High Temperature Structural and Mechanical Properties of Hard Metal Doped CrN$_x$ and TiN$_x$ Coatings: Synchrotron Radiation and DFT Assisted Studies

Ehsan Mohammadpour, BSc, MSc

This thesis presented for the degree of

Doctor of Philosophy

School of Engineering and Information Technology,

Murdoch University, Western Australia

2018
I declare that this thesis is my own account of my research and contains as its main content work which has not been previously submitted for a degree at any tertiary education institution.

Ehsan Mohammadpour

2018
Acknowledgments

I would like to thank my supervisors Dr. Zhong-Tao Jiang, Professor Bogdan Z Dlugogorski and Dr. Mohammednoor Altarawneh for bringing this research topic to my attention, for their encouragement and patient supervision during the past three years of study. Their knowledge, mentorship, encouragement and dedication have provided a fundamental driving force for the present study.

I am grateful to Murdoch University for the award of International Postgraduate Scholarship, which provided essential financial support for my research work and living expense. This work was also supported by Grant of computational time from National Computational Infrastructure (NCI) and the Pawsey Supercomputing Centre in Perth, Australia.

Thanks also to Dr. Matthew Rolls, Dr. Justin Kimpton and other colleagues for their assistance with data preparation, and all participants and the team members of the Surface Analysis and Materials Engineering Research Group (SAMERG) and Fire Safety and Combustion Kinetics Research Group, School of Engineering and Information Technology. Finally, I would like to acknowledge the patience and support of my wife during my years of study.
Dedications

To My Family
Abstract

This thesis presents a series of scientific studies exploring the thermal stability of CrN and TiN based metal nitride hard coatings. Vacuum sputtered Cr$_{1-x}$Al$_x$N (14 < x < 21 at.%), Cr$_{1-x}$Si$_x$N (5 < x < 18 at.%), Cr$_{1-x}$Ni$_x$N (13 < x < 40 at.%) and Ti$_{1-x}$Si$_x$N (0 < x < 4 at.%) thin film coatings, in the temperature range of 25 – 800 °C, were studied using (1) synchrotron X-ray powder diffraction beamline at Australian Synchrotron (SR-XRD), (2) nanoindentation tests, (3) X-ray photoelectron spectroscopy (XPS), and (4) Field Emission Scanning Electron Microscope (FESEM) imaging. Rietveld refinement method has been applied to SR-XRD patterns to quantitatively analyse the phase evolution and the changes of microstructure in the coatings. First principal calculations via density functional theory (DFT) and quasi-harmonic approximation (QHA) methods were used to calculate the structural and mechanical properties of metal nitrides at ground state and high temperatures up to 2800 °C. This study also presents a novel model which can predict the mechanical properties of such hard coatings at high temperatures.

Adding Al to CrAlN coatings improved microstructural and mechanical properties for ~14-21% Al content. Rietveld analysis indicated various crystalline phases in the coatings that included: CrN, AlN, α-Cr with a small amount of AlO$_2$ and Al$_2$O$_3$ over 25 – 700 °C range. Al doping improves resistance to crystal growth, stress release and oxidation resistance of the coatings. Al doping also enhances the coating hardness and elastic modulus up to 42 and 438 GPa. First-principles and QHA method on bulk CrN and AlN were incorporated to predict the thermo-elastic properties of Cr$_{1-x}$Al$_x$N thin film coating in the temperature range of 0 - 1500 °C. The simulated results at T= 1500 °C give a predicted hardness of $H = \sim$41.5 GPa for a ~21% Al doped Cr$_{1-x}$Al$_x$N coating.

Adding Si to CrN reduced the crystallite size; stabilised the microstructure; modified coating softening resistance, and improves the hardness of CrN coatings up to 36 GPa. Although the coatings containing Ni have not shown a stable microstructure at high temperatures, changes in hardness and elastic modulus after heating are negligible. Formation of (Cr,Si)N and Ni(Cr) solid solutions are also postulated by studying the changes in lattice constants of CrN during heat treatment and comparing to estimated values from QHA calculations. The hardness of the CrN and Ni phases up to 930 °C was estimated by correlating the hardness with the bulk and shear modulus of these phases. The simulated hardness results predict hardness of $H \approx$20 and $\approx$6 for CrN (930 °C) and Ni (330 °C), respectively.

The influence of substrate bias voltage, ranged from -30V to -80V, on the thermal stability and mechanical properties of the TiSiN coatings were investigated. As-deposited TiSiN coatings consist of cubic TiN in the form of (Ti,Si)$_2$N solid solutions. Increasing substrate bias voltage up to -80 V during Ti–Si–N deposition resulted in significant changes in Si content, surface morphology, phase composition, microstructure and Oxidation resistance of the coatings. TiO$_2$ and Ti$_2$O$_3$ were identified above 600 °C for the samples deposited at lower bias voltages. Oxidation resistance and thermal stability of the TiSiN coatings were improved as the bias voltage increased beyond -40V. As the substrate bias voltage increases from -30V to -80V, Si content reduced from 4% to 0; hardness and Young’s modulus of the coatings constantly
improved from 23 GPa to 33 GPa and 310 GPa to 450 GPa, respectively, corresponding to almost 50% increase.

DFT-QHA algorithm was used to calculate phonon spectra, electronic properties, elastic constants ($C_{ij}$) and thermodynamic properties of TiN within the temperature range of 0-2830 °C and under a pressure range 0-60 GPa. QHA method, as implemented in the Gibbs2 code, is utilised to accurately estimate thermal expansion coefficients, entropies, heat capacity values and Debye’s temperature. A similar approach was used to investigate electronic properties and stability phase diagrams the cubic boron nitride (c-BN) surfaces. Enthalpy of formation of c-BN was estimated to be -2.816 eV. The c-BN(100) surface offers separate B and N terminations, whereas c-BN(111) and c-BN(110) are truncated with combinations of boron and nitrogen atoms. Optimised geometries of surfaces display interlayer displacements up to the three topmost layers. Bulk c-BN and its most stable surface c-BN(100)$_N$ possess no metallic character, with band gaps of 5.46 and 2.7 eV, respectively. We find that only c-BN(100)$_B$ configuration exhibits a metallic character. c-BN(110)$_N$ and c-BN(111)$_N$ surfaces display corresponding band gaps of 2.5 and 3.9 eV and, hence, afford no metallic property.

The presented microstructural and mechanical analysis of metal nitride coatings using SR-XRD data along with the proposed methods to predict mechanical properties at high temperatures can be used to design superhard coatings with sophisticated microstructure and superior thermal stability at elevated temperatures.
Table of Contents

Acknowledgments ...................................................................................................................... ii
Dedications .................................................................................................................................. iii
Abstract ..................................................................................................................................... iv
Table of Contents ...................................................................................................................... vi
Contribution Toward Publication .............................................................................................. x
Statement of Contribution ........................................................................................................ xii
Symbols and Abbreviations .................................................................................................... xix
List of Figures ........................................................................................................................... xxi
List of Tables ............................................................................................................................. xxv
1. Chapter 1: Introduction ....................................................................................................... 1
   1.1. General Overview ....................................................................................................... 2
   1.2. Research Motivation ................................................................................................. 3
   1.3. Objectives ................................................................................................................... 5
   1.4. Thesis Layout .......................................................................................................... 6
   1.5. References ................................................................................................................. 7
2. Chapter 2: Review Of Relevant Literature ....................................................................... 10
   2.1. Introduction ............................................................................................................... 11
   2.2. Different Types of Metal Nitrides ............................................................................. 12
   2.3. Hardening Mechanism in Metal Nitride Thin Films ................................................ 14
   2.4. Recent Advances in Depositing Hard Coatings ....................................................... 21
   2.5. Thermal Stability of Hard Coatings .......................................................................... 31
   2.6. Effects of Deposition Parameters .............................................................................. 38
   2.7. The Role of Computational Simulation .................................................................... 45
   2.8. Summary ................................................................................................................... 50
   2.9. References ................................................................................................................. 52
3. Chapter 3: Methodology ................................................................................................... 62
   3.1. Overview ..................................................................................................................... 63
   3.2. Experimental Configurations .................................................................................... 63
      3.2.1. Magnetron sputtering Technique ....................................................................... 63
      3.2.2. Synchrotron radiation X-Ray diffraction (SR-XRD) ........................................ 67
      3.2.3. SR-XRD data collection .................................................................................... 68
      3.2.4. Analysis of XRD data ....................................................................................... 69
      3.2.5. Scanning electron microscopy ......................................................................... 71
3.2.6. X-ray photoelectron spectroscopy (XPS) .......................................................... 72
3.2.7. Nanoindentation tests .......................................................................................... 73
3.3. Computational Techniques .................................................................................... 75
  3.3.1. Structural optimisation ..................................................................................... 78
  3.3.2. Phonon density of state .................................................................................. 78
  3.3.3. Thermo-elastic properties ............................................................................... 79
3.4. References ............................................................................................................. 80
4. Chapter 4: Electronic Properties and Stability Phase Diagrams for BN Surfaces ...... 83
  4.1. Abstract .................................................................................................................. 84
  4.2. Introduction ............................................................................................................. 85
  4.3. Methodology .......................................................................................................... 87
    4.3.1. Structural optimisation of $c$-BN .................................................................. 87
    4.3.2. Quasi-harmonic approximation (QHA) calculations ..................................... 88
    4.3.3. Ab initio atomistic thermodynamics .............................................................. 88
  4.4. Results and Discussions ....................................................................................... 89
    4.4.1. Properties of Bulk $c$-BN at 0 K .................................................................. 89
    4.4.2. Thermo-elastic properties of $c$-BN. ............................................................... 92
    4.4.3. Geometry of low index surfaces of cubic BN ............................................... 97
    4.4.4. Stability phase diagrams for $c$-BN surfaces ............................................... 105
  4.5. Conclusions .......................................................................................................... 106
  4.6. References ............................................................................................................. 107
5. Chapter 5: Thermo-Mechanical Properties of Titanium Nitride .............................. 110
  5.1. Abstract .................................................................................................................. 111
  5.2. Introduction ............................................................................................................. 112
  5.3. Theoretical Method ............................................................................................... 114
  5.4. Results and Discussions ....................................................................................... 115
    5.4.1. Bulk TiN ........................................................................................................ 115
    5.4.2. Mechanical properties .................................................................................. 116
    5.4.3. Electronic properties ..................................................................................... 118
    5.4.4. Phonon spectra ............................................................................................. 121
    5.4.5. Thermodynamic properties ......................................................................... 122
  5.5. Conclusions .......................................................................................................... 134
  5.6. References ............................................................................................................. 134
Contribution Toward Publication

The research work embodied in this thesis contains published joint-authored papers as listed below. I am the principal contributor in the publications. I have included as part of the thesis a written statement, endorsed by my supervisors, attesting to my significant contributions to these joint publications.


The list below itemises the publications to which I have contributed during the course of the PhD study, but fall outside the scope of this thesis.


Statement of Contribution


<table>
<thead>
<tr>
<th>Author’s Name</th>
<th>Contribution</th>
<th>Overall Percentage (%)</th>
<th>Signature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ehsan Mohammadpour</td>
<td>1- Analysed the Synchrotron diffraction patterns, calculated the crystallite size, microstrain in the coatings at high temperatures 2- Prepared the manuscript 3- Revised the manuscript according to supervisors and co-authors comments</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Zhong-Tao Jiang</td>
<td>Project leader, SR-XRD experiments, data analysis and manuscript preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mohammednoor Altarawneh</td>
<td>Manuscript preparation</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Zonghan Xie</td>
<td>Supervised indentation tests</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zhi-feng Zhou</td>
<td>Supervised the preparation of hard coating samples</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nicholas Mondinos</td>
<td>Manuscript preparation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Author’s Name</th>
<th>Contribution</th>
<th>Overall Percentage (%)</th>
<th>Signature</th>
</tr>
</thead>
</table>
| Ehsan Mohammadpour| 1- Analysed the SR-XRD data using Rietveld analysis to investigate the effect of Al content on the phase composition and microstructure of CrAlN at high temperatures  
2-Analysed indentation data to explore the effect of Al on the hardness of CrAlN coatings in as-deposited and heated conditions  
3-Modeled the thermo-mechanical properties of CrN and AlN phases at high temperatures using quasi-Harmonic Approximation method  
4-Predicted the hardness of CrN and AlN phases at high temperatures combining the experimental and computational data  
5-Prepared the manuscript | 70 | Mohammadpour |
<table>
<thead>
<tr>
<th>Name</th>
<th>Role</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zhong-Tao Jiang</td>
<td>6-Revise the manuscript according to supervisors and co-authors comments</td>
<td></td>
</tr>
<tr>
<td>Mohammednoor Altarawneh</td>
<td>Project leader, SR-XRD experiments, data analysis and manuscript preparation</td>
<td>30</td>
</tr>
<tr>
<td>Nicholas Mondinos</td>
<td>Manuscript preparation</td>
<td></td>
</tr>
<tr>
<td>M. Mahbubur Rahman</td>
<td>Discussion and analysis, Manuscript preparation</td>
<td></td>
</tr>
<tr>
<td>H. N. Lim</td>
<td>Manuscript preparation</td>
<td></td>
</tr>
<tr>
<td>N. M. Huang</td>
<td>Manuscript preparation</td>
<td></td>
</tr>
<tr>
<td>Zonghan Xie</td>
<td>Supervised indentation tests</td>
<td></td>
</tr>
<tr>
<td>Zhi-feng Zhou</td>
<td>Supervised the preparation of hard coating samples</td>
<td></td>
</tr>
<tr>
<td>Bogdan Z. Dlugogorski</td>
<td>Manuscript preparation</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Author’s Name</th>
<th>Contribution</th>
<th>Overall Percentage (%)</th>
<th>Signature</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ehsan Mohammadpour</strong></td>
<td>1-Optimise the atomic structure of BN using DFT method</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-Determine the electronic properties of BN surfaces</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3-Explore the surface stability of BN</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4-Prepared the manuscript</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5-Revised the manuscript according to supervisors and co-authors comments</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Mohammednoor Altarawneh</strong></td>
<td>Manuscript preparation</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td><strong>Zhong-Tao Jiang</strong></td>
<td>Manuscript preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Nicholas Mondinos</strong></td>
<td>Manuscript preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Bogdan Z. Dlugogorski</strong></td>
<td>Manuscript preparation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Author’s Name</th>
<th>Contribution</th>
<th>Overall Percentage (%)</th>
<th>Signature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ehsan Mohammadpour</td>
<td>1-Optimise the atomic structure of TiN using DFT method</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-Determine the electronic properties of TiN surfaces</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3-Model the thermo-elastic properties of TiN at high temperatures using quasi-harmonic approximation method</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4-Prepared the manuscript</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5-Revised the manuscript according to supervisors and co-authors comments</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mohammednoor Altarawneh</td>
<td>Manuscript preparation</td>
<td>30</td>
<td>X</td>
</tr>
<tr>
<td>Jomana Al-Nu’airat</td>
<td>Manuscript preparation</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Zhong-Tao Jiang</td>
<td>Manuscript preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nicholas Mondinos</td>
<td>Manuscript preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bogdan Z. Dlugogorski</td>
<td>Manuscript preparation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Author’s Name</th>
<th>Contribution</th>
<th>Overall Percentage (%)</th>
<th>Signature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ehsan Mohammadpour</td>
<td>1-Study the effect of Ni and Si on the microstructure and phase composition of coatings using mainly Rietveld Refinement method</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-Analyse the mechanical properties of coatings using indentation data</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3-Find the connections between the microstructure properties such as microstrain, and hardness of the coatings</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4-Prepared the manuscript</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5-Revised the manuscript according to supervisors and co-authors comments</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zhong-Tao Jiang</td>
<td>Project leader, SR-XRD experiments, data analysis and manuscript preparation</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Mohammednoor Altarawneh</td>
<td>Manuscript preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Matthew Rowles</td>
<td>Manuscript preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sunghwan Lee</td>
<td>Manuscript preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Name</td>
<td>Role</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zhi-feng Zhou</td>
<td>Supervised the preparation of hard coating samples</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H. N. Lim</td>
<td>Manuscript preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N. M. Huang</td>
<td>Manuscript preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nicholas Mondinos</td>
<td>Manuscript preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bogdan Z. Dlugogorski</td>
<td>Manuscript preparation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Symbols and Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td>Angstrom (10−10 m)</td>
</tr>
<tr>
<td>B</td>
<td>Bulk modulus</td>
</tr>
<tr>
<td>BCC</td>
<td>Body-centred cubic</td>
</tr>
<tr>
<td>(C_p)</td>
<td>Constant-heat capacity</td>
</tr>
<tr>
<td>(C_v)</td>
<td>Heat capacity at constant volume</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>(E)</td>
<td>Young’s modulus</td>
</tr>
<tr>
<td>(E_f)</td>
<td>Enthalpy of formation</td>
</tr>
<tr>
<td>F(V,T)</td>
<td>Helmholtz free energy</td>
</tr>
<tr>
<td>FCC (or fcc)</td>
<td>Face-centred cubic</td>
</tr>
<tr>
<td>(G(T,p))</td>
<td>Gibbs free energy</td>
</tr>
<tr>
<td>g(w)</td>
<td>Phonon density of states</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized gradient approximations</td>
</tr>
<tr>
<td>(H)</td>
<td>Hardness</td>
</tr>
<tr>
<td>(h)</td>
<td>Planck’s constant (6.63 × 10^{-34} J.s)</td>
</tr>
<tr>
<td>(K)</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>(k_B)</td>
<td>Boltzmann constant (1.38 × 10^{-23} m^2kg.s^{-2}K^{-1})</td>
</tr>
<tr>
<td>MeN</td>
<td>Metal nitride</td>
</tr>
<tr>
<td>LDA</td>
<td>Local-density approximations</td>
</tr>
<tr>
<td>PDOS</td>
<td>Partial density of states</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
</tr>
<tr>
<td>QHA</td>
<td>Quasi-harmonic approximation</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>SR-XRD</td>
<td>Synchrotron radiation X-ray diffraction</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Thermodynamic Grüneisen ratio</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stress</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Thermal expansion coefficient</td>
</tr>
<tr>
<td>$\theta_D$</td>
<td>Debye temperature</td>
</tr>
</tbody>
</table>
List of Figures

Figure 2.1. Schematic structure of hard nanocomposite coatings for 2D systems: (a) nanosize layers and (b) columnar nanograins; and 3D systems: (c) nanocrystals covered with amorphous phase and (d) mixture of nanograins [44] ............................................................ 16
Figure 2.2. (a), (b) and (c) film crystallinity-concentration graphs of transition regions for A1-BxN compounds [44] .............................................................................................................. 17
Figure 2.3. Effect of grain size on the total material hardness [47] ........................................... 19
Figure 2.4. Lattice parameters of fcc-CrAlN phase as a function of Al content (at. %) .......... 23
Figure 2.5. Hardness of the Cr1-xAlxN coatings as a function of Al/Cr ratio measured by nanoindentation .................................................................................................................. 24
Figure 2.6. Hardness of the Cr1-xSi1-xN coatings as a function of Si at.% concentration measured by nanoindentation ............................................................................................................ 27
Figure 2.7. Lattice parameters of fcc-CrSiN phase as a function of Si content (at. %) ........... 28
Figure 2.8. Coating Hardness after annealing at different temperatures .............................. 35
Figure 2.9. Effect of Ti concentration on the hardness of annealed Cr(Ti)AlN coatings [98] 36
Figure 2.10. Influence of substrate to chamber wall distance on the mechanical properties of CrAlN coatings [112] ........................................................................................................... 42
Figure 2.11. Hardness and Young’s modulus of CrAlN coatings deposited with various pulsing frequencies [115] ........................................................................................................... 44
Figure 2.12 Crystal structures: (a) CrN and (b) TiN (dark blue, light blue and grey spheres denote Cr, Ti and N atoms, respectively). ............................................................................... 46
Figure 2.13. Calculated pressure-temperature phase diagram of CrN based on the GGA+U and LDA+U. Schemes compared to experiment (open circles and squares). [123] .......... 47
Figure 2.14. Comparison between isostructural mixing enthalpies H(x) and d²H(x)/dx² of B1- Cr1-xAlxN and Ti1-xAlxN [128] ......................................................................................... 49
Figure 2.15. The calculated cubic elastic constants of Ti0.5Al0.5N [129] ................................... 50
Figure 3.1 Closed field unbalanced magnetron sputter ion plating (CFUBMSIP) system manufactured by Teer Coatings Ltd design ............................................................................. 64
Figure 3.2 NEON 40 EsB instrument at Curtin University ..................................................... 72
Figure 3.3. Schematic of indentation deformation at peak load and after unloading ............. 74
Figure 3.4. A flowchart of the DFT iteration scheme ............................................................ 77
Figure 3.5. Calculated phonon DOS for TiN and experimental phonon dispersion obtained from neutron diffraction of bulk TiN [20] ..................................................................................... 79
Figure 4.1. (a) c-BN unit cell (read and black spheres denote B and N, respectively), (b) energy versus volume curve for bulk c-BN ................................................................. 90
Figure 4.2. Total and partial density of states for (a) BN, (b) B and (c) N atoms in bulk c-BN. ................................................................................................................................. 92
Figure 4.3 Phonon density of states for c-BN. Dashed-line responds to theoretical calculations of Srivastava et al. [37] ................................................................. 94
Figure 4.4 Dependence of Bulk modulus of c-BN on temperature and pressure. Empty squares correspond to theoretical calculations of Albe et al. [38] at 0 K. ....................... 94
Figure 4.5 Heat capacity (a) and thermal expansion (b) of c-BN as a function of temperature. Empty squares, rectangles and circles correspond to the theoretical calculation of Solozhenko et al. [39] and Tohei et al. [40], respectively.

Figure 4.6 (a) Dependence of V/V₀ on pressure and (b) temperature. Empty squares, circles and rectangles represent experimental data by Grimsditch et al. [41], Knittle et al. [42] and theoretical by Knittle et al. [42].

Figure 4.7 Geometries of optimised c-BN slabs (red and black spheres denote B and N, respectively).

Figure 4.8 Plot of inter-planar spacing (a) c-BN(110) BN and (b) c-BN(100) B and c-BN(100) N.

Figure 4.9 DOS of the c-BN(100) B surface: (a) DOS for entire surface, (b) PDOS on B atoms and (c) PDOS on N atoms.

Figure 4.10 DOS of the c-BN(100) N surface: (a) DOS for entire surface, (b) PDOS on B atoms and (c) PDOS on N atoms.

Figure 4.11 DOS of the c-BN(110) BN surface: (a) DOS for entire surface, (b) PDOS on B atoms and (c) PDOS on N atoms.

Figure 4.12 DOS of the c-BN(111) BN surface: (a) DOS for entire surface, (b) PDOS on B atoms and (c) PDOS on N atoms.

Figure 4.13 Stability phase diagram of c-BN surfaces.

Figure 5.1 Crystal structure of TiN (Blue and grey spheres denote Ti and N atoms, respectively).

Figure 5.2. DOS and PDOS of c-TiN under pressures of (a) 60 GPa, (b) 33 GPa and (c) 0 GPa. Fermi level is located at 0 eV.

Figure 5.3. Calculated phonon DOS for TiN and experimental phonon dispersion obtained from neutron diffraction of bulk TiN [32].

Figure 5.4. Heat capacities (Total heat capacity C, Cᵥ and Cₚ) for TiN with respect to various temperatures and pressures: (a) C versus T at 1 atm, (b) Cᵥ versus P at a constant T (isotherms), (c) Cᵥ versus T at constant P (isobars) and (d) Cₚ versus T at constant P (isobars).

Figure 5.5. Calculated V/V₀ as a function of (a): T at different fixed P (isobars) Expt [35] are at 1 atm, and (b) P at different fixed T (isotherms).

Figure 5.6. Volume thermal expansion for TiN as a function of (a) T at different fixed P (isobars) and (b) P at different fixed T (isotherms).

Figure 5.7. Entropy of TiN as a function of (a): T at different fixed P (isobars) – Expt. [35] are at 1 atm. and (b): P at different fixed T (isotherms).

Figure 5.8. Bulk modulus of TiN as a function of (a) T at different fixed P (isobars) and (b) P at different fixed T (isotherms)– Calc. [15] at 1 atm.

Figure 5.9. Debye temperature of TiN as a function of (a): T at different fixed P (isobars) and (b): P at different fixed T (isotherms).

Figure 6.1 Experimental SR-XRD and Rietveld refinement profile of TiN coating at 800 °C. The hkl values for each phase are indicated by the small vertical bars.

Figure 6.2 SR-XRD patterns of the as-deposited TiSiN coatings at varying bias voltages at room temperature. The dashed vertical lines indicate substrate peaks.
Figure 6.3 (a) Si 2p and (b) N 1s XPS diffractograms of sputtered TiSiN coatings deposited at various bias voltages. ............................................................................................................. 150
Figure 6.4 SR-XRD patterns of TiSiN coatings deposited at various bias voltages, measured at 800 °C. The dashed vertical lines indicate substrate peaks................................................................. 151
Figure 6.5 TiN lattice constants in TiSiN coatings deposited at various bias voltages, within the experimental temperature range of 25-800 °C ............................................................................................................. 153
Figure 6.6 Schematic summary of the phase evolution for TiSiN coatings obtained from the in situ experiment analysis........................................................................................................................................ 154
Figure 6.7 (a) crystallite size and (b) microstrain of TiN phase as a function of measurement temperature, obtained from the analysis of in situ experiments. ................................................................. 156
Figure 6.8 FESEM images of TiN and TiSiN coatings deposited at different bias voltages. 157
Figure 6.9 Hardness and Elastic modulus of TiSiN samples as a function of bias voltage, derived from nanoindentation experiments................................................................. 159
Figure 6.10 The residual stress for TiN(111) in TiSiN coatings as a function of bias voltage compared to TiN coating at various temperatures ............................................................................................................. 160
Figure 7.1. SR-XRD patterns of (a) CrN-M2ST and (b) CrAlN-M2ST samples at different temperatures ........................................................................................................................................ 173
Figure 7.2 Refined SR-XRD pattern of CrAlN coating at 700 °C ................................................................. 176
Figure 7.3 Williamson-Hall plots for CrN phase in (a) CrN-M2ST and (b) CrAlN-M2ST samples at different temperatures ........................................................................................................................................ 178
Figure 7.4. Calculated (a) strains vs. T and (b) crystallite size vs. T for CrN phase in the CrN-M2ST and CrAlN-M2ST samples ........................................................................................................................................ 180
Figure 8.1 Experimental SR-XRD and Rietveld refinement profile of C1 coating at 700°C. The allowed hkl values for each phase are indicated by the small vertical bars. ................................................................. 196
Figure 8.2 SR-XRD diffraction patterns at ~ 25 °C of as-deposited Cr_{1-x}Al_{x}N coatings with various Al contents. The dashed vertical lines indicate substrate peaks. The high intensity peak at 2θ = 23.5 which belongs to Steel substrate was omitted to avoid overlapping with above diffraction patterns ........................................................................................................................................ 197
Figure 8.3 SR-XRD diffraction patterns at 700 °C of Cr_{1-x}Al_{x}N coatings with various Al contents. The dashed vertical lines indicate substrate peaks. ........................................................................................................................................ 199
Figure 8.4 CrN and c-AlN lattice constants, from Rietveld analysis, in Cr_{1-x}Al_{x}N coatings as a function of the in-situ experiment temperature ........................................................................................................................................ 200
Figure 8.5 Effect of temperature on the CrN phase in the Cr_{1-x}Al_{x}N coatings, from Rietveld analysis: (a) crystallite size (b) microstrain ........................................................................................................................................ 202
Figure 8.6 Effect of temperature on the residual stress, from equation (8.2), for CrN (200) orientation in Cr_{1-x}Al_{x}N coating ........................................................................................................................................ 203
Figure 8.7 The change in energy of primitive unit cells for bulk CrN-NM, CrN-M and AlN as a function of cell volume ........................................................................................................................................ 205
Figure 8.8 Theoretical and experimental lattice constants: (a) CrN and (b) c-AlN phases. ................................................................. 208
Figure 8.9 Simulated hardness values as a function of temperature for bulk CrN-m, CrN-nm and c-AlN. Nanoindentation hardness data, at high temperature for Al_{0.7}Cr_{0.3}N thin film coatings and room temperature for current Cr_{1-x}Al_{x}N coatings ........................................................................................................................................ 214
Figure 9.1 Whole pattern profile modelling for C7#Ni coating at 970 K (R_{wp}=14.28) .......... 228
Figure 9.2 Diffraction patterns of C1 and CrSiN coatings: (a) as-deposited condition at 300 K and (b) at 970 K. The dash lines indicate main substrate peaks. The peaks marked with ‘x’in fig. 9.2a indicate phase modifications of substrate. 232

Figure 9.3 Diffraction patterns of CrNiN samples: (a) as-deposited condition at 300 K and (b) at 970 K. The dash lines indicate main substrate peaks. 234

Figure 9.4 Lattice constants of CrN in CrSiN and CrNiN at different temperatures. 237

Figure 9.5 Effect of Cr content on lattice constants of Ni in CrNiN. Included are data from QHA model. 238

Figure 9.6 Changes in (a) volume-weighted mean crystallite sizes and (b) microstrain for CrN in CrSiN and CrNiN coatings as a function of temperature. 240

Figure 9.7 Calculated hardness for pure CrN and Ni phases [from indicated references], and CrNiN coatings. Included are experimental hardness of CrNiN samples. 246

Figure 10.1. Proposed laboratory set-up including tubular furnace reactor. 260

Figure 11.1 In situ SR-XRD data for TiN coating heated from 25 to 800 °C in air. 265

Figure 11.2 In situ SR-XRD data for TiSiN-30 coating heated from 25 to 800 °C in air. 265

Figure 11.3 In situ SR-XRD data for TiSiN-40 coating heated from 25 to 800 °C in air. 266

Figure 11.4 In situ SR-XRD data for TiSiN-50 coating heated from 25 to 800 °C in air. 266

Figure 11.5 In situ SR-XRD data for TiSiN-60 coating heated from 25 to 800 °C in air. 267

Figure 11.6 In situ SR-XRD data for TiSiN-70 coating heated from 25 to 800 °C in air. 267

Figure 11.7 In situ SR-XRD data for TiSiN-80 coating heated from 25 to 800 °C in air. 268

Figure 11.8 In situ SR-XRD data for C1 coating heated from 25 to 700 °C in air. 270

Figure 11.9 In situ SR-XRD data for C2-14%Al coating heated from 25 to 700 °C in air. 270

Figure 11.10 In situ SR-XRD data for C3-17%Al coating heated from 25 to 700 °C in air. 271

Figure 11.11 In situ SR-XRD data for C4-21%Al coating heated from 25 to 700 °C in air. 271

Figure 11.12 Stress in CrN structure for (111) orientations as function of temperature. 272

Figure 11.13 Stress in CrN structure for (200) orientations as function of temperature. 272

Figure 11.14 Stress in CrN structure for (311) orientations as function of temperature. 273

Figure 11.15 The Hardness (H) measured at room temperature for as-deposited and heated samples. 274

Figure 11.16 The Elastic modulus (E) measured at room temperature for as-deposited and heated samples. 275

Figure 11.17 The resistance to deformation (H^3/E^2) measured at room temperature for as-deposited and heated samples. 275

Figure 11.18 In situ SR-XRD data for C2#Si coating heated from 300 to 970 K in air. 277

Figure 11.19 In situ SR-XRD data for C3#Si coating heated from 300 to 970 K in air. 278

Figure 11.20 In situ SR-XRD data for C4#Si coating heated from 300 to 970 K in air. 278

Figure 11.21 In situ SR-XRD data for C5#Ni coating heated from 300 to 970 K in air. 279

Figure 11.22 In situ SR-XRD data for C6#Ni coating heated from 300 to 970 K in air. 279

Figure 11.23 In situ SR-XRD data for C7#Ni coating heated from 300 to 970 K in air. 280

Figure 11.24 (a) Hardness and (b) elastic modulus for CrNiN and CrSiN coatings in as-deposited and annealed conditions. 281

Figure 11.25 Resistance to deformation for CrNiN and CrSiN coatings in as-deposited and annealed conditions. 282
List of Tables

Table 3.1 Peak types for symmetric functions in TOPAS ....................................................... 70
Table 4.1 Lattice parameter and Bulk modulus of BN compared to other analogous theoretical and experimental results................................................................. 93
Table 4.2. Bader's charges on B and N atoms. Subscript numbers refer to the first, second and third layers...................................................................................................................... 105
Table 5.1 Calculated lattice constant (a), elastic constants (C_{ij}), bulk modulus (B), shear modulus (G), elastic modulus (E), Zener anisotropy factor (A) and Poisson ratio (\(\nu\))............. 116
Table 6.1 Elemental compositions of TiN and TiSiN unbalanced magnetron sputtered coatings, deposited at different bias voltages, acquired via XPS survey scans. .................... 148
Table 7.1. Contents of coating sample obtained from XPS measurements........................................ 172
Table 7.2. Calculated strain and crystallite size of CrN phase in the CrN-M2ST and CrAlN-M2ST samples at different temperatures (T)......................................................................... 179
Table 8.1. Elemental composition of the Cr_{1-x}Al_xN coatings determined by XPS................. 194
Table 8.2. Nanoindentation, at 25°C, of Cr_{1-x}Al_xN coatings: as-deposited and heated samples. ................................................................................................................................................ 204
Table 8.3. Lattice constant from experimental SR-XRD and DFT calculations ......................... 206
Table 8.4. Calculated elastic constants (C_{ij}), bulk modulus (B), Young's modulus (E), Poisson ratio (\(\nu\)) of CrN (non-magnetic and spin-polarized) and c-AlN phases. Calculated and experimental data from the literature are denoted by \(c\) and \(e\), respectively......................... 210
Table 8.5 DFT calculated hardness, at T = 25 °C, of bulk CrN, AlN based on \(d_{ij}\). Current project and literature experimental data included for comparison........................................ 211
Table 9.1 Surface chemical composition of coatings with different Ni and Si content determined by XPS ................................................................................................................ 226
Table 9.2 Relative phase composition (wt. %) of CrNiN coatings at 970 K............................... 234
Table 9.3 \(h\text{-Cr}_2\text{N lattice constants (a and c) based on Rietveld models of C1 and C5#Ni coatings.} \)........................................................................................................................................ 238
Table 9.4 Hardness, elastic modulus and resistance to deformation from nanoindentation measurements made at 300 K.......................................................................................... 242
Table 9.5 Dependency of elastic modulus on crystallographic directions in CrN and Ni based on experimental (\(c\)) and computed (\(c^{\prime}\)) elastic constants at room temperature........................................... 244
Table 9.6 Calculated hardness (\(H_{cal}\)) for CrN and Ni phases from equation (5.2).............. 245
Table 11.1 \(hkl\) values for major phases in SR-XRD diffractograms as shown in Figure 11.1-Figure 11.7 ........................................................................................................................................ 264
Table 11.2 \(hkl\) values for major phases in SR-XRD diffractograms as shown in Figure 11.8-Figure 11.11 ........................................................................................................................................ 269
Table 11.3 k-points grids, used in the VASP simulation, for elastic constants of CrN-m. ... 276
Table 11.4 k-points grids, used in the VASP simulation, for elastic constants of CrN-nm. 276
Table 11.5 \(hkl\) values for major phases in SR-XRD diffractograms as shown in Figure 11.18-Figure 11.23 .......................................................... 277
Chapter 1

Introduction

This chapter sets the stage for the whole thesis, encompassing detailed research motivations, objectives, as well as a brief outline of the dissertation.
1.1. **General Overview**

In the modern industry, machine components are often subjected to a highly complex thermo-mechanical loading and corrosive environments [1]. Mechanical performance of tools, usually made of special types of steel, reduces significantly at high temperatures due to aggressive wear and corrosion which affects the service life and increases the material costs [2]. In the tooling industry, as the cutting speed increases and the working fluid decreases, the demand continues to increase for high-performance hard coatings to protect cutting tools and die casting dies [3]. Product development in various engineering industries has close relations with innovations in surface enhancement techniques. Advanced hard coating materials and modern deposition techniques are the main requirements for the fabrication of tools and components that withstand aggressive working environment [4]–[6]. Currently, hard transition metal nitride coatings found widespread technological uses as oxygen diffusion barriers, corrosion and wear resistant coatings on cutting, moulding, milling and screw-threading tools. Transition metal nitrides like TiN or CrN deposited using PVD (Physical Vapour Deposition) technology have been widely used as hard protective coatings due to good wear and corrosion resistance, in order to contribute to a reduction of costs and increase of operating efficiency [7]–[9].

Both the technological process of hard coating production and their properties, i.e. hardness, wear and oxidation resistance are continuously being improved [10]. Due to the increased severe mechanical and thermal loading on cutting tools, coatings are required to maintain high hardness, and good wear and oxidation resistance at even higher temperatures. The temperature of the tool tip can reach 1000 °C during high-speed machining, and therefore, the oxidation resistance of hard coatings should be increased up to approximately 1000 °C [11].
Industrial coatings have been used in a wide variety of industrial purposes such as wear and corrosion resistance protection, anti-reflective and decorative applications. The coatings explored in the present study exhibit high mechanical properties including hardness and oxidation resistance at elevated temperatures which have widespread applications as protective coatings on cutting and moulding tools [12], [13].

This thesis presents a series of scientific studies on experimental and modelling aspects of transition metal nitrides based thin film coatings designed for mechanical applications. It aims to develop prediction tools for estimating the mechanical properties of such coatings at high temperatures considering their complex microstructure and deposition conditions.

1.2. Research Motivation

Protective hard coatings and sputtering techniques have been developed to coat cutting and moulding tools. These coatings are the subject of extensive research activities to improve the performance and increase the service lifetime of machining tools [1],[14]. The development of these coatings has increased significantly in the last 15 years thanks to their scientific and industrial applications [15]. A combination of superior mechanical and chemical properties, such as high fracture toughness, high oxidation resistance and high thermal and chemical stability make them favourable in engineering applications [15].

To enhance the physical and mechanical properties of the hard coatings, several approaches including alloying and sophisticated nanoscale design were utilised [16]. Ternary transition metal nitrides such as CrAlN, TiSiN and TiAlN exhibited superior mechanical and structural properties such as excellent hardness and thermal stability [4]. Nonetheless, further
improvements are still required to increase the stability and oxidation/corrosion resistance of metal nitride hard coatings for demanding forming or machining applications.

Sophisticated film architecture has been extensively studied to fabricate high-performance protective coatings. Complex coatings systems like multilayers, superlattice, and nanocomposite coatings exhibited superior properties compared to conventional coatings in industry. Coatings with designed macrostructure with complex grain boundary systems seem to be harder hardness [17] and remain hard up to elevated temperatures due to their improved structural stability at high temperatures. Those boundaries effectively stop atomic and vacancy migration and thus improve the hardness of the coating system. Protective coatings that contain different crystalline phases could withstand a high level of external tensions because different phases deform via different sliding systems.

Thermal stability is a general term used to describe the change (or not) of material properties as a function of temperature [15]. These properties include oxidation, structure, composition, mechanical properties, etc. for example, a superhard coating may exhibit high thermal stability if hardness and grain size remain unchanged upon annealing up to elevated temperatures. These properties highly depend on nanostructure and composition of any certain coating. Oxidation and corrosion resistance of the coating may strongly affect the thermal stability of the coating. Phase/structure transition in the coating can alter its mechanical and chemical stability [18].

Several studies have focused on the microstructure and mechanical properties of as-deposited nanocomposite coatings. Some investigated the changes in microstructure and composition of annealed and cooled down coatings [19], [20]. However, there are only a few studies on the real-time microstructural evolution at high temperatures due to the laboratory and instrumental limitations [21]. These studies are essential to investigate the real-time changes in the microstructure of nanocomposite coatings featuring complex nanostructures, solid solutions
and preferred orientations. It is vital to investigate the presence of phases which are only stable at elevated temperatures and may affect the oxidation resistance and mechanical performance of the coatings.

1.3. Objectives

The focus of the present study is to investigate the thermal stability of the designed monolayered CrN and TiN based quaternary coatings. The main difference of this study compared to the standard post-annealing testing is the possibility to estimate the residual stress in complex metal nitride coating systems at high temperatures, and identify metastable structures which may exist only at high temperatures. To achieve this, the thesis aims to fulfil the following objectives:

1. Studying the microstructure and mechanical properties of metal nitride coatings in the temperature range 25-800 °C: in situ synchrotron radiation powder diffraction (SR-XRD) beamline, Rietveld refinement, XPS, FESEM, Nanoindentation methods were employed to quantitatively investigate the phase composition, microstructure and mechanical properties of thin film coatings as a function of temperature in an atmospheric environment.

2. Predicting the mechanical properties of hard coatings at high temperatures: Density Functional Theory (DFT) calculations and Quasi-harmonic approximation (QHA) are employed to estimate thermo-mechanical properties of several hard metal nitrides in temperatures up to 1500 °C.
1.4. **Thesis Layout**

This dissertation represents a coordinated study assessing the thermal stability of transition metal nitride hard coatings. The following chapter (Chapter 2) presents a comprehensive literature review designed to briefly describe the recent significant developments in designing and depositing hard thin film coatings, evaluate the thermal stability of hard coatings, explain the effect of sputtering parameters on the properties of the coatings and describe the role of computational simulations on the better understanding of thermodynamic properties of hard coating systems, and point out the research gaps in hard metal nitride coating area.

Chapter 3 illustrates the main experimental and computational techniques employed within the scope of this study. Chapter 4 and 5 are focused on the of DFT and QHA approaches and implementation of these techniques on boron nitride and titanium nitride in cubic structures. Chapter 4 demonstrates the capabilities of DFT method in predicting the optimised atomic structure of cubic BN phase and calculating the electronic, surface stabilities, heat of formation and thermo-mechanical properties of BN. Chapter 5 illustrates the calculated electronic, phonon dispersion and thermo-mechanical properties of TiN in temperature range 0-3100 K using QHA method. The calculated properties including heat capacity, bulk modulus, elastic constants, Helmholtz free energy, Gibbs energy, thermal expansion coefficient and Debye temperature were compared and validated by available literature.

Chapter 6 represents the influence of substrate bias voltage on the microstructure, and mechanical properties of magnetron sputtered Ti$_{1-x}$Si$_x$N coatings. The calculated theoretical data on TiN were used in this chapter to explain the formation of solid solutions in TiSiN coating systems.
Chapter 1: Introduction

Chapters 7 and 8 present a systematic investigation of the structural and thermal stability of magnetron sputtered CrN and Cr\(_{1-x}\)Al\(_x\)N coatings using high temperature SR-XRD diffraction patterns and Rietveld refinement method. A model based on QHA calculation and atomic bond potentials is presented in Chapter 8 to predict the hardness of CrN and AlN at high temperatures.

Chapter 9 illustrates the influence of Ni and Si on the thermal stability of magnetron sputtered CrN based coatings and presents a model based on elastic constants to predict the hardness of coatings at high temperatures. Chapter 10 draws the concluding remark of this thesis and provides suggestions and recommendations for future investigations.

1.5. References


Chapter 1: Introduction


This chapter contains a broad review of the current advances in the design and fabrication of hard metal nitride coatings. It provides detailed explanations on the effect of alloying elements such as Al, Si, Ni, etc. on the thermal stability of TiN and CrN based hard coating systems.
2.1. Introduction

In the modern industry, machine components are often subjected to a highly complex thermo-mechanical loading and corrosive environments. Especially, wear and corrosion appear to have a significant influence on machine performance, reducing the lifetime and increasing the material costs. In such cases, often special steels are utilised and material prices are rising substantially. Transition metal nitrides such as TiN and CrN have had wide-ranging industrial applications as diffusion barriers against oxidation and corrosion at high temperatures and wear resistant coatings on various cutting, milling, screw-threading tools and mechanical components [1]. Transition metal nitrides like TiN or CrN deposited using PVD (Physical Vapour Deposition) technology have been widely used as hard protective coatings due to excellent wear and corrosion resistance, to contribute to a reduction of costs and increase of operating efficiency [2]. In fact, technological developments in several industries are closely related to advances in surface engineering and coating engineering techniques. Recent advances in designing nanostructured coating materials and coating deposition techniques enabled manufacturers to produce tools that withstand aggressive environments and harsh working conditions [3]. Both the technological process of their production and their properties, i.e., hardness, wear and oxidation resistance, however, are continuously being improved. The oxidation resistance should be increased up to approximately 1000 °C because during high-speed machining the temperature of the tool tip can reach 1000 °C and the coating should be stable at such high temperatures.
2.2. Different Types of Metal Nitrides

In general, ternary nitride coatings with cubic B1 structure have been used for practical purposes because of their excellent properties. Research interests on metallic nitride based thin film coatings in pure states and with various dopants have received substantial attention because of their high hardness, good electrical and thermal conductivity, high melting points, high surface acoustic velocity, are corrosion resistant, oxidation resistant, have excellent chemical and thermal stability and physical robustness. Due to this unique combination of numerous properties, several researchers studied the microstructure and properties of these coatings [4]–[14].

Hard coating materials can be synthesised via reactive magnetron sputtering, cathodic arc ion plating, and beam plasma-assisted physical vapour deposition. PVD processes involve an intense ion bombardment that generates a high level of defects and compressive stresses in the film that lead to high hardness. The increased hardness enabled quick implementation of the first generation of PVD coatings, such as TiN, Ti(CN), and ZrN, on tools made of high speed steels and of cemented carbides, which were used at moderate cutting conditions. The hard coating materials can also be produced by a combination of a hard, and relatively brittle nitride with a soft metal to attain a better fracture toughness. This concept was primarily used to fabricate cemented carbide (WC–Co) where WC delivers the high hardness while cobalt metal refines the fracture toughness.

The stress-dependent component of hardness progressively reduces when the tool is used at increased cutting speeds and, thus, exposed to high thermal loads. Not surprisingly, development efforts turned towards other hardening mechanisms and were directed at coatings that could maintain a functional hardness over a wider range of metal cutting conditions.
Superhard nanocomposite coatings were designed with the combination of a hard transition metal-nitride (TiN, W2N, VN, …) and a covalent nitride (Si3N4, BN, etc.). These types of coatings show a thermodynamically driven, strong spinodal segregation which results in high thermal stability of the nanostructure along with the superhardness (hardness >40 GPa) at high annealing temperatures. Considerable improvement in high-temperature properties can be achieved in more complex coating systems by adding alloying elements. Most current commercial multicomponent coatings are thermally stable ternary or quaternary coatings and nanostructured compounds made of carbides and nitrdes of transition metals, like Ti and Zr, with dopants elements such as Al, Cr, Hf, Si, Y, Ni, Ta, Nb, and V [15]. Typical examples include TiAlN, TiZrN, TiAlCrN, TiAlSiN, CrN, CrAlN, CrSiN, ZrN, B4C, TiB2, and others [16]. For example, the addition of Yttrium to a ternary nitride coating improved the thermal stability of the system [17]. Ni can increase the toughness of system and be successfully doped in TiN/SiNx system where Ni content changed from 0 to 39.8 at.% to balance the hardness and toughness of the coatings [13].

TiN and CrN have been successfully applied to the moulding dies, wear components, and cutting tools. CrN is known to be superior to TiN in corrosion and wear resistance, friction behaviour, and toughness [18]. A significant advantage of CrN is that the internal stresses are very low, due to which coatings with thicknesses more than 40 μm can be deposited on a variety of engineering substrates.

Addition of Al or Si into TiN and CrN coating systems can enhance mechanical properties and tribological properties, thermal stability and oxidation resistance of hard coating [19],[20]–[28]. These dopants can stabilise the metal nitride with fcc-cubic crystal structures in certain concentration ranges. Studies on TiAlN and CrAlN coatings showed that the addition of Al improves the mechanical properties and oxidation resistance of binary CrN and TiN coatings.
as both the chromium and aluminium could form protective oxides which suppressed oxygen diffusion. Also, CrAlN coatings showed better tribological properties in comparison with TiAlN, promising applicability in high speed machining, and higher oxidation resistance than TiAlN. At high temperatures, the outward diffusion of Cr and Al atoms (ions) into the coating surface forms an adhesive oxide layer of Cr$_2$O$_3$ and Al$_2$O$_3$ which prevent oxygen diffusion and improve the high temperature oxidation resistance up to 700–800 °C [29],[25]. For example, the presence of Cr$_{0.50}$Al$_{0.50}$N coating layer protected the substrate from oxidation at temperatures up to 900–1100 °C [30]. CrAlN coatings exhibited fine columnar grains during deposition. The columnar grain structure showed better performance comparing to dense and equiaxial microstructures. The columnar structure can undergo severe loading by inter-granular shear sliding. Shear sliding reduces stress concentration and increases damage resistance of the hard coating [31]. It would be possible to obtain incredible hardness of about 48 GPa if a certain amount of Al were added to CrN coatings [27].

2.3. Hardening Mechanism in Metal Nitride Thin Films

The principal feature of a machining tool is high hardness, and protective hard coatings must illustrate significant hardness, strength, toughness, adhesion, and low friction. The coating system should keep its properties at high temperatures which means excellent thermal stability. Hardness is the resistance of the material to plastic deformation [32]. There are different calculation methodology to measure coating hardness such as (1) the Oliver and Pharr method [33]; (2) the deformation energy method [34]; (3) the force indentation function method [35], (4) the Joslin–Oliver method [36] and (5) the energy density method [37]. Since mentioned methods are based on different assumptions and theories, reported hardness values may differ using different evaluation method. Hardness value could be influenced by residual stress inside
the coating layer during deposition of superhard coatings. This residual stress can lead to a
significantly overstated hardness value [38]. Therefore, it is recommended to measure thin film
hardness after annealing in a range of 400 to 500 °C [39]. The other factor which may interfere
with the hardness measurements of coatings is the substrate hardness. Hence, it is more
accurate to keep the indentation depth to less than 10% of the coating thickness [40].

Fracture toughness is another parameter that plays a role in the coating durability. It shows the
resistance of the material against the growth of existing cracks. However, a standard
quantitative evaluating of fracture toughness has not been developed yet [41],[42]. It was
shown that the hardness of nanocomposite coatings such as TiN/Si₃N₄ are several times greater
than each constituent’s hardness. One way to classify hard coatings is to define three main
groups based on hardness ranges: (1) the hard coatings with hardness less than 40 GPa; (2) the
superhard coatings with hardness between 40 and 80 GPa; and (3) the ultrahard coatings with
hardness more than 80 GPa [38], [43]. An ideal coating would be hard yet sustaining a sudden
impact without catastrophic failure. That is why hard-yet-tough ceramic coating has been the
focal point of research for the last few decades. Fabricating such a coating is difficult because
of the natural conflict between hardness and toughness, or an increase of hardness usually goes
at the expense of toughness.

It was mentioned that hardness is the resistance of a material to plastic deformation. For coarse-
grained ceramics, plastic deformation occurs predominantly through dislocation. Under this
circumstance, increasing the resistance to the dislocation movement is the essence of
hardening. However, for fine-grained ceramics (e.g., ceramics with a grain size less than 10
nm or amorphous phase), deformation by grain boundary microcracking and sliding (i.e., quasi-
plasticity) is the primary cause of strength decline [13]. Several strengthening mechanisms are
active in hardening ceramic coatings: (i) Hardening via grain size refinement, (ii) Hardening
via grain boundary reinforcement, (iii) Hardening via solid-state solution and precipitation, (iv) Hardening via ion bombardment, (v) Hardening via multi-layering [32]. Based on the mentioned hardening mechanisms, there are four main nanostructure coatings, which exhibit enhanced hardness as illustrated in Figure 2.1. These structures can be summarised as (1) multilayers of different coatings with nano-size period distance ($\lambda$), (2) the structure consists of grains in columnar microstructure, (3) a nanograin crystalline structure inside a thin tissue phase (amorphous) and (4) different orientations of nanograins from one or more phases [44].

Figure 2.1. Schematic structure of hard nanocomposite coatings for 2D systems: (a) nanosize layers and (b) columnar nanograins; and 3D systems: (c) nanocrystals covered with amorphous phase and (d) mixture of nanograins [44]

Figure 2.2(a-c) schematically demonstrate transition regions of a typical $\text{A}_{1-x}\text{B}_x\text{N}$ coating. For such a system, hardness enhancement may occur when the crystalline phase converts to an amorphous phase as shown in Figure 2.2(a). Similar hardness improvements could take place when grains with certain crystal orientation alter to another preferred orientation and/or one crystalline phase change to another crystalline phase. For example, $\text{Ti}_{1-x}\text{Al}_x\text{N}$ results in nanocrystals of TiN and AlN for $x = 0$ and $x = 1$, respectively. [44]
Nanostructured coatings usually are prepared using energetic ion bombardment with improved hardness and nano-grain structure. This ion bombardment creates high density and large compressive stresses and improves hardness, morphology, and nanostructure of the coatings [45]. There are nanocomposite coatings developed based on thermodynamically driven phase segregation which is always comprised of two phases: nanocrystalline grains (The primary phase) embedded in a continuous amorphous or nanocrystalline matrix (secondary phase). The primary and secondary phases which are usually in forms of nanocrystalline metal nitrides and
amorphous phases, respectively, have to be immiscible [46]–[49]. It is also possible to promote the high temperature properties of the nanocomposite coating by designing multilayers of transition-metal nitrides known as the superlattice.

The nanocomposite microstructure is partly responsible for the hardness increase of MeN coatings. In MeN/SiNx system with a particular concentration of silicon, the formation of a SiNx mono-layer at the grain boundaries of the MeN nanograins (4–10 nm) hinders the movement/propagation of dislocations [50]. The maximum hardness corresponds to the percolation of the SiNx amorphous phase. Solid solution effect could also contribute to the improved hardness of these coatings. Hardening observed in the Me–Si–N and Me–Al–N system, is also related to the substitution of Me atoms by Si (or Al) atoms in the MeN lattice. Since the atomic radii of Si or Al and Me are different, the incorporation of the solute element (Si or Al) in the solvent (MeN) distorts the crystalline lattice. The solute atoms tend to diffuse and segregate around dislocations in a way to reduce the overall strain energy and improve the resistance to slip. The fact that the total lattice strain must increase if a dislocation is torn away from them results in higher strength.

Dislocation induced hardening is the main hardening mechanism when the crystallite size (d) is more than 10 nm. For crystal sizes larger than 10 nm, nanograin hardening mechanism is dominant. Figure 2.3 shows that dislocation and nanograin hardening mechanism reach an optimal value at a critical grain size.
Figure 2.3 shows that maximum hardness for a coating occurs when the grain size ($d_c$) is close to 10 nm. The grain size values before and after critical grain size (maximum hardness) exhibit a gradual transition. At $d > d_c$, intragranular processes dominated by the dislocations are active, and the Hall–Petch law [51] describes the effect of grain size ($d$) on hardness ($H$) assuming the initial hardness ($H_0$) and material constant ($K$) are known.

$$H(d)=H_0+Kd^{-1/2} \quad (2.1)$$

While, at $d < d_c$, the intergranular processes such as atomic interactions between grains or small-scale sliding in grain boundaries are more active. Dislocation density decreases as the grain size is in nanoscale. Nanograin structure obstructs the dislocation activities and enhances hardness [52]. At $d<d_c$, there is no dislocation in the grain since grain size is smaller than dislocation length. On the contrary, grain boundaries are much more dominant over those inside grains when $d>d_c$. In this case, deformation mainly occurs because of grain boundary sliding. When grain size decrease, accumulation of defects in the grain boundaries activates structure softening. At this stage, grain boundaries act as quick diffusion path for atoms and vacancies.
under external stress [53]. It means any further increase in hardness is only possible through delayed grain boundary sliding. Nanoscale multilayered coatings have shown similar hardness enhancement due to limited dislocation movement [4],[6]. Hard composite coatings with nanoscale crystallite structure exhibit excellent nanocrack hindering as well as high fracture toughness [48]. Observations showed that a certain level of diffusion and sliding at grain boundaries could improve the coating’s toughness [47]. To design a nanostructured coating with enhanced mechanical and physical properties, it is crucial to consider material behaviour at the nanoscale.

Nanostructured hard coatings with stable mechanical properties at high temperatures can also be formed as a result of spinodal decomposition and diffusion-driven microstructural reorganisation [6] which is motivated by thermodynamic phase segregation. This process is based on thermodynamic laws and controlled with a diffusion rate and leads to the creation of a self-organised and temperature-dependent stable nanostructure. Some of the nanocomposite coatings have shown an exciting self-hardening/self-organisation behaviour in the temperature range of 500 to 600 °C [6], [54]–[56]. For instance, TiN coatings doped with Si such as TiSiN and TiAlSiN thin films showed maximum hardness after were annealed at abovementioned temperature rage and undergone spinodal phase separation [57]. It seems a combination of a certain affinity between deposited phases of the coating and a wide miscibility gap at high temperatures are the necessary conditions for a coating to undergo spinodal separation and exhibit high hardness and thermal stability.

It is essential to optimise the nanocrystal structure regarding their size, volume fraction, and distribution to obtain a combination of high mechanical strength and good toughness. For example, the distance between neighbour nanograin is a critical factor. A large intergranular distance increases the chance of crack propagation in the matrix. On the contrary, a very short
intergranular distance leads to high level of atomic interaction in the adjacent nanograins. Results showed that it is more efficient to have grains with a random orientation to have better nanograins sliding in the amorphous matrix which helps to release strain and enhance high toughness. Amorphous phase can also play a prominent role in the properties of the nanocomposite coating. (1) Its flexible structure prevents the creation of dangling bonds, vacancies, and other atomic scale defects and promotes uniform strains in the matrix. (2) Improve coating toughness via changing the direction of nanocracks, terminate nanocracks and boost grain boundary sliding.

2.4. Recent Advances in Depositing Hard Coatings

Recent reports showed that it is better to employ more complicated hard coating by adding specific elements which make ternary, quaternary or even more complex systems. For example, adding Si or Al to transition metal nitride such as Ti, Cr, Zr, Hf, V, Nb, Ta, … is an effective method to fabricate hard/superhard nanocomposite coatings [58]–[61]. In those systems, a combination of nanocrystals of hard transition metal nitrides such as TiN, CrN, W2N, BN embedded in an amorphous matrix, e.g., a-Si3N4, a-BN and a-C increases the grain boundary complexity and enhance the coating hardness. Complex coatings such as TiSi2, nc-TiN/a-SiNx and nc-TiSi2 systems [62] deposited via plasma chemical vapour deposition retained their superhardness in range of 80 to 105 GPa and remained hardness up to 900–1000 °C.

For example, Al dopant concentration displayed substantial influence on hardness, lattice parameter, and microstructure of CrN and TiN coatings [63]–[65]. Studies on crystal structures, phase composition, lattice parameters and microstructures of ternary nitride films of CrAlN and TiAlN coatings deposited by various PVD methods showed that face-centered cubic CrN phase with the NaCl structure (B1) is the dominant structure in such coatings when the Al
content is below 0.66 at.% [20], [63]. In contrast, hexagonal Cr\(_{1-x}\)Al\(_x\)N solid solutions (h-AlN) with wurtzite structure (B4) started to form at higher Al contents (x>0.7) which showed detrimental effects on the hardness, wear resistance and oxidation resistance of CrAlN film. CrN lattice parameter (x<0.6) decreased continuously as Al content increases from 4.16 Å to 4.13 Å as shown in Figure 2.4 as the Al atoms substitute the Cr atoms in CrN lattice. Al doping may continuously improve the coating hardness as long as the NaCl type CrAlN is stable. However, the hardness of coatings in the wurtzite structure reduced as Al concentration increased from 0.6 to 1. Transition metal nitrides exhibit different solubility limits for AlN [6], where the face-centered cubic (fcc) crystal structure desired for wear resistant PVD hard coatings changes to the thermodynamically stable hexagonal wurtzite structure [7] via an intermediate transition region where both structures occur. However, to study the structure-property evolution of these hard ternary coatings over wide compositional ranges requires many deposition runs with several sputter targets. It was shown that Al has a similar effect on the cubic structure of TiN thin films [65]. Observations showed that lattice constant of TiN phase reduce as Al content increased. They also attributed this lattice constant shrinking to the substitution of bigger Ti with Al atoms in face-centered cubic TiN structure and formation of a solid solution. The critical composition for the phase transition in TiAlN from B1 cubic-type structure to B4 wurtzite-type structure was around 65.3 mol.% AlN.
Figure 2.4. Lattice parameters of fcc-CrAlN phase as a function of Al content (at. %)

Figure 2.5 shows the changes in coating hardness as a function of Al/Cr ratio as reported in several studies on CrAlN coatings deposited by PVD techniques. Results show that there is a correlation between coating hardness and Al concentration in the CrN coating. Maximum hardness has reached when the Al/Cr ratio is in the range of 1 to 2. Studies of Bagcivan et al. [2], [66] showed that deposition technique also affects the coating hardness significantly. The highest hardness in Figure 2.4 was obtained in a coating deposited by a middle frequency magnetron sputtering ion plating technique at 200 °C. Same coatings deposited via high power pulsed magnetron sputtering method contained hexagonal AlN (for Al/Cr ratio=1) caused lower hardness of the coatings.

Ding et al. [18] used reactive unbalanced magnetron sputtering technique to deposit 300 nm thick CrAlN coatings with a preferred orientation along CrAlN(111), crystallised in rocksalt-
type cubic structure. The highest crystallinity was observed at the Al/Cr atomic ratio of around 0.3. Figure 2.4 shows the hardness evolution of the coatings as a function of Al content. Results show the improvement in hardness and Young’s modulus as the of Al/Cr ratio increases to about 0.5 with maximum hardness and Young’s modulus of about 30 GPa and 270 GPa, respectively [67],[68]. The wear resistance of all the CrAlN coatings enhanced up to six times compared to the pure chromium nitride coating deposited under similar conditions.

Figure 2.5. Hardness of the Cr$_{1-x}$Al$_x$N coatings as a function of Al/Cr ratio measured by nanoindentation

CrAlN coatings designed by Ding et al. [69] and deposited on a high speed steel substrate by lateral rotating cathodes arc deposition system showed extreme hardness as shown in Figure 2.5. The main advantages of this system compared to conventional vacuum arc systems comprise a substantially improved target utilisation rate thanks to the even target erosion and target cleaning in this system before coating deposition. Coatings deposited by cathodes arc
deposition with Al/Cr=1.7 showed minimum crystallinity and maximum hardness of 40 GPa which is remarkable compared to the hardness of CrN of 18 GPa. All the as-deposited CrAlN coatings showed a higher \( \frac{H}{E^2} \) value than that of the chromium nitride coating (at Al/Cr=0) deposited under similar conditions, which indicates a better resistance to plastic deformation and a more promising practical applicability of the CrAlN coatings. The wear performance of the CrAlN coatings is much better, with wear rate 2–3 orders in magnitude lower, than the TiAlN coatings, deposited by the same technique, under ambient conditions. In high speed machining tests, an evident better performance of the CrAlN-coated WC end-mills was demonstrated than that of the TiAlN-coated ones for cutting a hardened steel material.

Deposition system and sputtering parameters can significantly affect the mechanical properties of the coatings. \( \text{Cr}_{1-x}\text{Al}_x\text{N} \) coatings developed by a reactive pulsed DC magnetron equipped with triangle-like segmented targets resulted in coatings with a maximum hardness of 25 GPa at \( x = 0.37 \) [70]. Using this deposition technique also reduced the solubility limit of AlN in the face centered-cubic \( \text{Cr}_{1-x}\text{Al}_x\text{N} \) solid solution to \( x = 0.61 \). The relatively low metastable solubility limit for AlN in CrN compared to the accepted limit of \( x = 0.77 \) [6] could be due to the high N\(_2\) fraction in the process gas. The more significant decrease in hardness for \( x = 0.44 \) is attributed to various ion flow inside the chamber. Samples located in the area with a high yield of ion-to-atom flux ratio probably experienced excessive ion bombardment and high defect densities resulting in a deteriorated hardness of 15.9 GPa.

There have been considerable efforts in recent years to synthesise nanocomposite thin films containing. One of the most promising coatings is nanocomposites film consisting of nanocrystalline (nc-) CrN phase embedded in an amorphous (a-) \( \text{Si}_3\text{N}_4 \) matrix which can show a hardness > 40 GPa. It was shown that the microstructure of CrSiN coatings is a mixture of CrN and Cr\(_2\)N when Si/(Cr+Si) is below 11.7%. Amorphous content of the coating become
dominant as the ratio is over 34% and the crystallinity of the coating fade gradually [71]. Solid solution hardening mechanism is also active in CrSiN coating when the Si/(Si+Cr) is about 11% in the coating film due to the substitution of the Cr atom with smaller Si atom in CrN lattice.

Maximina hardness of 38 GPa and the $H^3/E^2$ ratio of 0.31 was reported in CrSiN coatings with microstructure of Cr(Si)N nanocrystallites embedded in an amorphous Si$_3$N$_4$ matrix nanocomposite and Si content of 6.7 at.% [72]. These coating series were deposited in a closed field unbalanced magnetron sputtering system and a substrate temperature of 200–220 °C. The nanocrystals of Cr(Si)N were measured in the range of 5-8 nm. Coatings with higher Si content (6.7 at.% <Si< 10 at.%) showed high performance in wear resistant applications with low COF values of 0.4–0.43 and wear rates of $5\times10^{-7}$ mm$^3$N$^{-1}$m$^{-1}$.

Wo et al. [73] used closed field unbalanced magnetron sputtering technique and tried to control the microstructure of the coatings to achieve high hardness and Young's modulus. Reported hardness for CrSiN coatings is shown in Figure 2.6. Their results showed that the highest hardness of 36 GPa was achieved at about 14 at.% Si concentration. They suggested that a combination of grain boundary strengthening by Si$_3$N$_4$ segregation, fine CrN nanocrystals, the formation of (Cr,Si)N solid solution and high compressive residual stress resulted in the hardness enhancement of the thin films.
Results of Mercs et al. [74] on CrSiN coatings deposited under the intense argon ion bombardment showed that the implantation of argon atoms in the coatings could increase the internal compressive stress and hardness of the coatings to 27 GPa. Silicon atoms in coating deposited with Si content < 0.92 at. % can partially substitute into the CrNx structure and caused both amorphisation of the coating, and lattice constant expansion as shown in Figure 2.7. However, the lattice expansion mechanism contradicts most of the studies on the formation of solid solution in Cr–Si–N coating systems, where (Cr, Si)N films exhibited a decrease in the lattice parameter [16] as shown in Figure 2.6. CrN nanograins with lattice parameters of 4.11 Å embedded in amorphous Si$_3$N$_4$ were detected in coatings with Si content >1.3 at.%. coatings showed the maximum hardness of 30 GPa when Si concentration is 2.2 at.% featuring a nanocomposite nc-CrN/a- SiN$_x$ structure. Further increase of the silicon content in the coating...

![Figure 2.6: Hardness of the Cr$_{1-x}$Si$_x$N coatings as a function of Si at.% concentration measured by nanoindentation](image-url)
resulted in coating softening caused by the rise in the fraction of amorphous SiNx phase in the coating composition.

Figure 2.7. Lattice parameters of fcc-CrSiN phase as a function of Si content (at. %)

Changing the deposition parameters such as sputtering power and bias voltage can significantly alter the microstructure of the coatings[75]. Coatings deposited at 0 bias voltage showed a monocrystalline structure. However, the nanocrystals started to merge and form columnar grains at higher bias voltages of -50 and -250 V. Lattice constant of CrN also showed opposite trends when Si content gradually increases which could be due to the limited solubility of Si in the CrN phase. It seems that Si can dissolve in CrN up to 9 at% [28]. Formation of Si$_3$N$_4$ phase starts at higher Si contents and is responsible for the creation of nanocomposite structure.
Another hardening mechanism is by depositing a multilayered structure of crystalline CrN\(_x\) and amorphous Si\(_3\)N\(_4\) on the substrates. For instance, Kim et al. [76],[77] sputtered multilayers of CrN and Si\(_3\)N\(_4\) with different Si contents of 5 and 10 at.% and superlattice periods (D) of 14 nm and 17 nm, respectively. Their results showed that coatings with higher Si content exhibited denser structure with reduced grain size. The hardness of CrSiN coatings increased to 24 GPa in the coating.

A similar study on the CrSiN coatings showed that the CrN lattice is profoundly influenced by Si concentration [78]. The result of this study showed that low level of Si (Si < 3 at.\%) does not change the crystallite size of CrN meaning that Si is soluble in CrN as shown in Figure 2.6. Further increase of Si content between 3 to 7 at.% leads to even smaller CrN grain size. When Si concentration is above 7 at.\%, it starts to segregate between CrN grains and furthered the crystallite size reduction. CrN lattice constant changed in range did not change significantly as the Si content of the coating changed and remained in the range of 4.105 Å to 4.090 Å. Coating hardness as shown in Figure 2.7 increased gradually as Si content of the coating increases to a maximum of 24 GPa when the solid solution hardening is the dominant hardening mechanism. Formation of SiN\(_x\) matrix with a hardness of about 18GPa at higher Si contents leads to overall softer coatings.

The microstructure of the CrSiN coatings in Zhang et al. [79] study deposited by medium frequency reactive magnetron sputtering also showed CrN structure transition from columnar nanocrystals to amorphous as the Si content increases. The coating hardness as a function of Si content is shown in Figure 2.6. The two hardness peaks were reported for coatings with different microstructures which suggest that different hardening mechanisms are active in coatings with various Si content. Coating with lower Si/(Cr + Si) ratio of 10% exhibited extremely fine CrN crystallines which hinders dislocation activities in CrN nanocrystals and
slow the grain boundary sliding [6,10]. Coating with Si/(Cr + Si) ratio of 36% showed the hardness of 23 GPa which could be due to relatively high compressive stresses in the thin film layer. XRD analysis confirms the excessive internal stresses as the Si content of the coating increases when the CrN (111) diffraction peaks start shifting toward lower angles. Results showed that the film with relative high stress might also exhibit remarkable hardness.

Hardness results of CrSiN coatings deposited by Benlatreche et al. [80] using dual magnetron sputtering system fluctuated as Si content of the coatings changes. The hardness of CrSiN coatings is plotted in figure 2.6 with a maximum hardness of 28 GPa at 7.5 at.% Si. They suggested that the solid solution hardening formation and accumulation of defects in coating lattice caused by atomic bombardment are the central hardening mechanisms. Deterioration of hardness at higher Si content of about 9 at.% was explained by the higher volume fraction of amorphous Si$_3$N$_4$ phase with poor mechanical properties.

Shah et al. [81] results showed that maximum enhancement of the hardness (28 GPa) and modulus (246 GPa) was obtained at 6.33 at.% Si content. Hardness improvement caused by the formation of CrN/Si$_3$N$_4$ nanocomposite was reported when Si content varies between 6.33 at.% and 14.88 at.% in the coatings. Further increases in Si content results in volume fraction of the amorphous Si$_3$N$_4$ matrix which leads to coating softening.

The alloying of CrAlN with silicon could significantly affect the grain size, the phase composition and the mechanical properties [14,15]. In such a quaternary CrAlSiN compound, Si tends to segregate as amorphous Si$_x$N$_y$ along the grain boundaries [14]. This effect leads to an improved oxidation resistance with the nanocomposite structure assuring the hardening of the materials even with a decrease of the intrinsic stresses. Polcar et al. [82] studied the CrAlN (Cr/Al ratio 0.8), CrAlSiN (Cr/Al ratio 1.16) and AlCrSiN (with Cr/Al ratio 0.53) coatings.
CrAlSiN and CrAlN exhibited cubic B1-type, while AlCrSiN exhibited a mixture of Cr(Al)N cubic phase together with the hexagonal AlN phase.

2.5. Thermal Stability of Hard Coatings

Thermal stability of hard nanocomposite coatings defines their ability to keep their nanostructure, phase composition, and hardness at high temperatures [49]. The performance of coatings for cutting tools depends highly on the hardness and the oxidation resistance at elevated temperatures as the temperatures may frequently reach above 1000 °C at the edge of cutting tools during metal machining and hot forming [8]. The high temperature applications result in oxidation of the coating, which affects their wear resistance and friction coefficient. It must be noted that as-deposited nanostructured nanocomposite coatings are thermodynamically unstable. If the coating temperature exceeds a critical value \( T_c \), nanostructure becomes unstable and gradually transforms into the conventional crystalline material as the diffusion and grain growth mechanism become dominant. When coating temperature is above the critical temperature \( T > T_c \), the coating loses its thermal stability and subsequently its resistance to oxidation, wear, corrosion and stress reduces considerably [1], [49], [52], [83], [84].

Several techniques have been used to measure the thermal stability of the coating. In some studies, hardness is used as the indicator of coating stability before and after annealing [35], [38], [85], [86]. Phase segregation and substrate/coating diffusion at high temperatures were also studied in several studies [87]–[91]. Some others focused on the effect of internal/external stresses on the as-deposited coating and the stress release during annealing process [92]. To
improve the oxidation resistance of these coatings, ternary compounds consisting of Al, Si, V, Nb, Cu, etc. have been added to the coating composition. It was shown that including elements with high thermal stability in the coating like Yttrium could improve the stability of the coatings. Modifying the interface structure through designing ternary coating system which exhibits Spinodal separations and immiscibility at high temperatures [87] is also possible. Embedding nanocrystalline phases in an amorphous phase matrix, such as nc–WC&WS₂/DLC [93], nc-TiN/a-Si₃N₄ [88], TiC/a-DLC with hardness of 32 GPa [94], 4–11 nm nc-TiN inside a-Si₃N₄ with hardness of 50–70 GPa [38] and 8–15 nm nc-TiCrCN inside a-DLC with hardness of 40 GPa [47].

Al can produce a sticky oxide layer on the coating layer, which improves its oxidation resistance and the Al-N bonds inside the coating layer increase its thermal stability [31]. It is possible to add Al in TiN coatings and improve the hardness and oxidation resistance. However, Al can cause drawbacks for specific applications, since it leads to higher friction coefficient and poor toughness [94]. It has been reported that the oxidation resistance of CrN and TiN coatings are limited up to about 650 °C. However, (Cr/Ti)AlN coatings are stable up to 900 °C in the air [95] due to the formation of a protective oxide layer, consisting of chromium and aluminium oxides, which eventually suppress the oxygen diffusion into the bulk, providing excellent oxidation resistance. The presence of aluminium oxide after the isothermal tests was identified only by testing the chemical composition of the surface oxide scale; the absence of Al₂O₃ peaks in XRD diffractograms suggested an amorphous nature of aluminium oxide. Lin et al. [9] showed that CrAlN film exhibited crystalline alumina only when annealed at 1000 °C.

Coatings consisted of cubic (c-) structured phases such as c-TiAlN and c-CrAlN have exhibited superior mechanical properties and oxidation resistance in comparison to traditional binary TiN
and CrN coatings [97], and have been successfully used in the industry. TiAlN coatings are widely used for metal machining because of its superior mechanical properties at elevated temperatures. CrAlN coatings show poor wear resistance at high-temperature. However, CrAlN coatings regarding corrosion and oxidation resistance are preferred [34] to TiAlN coatings. In short, there is an opening for functional coatings having both high hardness and good oxidation resistance at elevated temperatures. With a similar Al content, c-CrAlN coatings exhibit higher oxidation resistance than c-TiAlN coatings owing to the formation of a dense $\text{Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$ mixture on the surface [52]. On the other hand, c-TiAlN coatings outperform c-CrAlN coatings regarding the capability of maintaining high hardness at temperatures between 600 to 950 °C because of spinodal decomposition [96].

Most of the coatings designed for high temperature applications rely on the formation of a protective oxide scale by interaction with the environment. This scale must fulfil several conditions: be stable, slow-growing, dense and adherent. It is well known that in an oxidation or corrosive environment Ti element often forms a porous non-protective oxide scale [61], and therefore the oxidation and corrosion resistance of titanium-based coatings are limited. Nevertheless, it has been demonstrated that the presence of Ti, even out-diffused from the substrate, would perturb the formation of the protective $\text{Al}_2\text{O}_3$ scale at high temperature (1000 °C) and consequently affect the coating oxidation resistance.

It has been reported that the activation energies at 923 K for the oxidation of TiN, CrN and TiAlN are 136, 225 and 471 kJ/mol, respectively [95]. Furthermore, the oxidation of CrN is controlled by the outward diffusion of Cr ions through the $\text{Cr}_2\text{O}_3$ layer formed on each CrN grain, and the oxidation of TiAlN is mainly controlled by the aluminium content [18,19]. It is therefore expected that the presence of Cr and Al in CrAlN coatings will significantly improve the oxidation resistance due to the formation of complex aluminium and chromium oxides,
which eventually suppress the oxygen diffusion [20]. The superior oxidation behaviour of CrAlN coatings is due to the strongly differing values of the Gibbs free energy for the oxide formation. Over a wide temperature range, Al$_2$O$_3$ is much more stable than Cr$_2$O$_3$ (i.e., for Al$_2$O$_3$, $\Delta G^\circ=\text{-378.2 kcal/mol}$ and Cr$_2$O$_3$, $\Delta G^\circ=\text{-252.9 kcal/mol}$).

Banakh et al. [20] investigated the oxidation resistance of CrAlN films in air at temperatures up to 900 °C. Coating characterisation results reveal the presence of a mixture of rhombohedral structured Al$_2$O$_3$ and Cr$_2$O$_3$ crystallises with similar lattice parameters. They concluded that with a sufficient supply of Al atoms, a mixed fully oxidised surface layer is formed. This layer then acts as a diffusion barrier to oxygen, thereby curtailing any further oxidation of the bulk nitride. The study of Thobor-Keck et al. [96] on CrSiN coatings showed that addition of 3 at.% Si to the CrN coating can enhance the oxidation temperature from 750 to 900 °C compared to pure CrN coating by hindering Cr$_2$N phase formation and CrN recrystallisation in the nanocomposite coating.

Mayrhofer et al. [24] developed Ti$_{1-x}$Al$_x$N ($x=0.5, 0.66$) coatings in cubic B1-type structure, with an approximately equal amount of Al and Ti in the film. Reduction of TiN lattice parameter in TiAlN coating from 4.23 Å to 4.17 Å confirms the formation of (Ti, Al)N solid solution. Figure 2.7 shows the hardness of pure TiN and Ti$_{0.34}$Al$_{0.66}$N coatings as a function of annealing temperature. Results show that TiAlN coating exhibits superiority to TiN regarding retaining mechanical properties. Interestingly, a hardness increase in multi-phase TiAlN coating between 600 and 1000 °C was detected which indicates the activation of age hardening mechanism in the coating. Spinodal decomposition of (Ti, Al)N solid solution into fcc-TiN and fcc-AlN domains at 800 °C restricted dislocation movement and caused an increase in coating hardness. The hardness of TiAlN coating drops at 1000 °C as the fcc-AlN converts into hcp-AlN with poor mechanical properties.
Barshilia et al. [95] measured the hardness of annealed samples and compared the oxidation resistance of CrN and CrAlN coatings in the air as shown in Figure 2.7. CrN and CrAlN coatings maintained their initial hardness of 18 and 33 GPa, respectively, up to 500 °C and then their hardness decreased sharply with the almost similar trend. CrN and CrAlN coatings showed the hardness of 7.5 and 22.5 GPa after annealing at 700 °C, respectively.

Chim et al. [97] investigated the hardness of TiAlN (Al/Ti ratio=1) and CrAlN (Al/Cr ratio=1) coatings after annealing. Results showed that CrN and TiN coatings possess lower hardness compared to CrAlN and TiAlN coatings at room temperature. Oxidation and softening of TiN and CrN thin films started at about 500 °C, while the oxidation temperature of TiAlN and CrAlN systems happened above 600 °C. CrN coating recovered its hardness in temperature range 700 to 1000 °C which could be due to the formation of a dense layer of \( \text{Cr}_2\text{O}_3 \) phase with a hardness of 30 GPa. CrAlN showed low oxygen content around 19 at.% after annealing.
at 1000 °C. Also, CrAlN hardness was remained almost constant in the range of 33 to 35 GPa up to 800 °C and showed even the highest hardness up to 1000 °C.

Forsén et al. [98] showed that adding Ti to AlCrN coatings can significantly enhance the thermal stability of the coatings up to 1100 °C as depicted in Figure 2.8. The oxidation resistance of the coatings at high temperatures deteriorated as the Ti content increased due to the formation of a TiO$_2$ layer on the coating surface. Coating with Ti$_{0.11}$Cr$_{0.28}$Al$_{0.61}$N composition showed superior oxidation resistance as well as acceptable mechanical properties after annealing at 1100 °C compared to more conventional Ti$_{0.33}$Al$_{0.67}$N one.

![Figure 2.9. Effect of Ti concentration on the hardness of annealed Cr(Ti)AlN coatings [98]](image)

Results depicted in Figure 2.9 shows that the hardness of the coatings increased after annealing between 800 to 1000 °C compared to as-deposited and lower annealing temperatures. Spinodal decomposition of the of the coatings into (Ti, Cr)N and Al-rich (Ti, Cr, Al)N solid solutions can efficiently prevent dislocation movements in the coating. Addition of Ti to the coatings
also suppressed the formation and growth of h-AlN and stabilised the cubic solid solutions lattice. Altogether, this results in improved high temperature mechanical properties. These studies showed that high thermal stability of a hard nanostructure coating depends on the chemical activity of the system. The phase composition should provide a thermodynamic driving force which results in spinodal phase separation [50]. For example, diffusion rate at grain boundaries and nanostructural resistance against recrystallisation are the primary sources of thermal stability and self-hardening of Nc-TiN/a-Si$_3$N$_4$ and nc-TiN/a-BN nanocomposite coatings. Immiscibility of the phases in those composites plays a vital role in their thermal stability up to 1000 °C [49]. Observations confirmed the formation of oxides such as SiO$_x$ and YO$_x$ at grain boundaries in nc-(Al$_{1-x}$Ti$_x$) N/a-Si$_3$N$_4$ and TiAlYCrN coating systems, respectively, have a critical impact on oxidation resistance improvement [1],[47].

Several studies investigated the improvement of the thermal and oxidation resistance of hard coatings beyond 1100 °C by incorporating large (substitutional) atoms like Yttrium and Zirconium. It has been suggested that these dopants can retard recovery, decomposition and recrystallisation processes which based on diffusion at high temperatures. Sánchez-López et al. [68], [99], [100], [101] studied the influence of the dopant nature on the tribological performance of CrAl(Y, Zr)N coatings deposited by direct current magnetron sputtering. Yttrium has been anticipated to efficiently improve the oxidation resistance of the coatings by segregating at fast diffusion paths and blocking the oxidation diffusion along grain boundaries [11], [15], [18–20]. Yttrium as a reactive element can reduce the accumulation of voids at the substrate/scale interface [21] and hinder the coating decomposition up to 1100 °C. Rojas et al. [67] investigate the oxidation resistance of CrAlYN coatings annealed in air at 1000 °C for 2 h. The deposited coatings consisted of cubic Cr(Al)N phase with a dense columnar microstructure that resisted the oxidation in air up to 1000 °C. Results showed that yttrium
reinforced the oxidation protection provided by aluminium against oxygen reactivity and successfully reduced the oxidation rate and modified the oxide growth mechanism. The addition of this element promotes the formation of a dense mixed (Cr, Al)-oxide top layer that avoids the inward diffusion of oxygen. Zirconium atoms did not diffuse together with Cr and Al which slow oxidation progresses.

2.6. Effects of Deposition Parameters

Several parameters should be considered in the process of coating deposition technique including coating application, cost, required properties, its thickness, temperature restriction, etc. The specific requirement should be considered to fabricate a nanocomposite coating with desirable properties. For example, the components of the coating must be deposited at the same time to successfully form the desired immiscible structure. The process of nano-segregation during coating deposition needs sufficient surface mobility which clearly shows the significance of the deposition conditions [49].

Hard thin films have been successfully produced through different physical vapour deposition (PVD) methods including DC magnetron sputtering [3,11,12], arc ion plating [13], and cathodic arc evaporation. The most convenient deposition process to produce nanocomposite coatings is magnetron sputtering based PVD techniques. Widespread hard/superhard nanocomposite coatings have been developed through sputtering techniques [19], [71], [102]–[105]. Also, although each deposition technique has its advantages, sputtering is known to be more suitable for industrial applications [106].

Sputtering techniques can overcome many difficulties if it is practised skilfully in the right application. It is quite practical to monitor the chemical composition of the resultant coating
by using Co-sputtering of single element targets. This feature allows independent control of each element or target source with available power density parameters. Sputtering deposition offers a wide range of target materials, better step coverage, uniform deposition, small shadow effect, and proper adhesion. Coating properties such as hardness, roughness, film density, and adhesion strength can be controlled using sputtering [107] and is a much safer method in comparison to CVD. In machine components, the primary challenge facing PVD applications is the complex geometry of the machine parts as well as the low deposition temperature. The low deposition temperature inhibits distortion and helps to maintain the mechanical properties of coating and substrate. Direct current or medium frequency reactive magnetron sputtering systems are suitable techniques to apply Cr$_{1-x}$Al$_x$N coatings are for these purposes.

Magnetron sputtering process gives us the power to determine the microstructure of coating. Microstructure design is possible through precise manipulation of sputtering parameters including substrate temperature, substrate ion current density, bias voltage, the partial pressure of reactive gas and stress release annealing temperature. One source of confusion is that in each deposition process includes many parameters that operate simultaneously and can change the structure and properties of the film. The magnetron configuration and substrate position play an important role in determining the ion-to-atom ratio at the substrate, and thus substantially influence the coating structure and properties [18]. It means that magnetron sputtering can produce a specific texture with controlled microstructure at low operating temperatures. As mentioned above, thermodynamic roles govern the deposition of nanostructured coatings. For instance, there is an exact temperature at which the crystalline phase will grow up to a particular diameter. Diffusion processes during sputtering are responsible for segregating system and also affected by operating temperature.
On the other hand, any more heating of coating results in significant grain growth and grain boundary segregation [108]. It was shown that nitrogen pressure could affect the crystallite size in the coating during the deposition of metal-nitride coating systems [109], [110]. Other factors such as the concentration of the elements are also profoundly influence the crystal size. This fact was observed in several systems such as TiN–Cu, nc-TiN/a-Si$_3$N$_4$, nc-TiB/a-Si$_3$N$_4$ and nc-W$_2$N/Si$_3$N$_4$ [48], [89], [111]. For example, CrAlN films can be easily produced by sputtering of elemental targets (Cr and Al) in the reactive gas ($N_2$) with the desired composition and controlled multilayer or compositionally graded structure. Under standard magnetron sputtering, the sputtered targets generate a range of species that include energetic ions (1–10%), and neutral atoms (e.g., Cr, Al). These species can chemically react with gas atoms that impinge on the substrate surface to form a compound film. Ion species in the sputtered metal flux can be used to increase the ion bombardment of the growing film by applying a negative substrate bias voltage. The energetic particle bombardment has been used to improve the adatom mobility and nucleation rate, thereby affecting the microstructure and properties of the growing films [17].

As mentioned above, the nanocomposite films can be sputtered from alloy/element targets. For instance, to apply continuous changes in the chemical composition of a two-phase nanocomposite coating, one has to co-sputter two targets made of different pure elements [106]. While one transition converts a crystalline phase to amorphous, another one could change a nanocrystalline phase to a different nanocrystalline phase. It may merely change the crystallographic orientations of grains which belong to the same material [44]. Each transition region matches a specific chemical composition which creates nanocrystal/amorphous or nanocrystal/nanocrystal coatings.
Lin et al. [112] investigated the dependence of the microstructure and properties on the substrate to chamber wall distance for CrAlN films deposited by pulsed closed field unbalanced magnetron sputtering (P-CFUBMS). P-CFUBMS has been used to produce a wide range of nitride and oxide thin films due to its high deposition rate (compared to conventional magnetron sputtering), the controllable stoichiometry of the film, and long-term deposition stabilisation [15,16]. Characterisation of CrAlN films showed that as the substrate to chamber wall distances increased from 127 and 152 mm to 229 mm during deposition, the preferred orientation of the coatings changed from (200) to most closed packed (111) plane, and at the same time, grain size decreased in the films. Results showed that the substrate to chamber wall distance had a strong influence on the ion flux in the discharged plasma. Higher ions flux for samples with a larger distance to the chamber wall (203 mm) facilitated ion bombardment on the substrate and led to higher atomic mobility on the substrate surface. This higher mobility increased the nucleation sites and resulted in coatings with denser structure, finer grain size, good wear resistance and improved hardness (30.55 GPa) and Young's modulus (353.87 GPa). Effect of substrate position on the measured mechanical properties of these coatings is shown in Figure 2.10.
Figure 2.10. Influence of substrate to chamber wall distance on the mechanical properties of CrAlN coatings [112]

During the sputtering process, energetic ions attack the surface of the growing film and their kinetic energy transfers to other atoms and excite them. Excited surface atoms move around until they settle down at energetically proper sites. Sufficient increase of ion bombardment and higher flux of energetic ions results in: (1) resputtering of the surface atoms that fill the voids; (2) forming of high density films with a smooth surface; and (3) increase nucleation sites and reduce the crystallites size in the film structure.

Khamseh et al. [113],[114] employed pulsed magnetron sputtering to produce highly energetic species by pulsing the power of the targets. CrAlN films deposited at higher pulse frequencies and increased energetic bombardment showed higher values of internal stress, and their grain size reduced continuously with increasing pulse frequency. A larger number of preferential nucleation sites and defects led to finer grain size down to approximately 20 nm, higher internal...
stress, slower multiplication and mobility of dislocations, and enhanced hardness of the CrAlN coating film up to 36 GPa according to the Hall–Petch relationship.

N$_2$/Ar gas flow ratio during sputtering can alter the microstructure of the coatings. For example, the N$_2$/Ar ratio of 30/10 can lead to a decrease in total sputtering gas pressure and intensify the energetic bombardment of the growing film. Higher energetic bombardment of the films increases the internal stresses and hardness 42GPa. The crystal structure also changes from NaCl-type in CrAlN coatings to mixed structures of wurtzite-type Cr$_2$N, wurtzite-type AlN and NaCl- type CrN phases at lower sputtering pressures (N$_2$/Ar=30/10) and higher pulse width. CrN coatings deposited at 60:40 ratio of Ar:N$_2$ content [81] showed the hardness value of 21 GPa due to the presence of a mixture of h-Cr$_2$N and CrN phases. Similar CrN coatings deposited in pure N$_2$ exhibits a high hardness of 27 GPa thanks to fine grain size (15 nm), reduction in surface roughness and lower defects density which increases the density of the coatings.

Lin et al. [115] studied the effects of pulsing the Cr and Al targets asynchronously and synchronously on the IEDs of the plasma, for different frequencies (100 kHz to 350 kHz) and duty cycles (65–90%). The stable cubic crystal structure at 100 kHz changes to a mixture of cubic and hexagonal phases in the films deposited synchronously at 250 and 350 kHz that reduced the overall coating hardness as shown in figure 2.11. The low level of N concentration and increased Al/(Cr+Al) ratio in the film resulted in the formation of the hexagonal phases consisting of h-AlN and h-Cr$_2$N ($\beta$-Cr$_2$N). Higher pulsed ion energy and a larger number of high energy ions in the plasma increased the point and line defects, residual stress and coating hardness. Some of the internal stresses may is due to the lattice distortion due to the presence of Al in the coating lattice.
In general, coatings with higher internal stress and finer crystallite size exhibit higher hardness. One way to improve these parameters is to increase the substrate bias voltage. For instance, in the study of Wüstefeld et al. [116] on Ti$_{1-x}$Al$_x$N, the indentation hardness of the coatings increased with increasing bias voltage (from -20 to -120 V) in all composition series. Studies on CrN based coatings showed that the bias voltage increment produces an increase in the Cr concentration, presenting low roughness, high adhesion strength, high hardness, high elastic modulus as well as higher H/E ratio. Studies of Benegra et al. [12] on TiN coatings showed higher compressive residual stress and lower average grain sizes were observed with an increase in the negative bias voltage applied to the substrate.
2.7. The Role of Computational Simulation

There have been significant advances and developments in characterisation and design of superhard coatings recently. However, there is still a vast distance between our abilities to control the coatings structure and resulted thermal stability. Coatings with different microstructure and phase compositions could exhibit similar hardness and different high temperature behaviour. Therefore, extensive research is required to clarify those observations further. It is not experimentally possible to investigate all the possible coating systems which may possess superior mechanical and thermal properties. Harsh operational conditions are sometimes not accessible under experimental conditions. Theoretical calculations can be an alternative approach to further study and characterise different combination of available candidates.

Density function theory (DFT) is a robust atomic simulation method. It can predict and optimise atomic structures based on electronic properties of the components. Knowing the electrical and structural properties of a coating is a significant advantage to predict physical and mechanical properties of the coating. Based on available experimental data, it is possible to optimise atomic models of the hard coating and study high temperature behaviour of the coating. According to the available literature, current laboratory equipment imposes several limitations for analysing hard coating at working condition. However, precise atomic modelling of the coating could be very helpful. It is widely accepted that quantum theory can describe most of the physical and chemical reactions. It has been demonstrated that the quantum mechanics can predict the total energy of a system consist of electrons and nuclei.

The first-principles, the total-energy calculation can predict the important quantities such as atomic structures and bonding energies, and may further provide critical information on
chemical reactions in the coating or on the coating surface. Recent advances in predicting phonons oscillations enable one to obtain thermo-elastic properties at elevated temperatures and pressures. Atomic modelling helps to understand the influence of elemental composition and phases structure of the nanocomposite coating on its thermal stability and oxidation resistance, to find superhard coating systems with high thermal stability properties, and provide electronic properties of investigated materials such as charge distribution, the density of states and band structure.

Transition metal nitrides including TiN and CrN have received considerable experimental and theoretical attention regarding their potential technological applications in industries thanks to excellent hardness, high melting point, high chemical and thermal stability and good wear and high corrosion resistance. Figure 2.12 shows the crystal structure of CrN and TiN.

![Crystal structures: (a) CrN and (b) TiN](image)

Figure 2.12 Crystal structures: (a) CrN and (b) TiN (dark blue, light blue and grey spheres denote Cr, Ti and N atoms, respectively).

First-principles calculations have been used to study the structural, electronic, phonon and thermodynamical properties of these metal nitrides [117], [118]. Other studies focused on the structural and mechanical properties of transition metal nitrides under high pressures and high
temperatures [119]. Phase transition if CrN from B1 type fcc to orthorhombic has been studied using different modelling techniques and different exchange correlation potentials [120]–[123]. CrN in the form of mono-nitride crystallised in the NaCl structure. CrN is the only member of the mononitrides which exhibits antiferromagnetism and Neel temperature about 273 K and reported magnetic moment of 1.4 $\mu$B [124]. Magnetic structure of CrN transfers from paramagnetic to antiferromagnetic. Figure 2.13 shows the pressure-temperature phase diagram of CrN based on the GGA+U and LDA+U methods.

![Phase diagram of CrN](image)

**Figure 2.13.** Calculated pressure-temperature phase diagram of CrN based on the GGA+U and LDA+U. Schemes compared to experiment (open circles and squares). [123]

This transition is also accompanied by an orthorhombic distortion of the rock-salt structure. The space group of orthorhombic CrN was determined as Pnma. Mavromaras *et al.* [124] studied the electronic and magnetic properties of rock-salt and orthorhombic structures of CrN by Self-consistent band structure calculations. Thermo-mechanical properties of CrN and TiN
has been investigated using various first-principle methods including electronic structure model [125], ab initio molecular dynamics [126] DLM-MD and static calculations [127].

CrAlN and TiAlN coatings have exhibited excellent oxidation resistance and mechanical properties and attracted industrial and academic interests. Alling et al. used first-principles calculations to investigate the stability of Cr$_{1-x}$Al$_x$N and Ti$_{1-x}$Al$_x$N systems [128]. Their results showed that Cr$_{1-x}$Al$_x$N is more stable against spinodal decomposition than Ti$_{1-x}$Al$_x$N. The mixing enthalpies of Ti$_{1-x}$Al$_x$N and substitutional disorder at the metal sublattice was studied using first principle calculations. Figure 2.14 shows the differences between the calculated mixing enthalpies and second concentration derivatives of Cr$_{1-x}$Al$_x$N and Ti$_{1-x}$Al$_x$N phases. Plots show that the calculated mixing enthalpy of Ti$_{1-x}$Al$_x$N is highly asymmetric and two to three times larger than Cr$_{1-x}$Al$_x$N mixing enthalpy for the most of the AlN fraction range. The shape of Cr$_{1-x}$Al$_x$N enthalpy curve is symmetric behaviour concerning equal fractions of CrN and AlN. The second concentration derivatives show more significant differences between these two phases. The second derivative of the Cr$_{1-x}$Al$_x$N curve behaves like a smooth parabola. On the other hand, the second derivative of Ti$_{1-x}$Al$_x$N changes from positive to very large negative values as the AlN fraction rises above x=0.50.
Tasnadi et al. [129] optimised the numerical methods to predict the elastic constants of Ti<sub>0.5</sub>Al<sub>0.5</sub>N alloy and concluded that the main three tensors are C<sub>11</sub> = 447 GPa, C<sub>12</sub> = 158 GPa, and C<sub>44</sub> = 203 GPa. Figure 2.15 presents the cubic-averaged elastic constants (C<sub>44</sub>) for the Ti<sub>0.5</sub>Al<sub>0.5</sub>N system. It can be seen that the cubic-averaged elastic constants converge faster concerning the number of atoms. They also conducted their proposed nine-dimensional analysis provides a less demanding technique to achieve convergence for the elastic constants.

In a similar study, the elastic stiffness constants of the Ti<sub>1-x</sub>Al<sub>x</sub>N alloys were calculated using a special quasi-random structure method [130]. Tasnádi et al. [131] presented a computational technique to investigate non-equilibrium vacancies in the metastable TiAlN system.
2.8. Summary

Industrial tools usually expose to extreme working conditions, such as high temperatures above 700 °C and oxidising/corrosive atmospheres. These conditions accelerate the degradation of the machinery, which significantly constrain their application and service life. The present literature review showed that hard coatings have exhibited outstanding potentials to expand oxidation and wear resistance of machining tools and engineering devices. Current literature review shows that TiN and CrN based hard coating system can improve the service life and efficiency of tools with their high thermal stability and oxidation resistance at high temperatures.
As discussed above, coating designing is an effective process to fabricate hard/superhard coatings with excellent thermal stability. Deep knowledge of the coating nanostructure and chemical properties of the coating constituents are vital parts of this process. Adding specific elements to the coating composition, modifying the interface complexity, creating an amorphous matrix are the well-known techniques to improve the thermal stability of hard coatings. Also, it is vital to find the connections between phase transition and nanostructure of the hard coatings since these parameters play a crucial role on the high temperature properties of the protective coating and stability of hard coatings.

Microstructural analysis and nanoindentation measurements clearly show that coating deposition technique and deposition parameters can improve the oxidation resistance and hardness of hard coatings. Therefore, several studies have been conducted to realise the effects of deposition parameters on the properties of hard coatings. However, the variety of deposition techniques such as magnetron sputtering and related deposition parameters, including the frequency, gas flow, substrate position inside the chamber, substrate bias voltage, deposition temperature and surface preparation, indicate that there are still a large number possibilities for future studies and examinations to find the optimum coating systems with the best protective properties.

In this work, we study hard/superhard nanocomposite magnetron sputtered metal nitride coatings using a combination of imperial and theoretical techniques. This study aims to investigate the effect of the sputtering parameter and composition on the coatings properties at high temperatures. Since high temperature mechanical properties of coatings are not measurable via experimental investigations, DFT and QHA calculations will be used to estimate mechanical properties of main phases in the coatings.
Chapter 2 - Review of relevant literature

2.9. References

Chapter 2 - Review of relevant literature


258, 2013.


[85] W. Herr and E. Broszeit, “The influence of a heat treatment on the microstructure and


Chapter 2 - Review of relevant literature


Chapter 2 - Review of relevant literature


Chapter 2 - Review of relevant literature


Chapter 3

Methodology

>This chapter presents an overview of the main experimental and computational techniques employed within the scope of this study. Specific details of experimental settings and computational conditions are mentioned in subsequent chapters.
3.1. Overview

The experimental work carried out in the present study can be classified as characterisation of 3d transition metal nitride thin film coatings (e.g., CrN, TiN, CrAlN, CrSiN, CrNiN and TiSiN) prepared by unbalanced magnetron sputtering. These coatings were tested for their microstructural/phase compositions and their mechanical properties analysed by synchrotron powder diffraction beamline, scanning electron microscopy, X-ray photoelectron spectroscopy (XPS), nanoindentation technique. This chapter also deals with the instrumentation and brief theoretical insights of various experimental techniques used for the characterisation of coatings. Characterisation of nanocomposite coatings needs high precision instruments. Investigation of the surface structure of these materials is essential because the surface chemistry of these coating materials is quite different from their bulk structures. Magnetron sputtered CrN and TiN coatings in Pure and doped conditions were studied in present work by means of several experimental techniques. The phase identification and quantitative analysis of the thin film coatings were performed at synchrotron powder diffraction beamline in the temperature range of 25 to 1000 °C. The synchrotron XRD (SR-XRD) was supported by XPS and SEM for surface chemical analysis and morphology, respectively. The mechanical properties of the coatings including the hardness and elastic modulus were measured by nanoindentation technique. This chapter contains a brief theoretical background for the various experimental techniques that have been used in this work.

3.2. Experimental Configurations

3.2.1. Magnetron sputtering Technique
CrN, CrAlN, CrSiN, CrNiN and TiSiN coatings with thicknesses of 2-4 µm were deposited using a Teer UDP 650 Closed Field Unbalanced Magnetron Sputter Ion Plating (CFUBMSIP) system with a four-target configuration (Figure 3.1). Unbalanced magnetron sputtering system can provide high deposition rates, high density, better uniformity, low substrate temperature and enhanced ionization efficiencies in the plasma compared to conventional sputtering system.

![Image](image1.jpg)

Figure 3.1 Closed field unbalanced magnetron sputter ion plating (CFUBMSIP) system manufactured by Teer Coatings Ltd design

M2 steel substrates were heat treated with a final hardness of 62 HRC. The substrates were polished, ultrasonically cleaned and then dried before being loaded into the vacuum chamber. The average surface roughness of the substrates was about 30 nm.

Before deposition, the background pressure was evacuated to $2.0 \times 10^{-6}$ torr, and sputter etching was carried out in an Ar gas environment at a bias voltage of -500 V for 30 min to remove surface oxides and other contaminants.
The deposition of CrAlN was conducted in mixed N\textsubscript{2} and Ar gases by reactive sputtering from Cr and Al targets. Two Cr targets, one Al target and one “dummy” Si target, were used. During deposition, the substrates were heated at 550 °C and rotated at a speed of 10 rpm. The bias voltage was set to -80 V. The working pressure of Ar/N\textsubscript{2} was kept approximately at 1.3 mtorr with the flow rate of Ar and N\textsubscript{2} at 50 and 60 sccm, respectively. A chromium wetting layer was first deposited. CrAlN coatings with varying Al contents were then grown by changing the currents of the Cr and Al targets.

CrSiN and CrNiN coatings with thicknesses of 1-2 µm were deposited onto M2 steel substrates using a closed-field unbalanced magnetron sputtering system (Teer Coatings Ltd, UK) with a four-target configuration. Pure chromium (Cr), silicon (Si) and nickel-chromium alloy (Ni:Cr=80:20 at.%) targets (99.9 % purity; 345×145×8 mm\textsuperscript{3} size) were used to synthesize the nitride coatings. In this experiment, two Cr, one Si, and one NiCr targets were installed in the coating system for deposition. High purity (99.999 %) Ar and N\textsubscript{2} gases were used as the working and reactive gas, respectively. The flow rates of these gases were controlled by MKS mass flow controllers. The vacuum chamber was pumped down to a background pressure of 4 \times 10^{-4} Pa before coating deposition. The pressure of the working gas was maintained at ~0.3 Pa during the sputtering process. The target-to-substrate distance was set to be 17 cm. The substrate rotation speed was 10 rpm during sputtering. In the first stage, the substrate was sputter cleaned by Ar plasma at a bias of -450 V (frequency 250 kHz) for 20 min, in order to remove the surface oxide layer or any contaminant. Then the bias voltage was reduced to be -80 V at a frequency of 250 kHz for deposition. The target current applied to each Cr target was fixed at 4.0 A (sputtering power ~1.2 kW). The Si or Ni content in the coatings could be controlled by adjusting the target current applied to Si or NiCr target. CrN, CrSiN and CrNiN thin films were deposited at various Ar/N\textsubscript{2} ratio by adjusting their flow rates. The
deposition time was 60 min. There was no external heating to the substrate holder during deposition.

The TiSiN hard coatings (9 samples) were deposited onto AISI M42 tool steel substrates (hardened to HRC 62) by using a closed-field unbalanced magnetron sputtering system with a four-target configuration. The steel substrates were finely polished (Ra ~0.02 μm), degreased, ultrasonically cleaned, and subsequently blown dry in flowing nitrogen gas. The magnetron sputtering system comprised three Ti targets (purity > 99.7 at%) and one Si target (purity > 99.9 at%). The size of the targets was 380 × 175 × 8 mm³. The coating equipment was furnished with a rotating substrate holder at a speed of 10 rpm to permit a homogeneous composition of the coatings, and the target-to-substrate distance was 17 cm. The vacuum chamber was pumped down to a background pressure less than 2×10⁻⁶ Torr before deposition. After that, the Ar working gas (purity 99.995 at%) pressure was set at ~1.3×10⁻³ Torr by controlling the flow rate (50 sccm) of Ar via an MKS mass flow controller. The DC current applied to each Ti target was fixed at 8.0 A (~2.3 kW for each Ti target), while the target current to the Si target was 2.5 A (sputtering power ~0.8 kW). The nitrogen content in the coatings was controlled using a closed-loop optical emission monitor (OEM) with a setting at 60 %, which regulated dynamically the flow of N₂ reactive gas (purity 99.995 at%) via a fast-responding piezoelectric valve. The pressure of Ar/N₂ mixed gases was 2×10⁻³ Torr. The deposition process of the hard coatings comprised three major steps: plasma ion cleaning, Ti adhesive layer (0.2 μm), TiN buffer layer (0.4 μm), TiSiₓN compositional gradient layer (0.3 μm), and TiSiN top layer (2 μm). The Si content in the compositional gradient layer was increased linearly in the thickness direction in order to accommodate the internal stress. The substrate holder was heated by a radiation heater (5 kW) located in the centre of the vacuum chamber, and the substrate temperature was maintained at 550 °C during deposition. The ion etching to the steel substrates
at the first stage (at a bias of -600 V) was employed for 30 min to remove the oxide layers on
the substrate surface. For the sputter deposition of Ti (10 min), TiN (30 min), and TiSi\textsubscript{x}N (20
min) layers, the bias voltage was reduced to -60 V. The top TiSiN layer was deposited for 120
min. The substrate bias was operated in a pulsed mode at a frequency of 250 kHz. In this case,
in order to study the effect of bias voltage, incremental bias voltages (from -30 V to -80 V) was
applied to the substrate holder when the TiSiN top layer (2 µm) was coated. The bias voltage
mainly determined the energy of ions that is bombarding the growing surface. For comparison,
a binary TiN coating of similar total thickness was prepared at a bias voltage of -50 V

3.2.2. Synchrotron radiation X-Ray diffraction (SR-XRD)

It has been shown during the past 20 years that synchrotron X-rays can determine the crystal
structures with extreme sensitivity, accuracy and precision. Synchrotron light exhibits a
number of remarkable properties such as high brightness, wide spectrum energy, tenability,
high polarised and emission in very short pulses [1]. Synchrotron radiation is $10^4$ - $10^{12}$ times
brighter than the conventional laboratory instruments. Synchrotron light exists in varying
energies from infrared light to hard x-ray, i.e. it offers a broad spectral range rather than a
sharply peaked spectrum. The wavelength can be tubed to any selected one with excellent
intensity. The radiation can be in a linear, circular or elliptical form based on the highly
polarised synchrotron light. For monochromatic diffraction, the incident energy can be chosen
using single-crystal monochromators. The radiation also has intrinsically small vertical
divergence and can be focused both horizontally and vertically to image the source.

Synchrotron radiation is produced when electrons are accelerated to 99.9997 % of the speed of
light by the linear. Those electrons are transferred to the booster ring to increase their energy.
Next step is to transfer the electrons to the outer storage ring. Then, magnetic fields are used to
deflect the trajectory of the electrons and cause them to give off energy in the form of electromagnetic radiation. A beam of light is produced at each deflection. The captured radiation is then focused to a specific wavelength and made available to the experimenter via a tangential beamline containing suitable optical components.

The storage ring consists of an ultra-high vacuum chamber (typically about $10^{-10}$ torr) in which an electron or positron current is maintained in a stable orbit at high energies by the use of a lattice of magnets. The charged particles are injected from an accelerator into the ring, at either the final operating energy or a lower one. In the latter case, the injected beam is subsequently accelerated to the desired energy. The particles are maintained in a closed orbit with the use of magnets. Dipolar magnets are used to bend the beam path, and multipolar magnets, such as quadrupoles, to provide focusing and hence maintain a stable orbit. In addition to these magnets, the lattice may contain insertion devices: magnet arrays placed in straight sections of the ring, which act as specialized radiation sources. The emission of synchrotron radiation leads to an energy loss from the stored particles, which is made up by the use of a radio-frequency cavity.

3.2.3. **SR-XRD data collection**

*In situ* SR-XRD experiments were performed on the Powder Diffraction beamline at the Australian Synchrotron with monochromatic X-rays, $\lambda = 0.827 \ \text{Å}$, verified by standard reference material (LaB$_6$ 660b) as supplied by the USA National Institute of Standards and Technology (NIST). The diffraction data were collected by a Mythen microstrip detector over the range of $10^\circ \leq 2\theta \leq 89^\circ$ in flat-plate asymmetric reflection geometry. The coated substrates were mounted on a Pt heating stage in an Anton Paar HTK-2000 high temperature furnace and aligned to the centre of rotation on the diffractometer. The heating rate was 10 °C/min from
ambient temperature up to 700 °C in air atmosphere. The temperature difference between the sample surface and Anton Parr furnace was calibrated manually before the *in situ* experiments carried out.

### 3.2.4. Analysis of XRD data

*In situ* SR-XRD measurements on CrAlN, CrSiN and CrNiN and TiSiN coatings were carried out as a function of temperature to observe changes in crystalline phase composition, lattice parameter, and crystallite size/strain. The experiments were performed on the Powder Diffraction beamline [2] at the Australian Synchrotron with monochromatic X-ray (λ = 0.82646 Å). The instrument was set up in the flat plate and fixed incident beam geometry, with the incident fixed between 4.1 to 5.9°. Data were collected over range 10° to 89° 2θ with a Mythen microstrip [3] in 2 Detector positions for 30sec in each position with movement of 0.5° between positions. The coated substrates were mounted on a Pt heating strip in an Anton Paar HTK-2000 high temperature furnace and aligned to the centre of rotation on the diffractometer. The specimens were heated in air from room temperature to 970 K at 10 K/min [4].

Structural determination is the process of finding an atomic arrangement that is periodic and would produce intensities that fit the experimentally observed pattern. Several parameters affect the peak intensities including the structural factors, multiplicities, Lorentz factor, polarisation and temperature factor, sample absorption, directional growth and extinction coefficients. Calculated intensity of a diffraction pattern, \( I_{\text{calc}} \), is defined as follows:

\[
I_{\text{calc}} = I_b + s \sum L_k |F_k|^2 \phi(2\theta_t - \theta_k)PA
\]

Where \( \theta \) is diffraction angle, \( s \) is the scale factor, \( L \) is multiplicity, \( P \) is preferred growth orientation, \( A \) is absorption factor, \( F \) is the structure factor, \( \phi \) is reflection profile function.
Chapter 3 – Methodology

Rietveld refinement [5] technique employs user-defined parameters to minimise the difference, $R_{wp}$, between and experimentally collected diffraction pattern and a model based on the assumed crystal structures and instrumental parameters:

$$R_{wp} = \frac{\sum |y_i(obs) - y_i(calc)|}{\sum y_i(obs)}$$  \hspace{1cm} (3.2)

where $y_i(obs)$ is the observed intensity and $y_i(calc)$ is the calculated intensity. In this study, Rietveld analysis was used to determine lattice parameters, preferred orientations, crystallite size, macrostrain, residual stress and quantitative phase composition analysis. The diffraction patterns were modelled using the Rietveld method [5] and the double-Voigt method (Table 3.1) as implemented in program TOPAS [6].

<table>
<thead>
<tr>
<th>Profile function</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaussian, $G_{UA}(x)$</td>
<td>$G_{UA}(x) = \left( \frac{g_1}{fwhm} \right) \text{EXP} \left( \frac{-g_2x^2}{fwhm^2} \right)$</td>
</tr>
<tr>
<td></td>
<td>where $g_1 = \sqrt{\frac{\ln(2)}{\pi}}$ and $g_2 = 4\ln(2)$</td>
</tr>
<tr>
<td>Lorentzian, Lua(x)</td>
<td>$L_{UA}(x) = \left( \frac{l_1}{fwhm} \right) / \left( \frac{l_2x^2}{fwhm^2} \right)$</td>
</tr>
<tr>
<td></td>
<td>where $l_1 = 2/\pi$ and $l_2 = 4$</td>
</tr>
<tr>
<td>PseudoVoigt, $PV_{UA}$</td>
<td>$PV_{UA} = \eta L_{UA}(x) + (1 - \eta) G_{UA}(x)$</td>
</tr>
</tbody>
</table>

In the above equations, $fwhm$ is the full width at half maximum, $\eta$ is the $PV_{UA}$ mixing parameter and $x$ is $(2\theta - 2\theta_k)$. $2\theta_k$ is the position of the $k^{th}$ reflection. An accurate description of peak shapes in a diffraction pattern was obtained by applying correctional functions for flat
plate, fixed incident beam geometry [7]–[9] as provided in the APPENDIX 1. Modelled peak shapes were used to determine the volume-weighted mean crystallite sizes ($L_{\text{vol}}$) and microstrain ($\varepsilon_0$) [10]. Phase quantitation was carried out on a relative basis using the approach of Hill & Howard [11]. It was assumed that the weight percent of a phase, $p$, in a mixture is proportional to the product of the scale factor, as derived in a multi-component Rietveld analysis of the powder diffraction pattern, knowing the mass and volume of the unit cell. For example, if all phases in a mixture are identified and crystalline, the weight fraction of phase $W_p$, is given by:

$$W_p = \frac{S_p Z M V_p}{\sum S_i Z W V_p} \quad (3.3)$$

where $S$ is scale factor, $Z$ is formula unit per unit cell of the phase, $M$ is the mass of the formula unit, and $V$ is the unit-cell volume. The initial structural parameters and atomic positions were taken from the Crystallography Open Database (COD) [12],[13] used for phase identification and Rietveld refinements.

### 3.2.5. Scanning electron microscopy

The surface morphology of the films was investigated with scanning electron microscopy (SEM) using a NEON 40 EsB instrument (Figure 3.2). The FESEM was operated at 5 kV. The elemental composition of the films was obtained by energy dispersive spectroscopy (EDS) from an OXFORD Link ISIS unit attached to the SEM.
3.2.6. **X-ray photoelectron spectroscopy (XPS)**

XPS data of all thin films was acquired using a Kratos Axis Ultra XPS spectrometer (Kratos, Manchester, UK) with Al-Kα monochromatic radiation ($h_\nu = 1486.6$ eV) source and at an operating power of ~10 mA and 15 kV. The XPS machine is also equipped with a cold stage and an Ar ion gun for etching and depth profiling. The samples were mounted on steel sample holder. The chamber pressure was reduced to $2.9 \times 10^{-9}$ Torr and maintained at that level during the analysis. XPS survey spectra were acquired with both etched (10 minutes of ion sputtering) and unetched samples. High resolution XPS spectra were recorded immediately after 6 minutes of Ar+ sputtering. Etching was done to remove any surface oxide and contamination layers. Pass energy of 20 eV was used for high resolution photoelectron lines measurement. CASA XPS (Version 2.3.15) software was used for processing and fitting the peaks of the XPS spectra.
3.2.7. Nanoindentation tests

Mechanical properties, such as Young’s modulus and hardness, of the thin films were measured by a depth-sensing indentation system (Ultra-Micro Indentation System, UMIS-2000, CSIRO, Australia) equipped with a Berkovich indenter. The indenter tip was calibrated by conducting single-cycling indentation tests on fused silica (a standard material having a known modulus of 72 GPa) at different loads. Load–unload tests were run in a closed-loop under load control to determine the mechanical properties of the samples. A maximum load of 20 mN was applied in 10 increments. The loading rate set to 2.5 mN/s represents the static response of the materials. Following each increment, there were 10 decrements, from which Young’s modulus and hardness were calculated. Five indentation tests were performed on each specimen.

An improved technique for hardness and elastic modulus determination were introduced which depends merely on the and resistance to deformation of the material [14]. This method uses a set of load-displacement nanoindentation curves (P-h curve) obtained during one cycle of loading-unloading without the need to image the hardness impression. A controlled load (P) is applied and monitored via an indenter which is in proper contact with the film surface, and the penetration depth (h) are measured during the loading-unloading cycles as typically shown in Figure 3.3.
Figure 3.3. Schematic of indentation deformation at peak load and after unloading

From the $P-h$ curve, maximum load ($P_{\text{max}}$), maximum displacement ($h_{\text{max}}$) can be determined as depicted in Figure 3.3. The hardness ($H$) can be defined as how resistant solid matter is toward various permanent shape changes when force is applied, and it can be estimated from the equation:

$$H = \frac{P_{\text{max}}}{A}$$

where $A$ is the area of the contact made by the indenter. Contact stiffness ($S$) is determined by differentiating the unloading curve at the peak load and can be connected to the reduced modulus ($E_r$) using the following formula:

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A}$$

Knowing the reduced modulus, one can calculate the elastic modulus of the indented material ($E$):

$$\frac{1}{E_r} = \frac{1-v^2}{E} + \frac{1-v_1^2}{E_1}$$

(3.4)

(3.5)

(3.6)
where $E_i$ and $v_i$ are the elastic modulus and Poisson’s ratio of the indenter.

### 3.3 Computational Techniques

Condensed matter physics and materials science are concerned fundamentally with understanding and exploiting the properties of systems of interacting electrons and atomic nuclei. It means that all the properties of materials can be obtained if proper computational setup is available for solving a given problem in quantum mechanics. However, the electrons and nuclei that make up the materials encompass a strongly interacting many-body system, and this means a direct solution of Schrödinger’s equation is an extremely impractical scheme [15], [16].

$$\left\{ \frac{\hbar^2}{8\pi^2m} \nabla^2 + V \right\} \Psi(r, t) = \frac{i\hbar}{2\pi} \frac{\partial \Psi(r, t)}{\partial t} \quad (3.7)$$

where $\Psi$, $m$, and $V$ represent wavefunction, particle mass, plank’s constant and potential energy, respectively.

Thus, various approximations have been done to simplify the Schrödinger equation in real calculations. A very significant simplification is the Bom-Oppenheimer adiabatic approximation. In their formalism, electronic and nuclear have separate coordinates in the many-body wave functions based on the fact that the electron has much less mass than the nuclei. Using this assumption, it is possible to compute the electronic structure at fixed nuclear positions. The importance of the Bom-Oppenheimer approximation became more evident later on when the density functional theory was introduced. Density function theory (DFT) has become an extremely useful tool in computational chemistry to study the molecular properties at the ground state. A schematic representation of a self-consistent loop in this numerical
method is depicted in Figure 3.4. Any self-consistency cycle assumes an initial guess for the electron density, \( \rho(r) \), is assumed which will be used to calculate the effective potential,

\[
\nu_{\text{eff}}(r) = \nu_{\text{en}}(r) + \int \frac{\rho(r')}{|r-r'|} dr' + V_{\text{xc}}[\rho(r)]
\]

(3.8)

Then, the diagonalisation of the Kohn-Sham equations happens

\[
\left[ -\frac{\hbar^2}{2m}\nabla_i^2 + \nu_{\text{eff}} \right] \psi_i = \varepsilon_i \psi_i
\]

(3.9)

which results in the evaluation of new electron density and total energy, \( E_{\text{tot}} \). At this stage, if the convergence criterion is not fulfilled (\( \Delta E > \varepsilon \)), the numerical process will be repeated incorporating the last \( \rho(r) \) to calculate new effective potential. When the criterion is satisfied (\( \Delta E < \varepsilon \)), various output quantities are computed.
Figure 3.4. A flowchart of the DFT iteration scheme.

The accuracy of the calculated values depends on the level of assumptions made, as well as the precision of the numerical simulation. This work applies the density function theory as numbered below.
3.3.1. Structural optimisation

Three-dimensional slab model enabled the investigations of bulk metal nitrides such as CrN, TiN, BN and metals such as Ni. VASP package [17] supported this kind of theoretical simulations, assisting all the structural optimisation and calculating all the energies and vibrational frequencies. All structural optimisations and calculations were performed with the generalised gradient approximations (GGA) as the exchange-correlation potential alongside with the Perdew-Wang 1991 (PW91) functional [18] as implemented in the VASP package. The total energy converged with a tolerance of $1\times10^{-7}$ Ha. All the parameters including the energy cut-off for plan waves, K-point sampling of Brillouin Zones for CrN, AlN, Ni, TiN and BN structures are explained in detail in chapters four, five and six and eight, respectively.

3.3.2. Phonon density of state

Phonon density of state for TiN, CrN and BN phases were calculated using Phonopy code [19] whereas force constants were calculated from VASP outputs. For the phonon calculations, a $2\times2\times2$ supercell of the conventional primitive cell was utilised with eight atoms at each volume grid. In calculations of force constants, atomic displacement distances vary within 0.01 Å. Figure 3.5 shows the calculated phonon density for cubic TiN against the experimentally obtained phonon dispersion.
In order to apply the QHA method within the Gibbs2 code, results from VASP and Phonopy codes were deployed as input to Gibbs2 to calculate all thermodynamic values [21]. Gibbs2 is a program for the calculation of the pressure and temperature dependence of the thermodynamic properties solid phases from ab initio data, within the framework of the quasi-harmonic approximation [22]. In a typical calculation, for a single phase, the user selects a grid of volumes encompassing the equilibrium geometry. At those fixed volumes, the rest of the structural parameters are relaxed, and E(V) curve is obtained, the static energy. QHA thermal model has been implemented together with the static energy curve, either the phonon density of states or the frequencies on a grid sampling the 1BZ are required at each volume.

3.3.3. **Thermo-elastic properties**

![Figure 3.5. Calculated phonon DOS for TiN and experimental phonon dispersion obtained from neutron diffraction of bulk TiN [20]](image-url)
The complete lack of anharmonicity in the harmonic model results into the unphysical behaviour of the materials such as zero thermal expansion, infinite thermal conductivity, etc. One way to account for anharmonic properties is to assume harmonic approximation at any given crystal volume which is the basic of QHA method. Although all the volumes are not corresponding to the equilibrium volume of the crystal [22].

The non-equilibrium Helmholtz free energy (F) of a crystal geometry \((x, V)\) in the QHA model is:

\[
F_{vib}^*(x, V) = \sum \frac{\omega_j}{2} + k_B T \ln(1 - \exp\left(\frac{\omega_j}{k_B T}\right))
\]  (3.10)

where \(\omega_j\) is volume independent phonons, \(k_B\) is the Boltzmann constant. For more details about the QHA modelling refer to Chapter 6.

3.4. References


Chapter 4

Paper I: Electronic Properties and Stability Phase Diagrams for Cubic BN Surfaces


*This chapter presents the electronic configuration and stability phase diagram of cubic BN*
4.1. Abstract

This contribution investigates structural and electronic properties as well as stability phase diagrams of surfaces of the cubic boron nitride (c-BN). Our calculated parameters for bulk c-BN agree reasonably well with both experimental and computed values available in the literature. Based on the energies of the three experimentally recognised phases of bulk boron, i.e., $\alpha$-B$_{36}, \beta$-B$_{105}$ and $\gamma$-B$_{28}$, we estimate enthalpy of formation of c-BN to be -2.816 eV. This value constitutes the first ever estimate for the enthalpy of formation of c-BN. The c-BN(100) surface offers separate B and N terminations (denoted as c-BN(100)$_B$ and c-BN(100)$_N$), whereas c-BN(111) and c-BN(110) are truncated with combinations of boron and nitrogen atoms (denoted as c-BN(111)$_BN$ and c-BN(110)$_BN$). Optimised geometries of surfaces display interlayer displacements up to the three topmost layers. Downward displacement of surface boron atoms signifies a common geometric feature of all surfaces. Bulk c-BN and its most stable surface c-BN(100)$_N$ possess no metallic character, with band gaps of 5.46 and 2.7 eV, respectively. We find that only c-BN(100)$_B$ configuration exhibits a metallic character. c-BN(110)$_BN$ and c-BN(111)$_BN$ surfaces display corresponding band gaps of 2.5 and 3.9 eV and, hence, afford no metallic property.
4.2. Introduction

Crystalline boron nitride (BN) exists in hexagonal (h-BN), cubic (c-BN) and wurtzite (γ-BN) configurations [1, 2]. Its stable structure under standard conditions assumes a hexagonal graphite-like structure [1]. Nearly two decades ago, 2-dimensional BN nanosheets were synthesised with a few layered structures of h-BN analogous to graphite [2], [3]. Bulk c-BN has also been synthesised under high pressure (> 2 GPa) and high temperature (> 1000 K) [1] via chemical vapour deposition techniques. BN nanosheets assume promising applications in many areas, including functional nanocomposites [4], catalysts supports, cutting machinery [4], electrical and optical nanodevices [5] and capturing of pollutants [6]. These unique applications are derived by the remarkable properties of BN, spanning outstanding mechanical properties (elastic modulus \(\approx 0.9\) TPa) [7], high thermal conductivity (up to 2000 W/mK) [7], chemical inertness, large surface area, excellent resistance to oxidation (up to 900 °C) [2] and a large band gap (4.7-6.0 eV) [8].

In comparison to diamond, c-BN displays some remarkable structural similarities and differences. For example, the diamond structure comprises two face-centred cubic (FCC) carbon cells whereas the c-BN incorporates one boron FCC (B FCC) cell and one nitrogen FCC (N FCC) cell. The bonding between atoms is entirely covalent in the case of diamond, while c-BN holds ionicity between 0.26 and 0.48 [9]. c-BN exhibits the largest heteropolar gaps among the III-V compounds. Structural properties of BN highly affect its physical parameters. Measurements by the soft X-ray spectroscopy and UV absorption techniques yielded an indirect band gap of around 6.4 eV [10]. On the other hand, theoretically-derived values widely scatter in the range of 3.9 eV to 10.5 eV [1], [9], [11], [12].
Literature offers detailed theoretical and experimental accounts of structural, optical and mechanical properties of bulk $c$-BN, including lattice constants, bulk moduli, cohesive energies, dielectric constants, and phonon frequencies [1], [13]–[15]. Analogously, surfaces of $c$-BN have been the subject of many theoretical investigations. These studies have mainly aimed to elucidate the structural relaxations in B- and N-terminated surfaces [16]. For example, Kadas et al. [10-11] found that B- and N-terminated (111) surfaces of $c$-BN experience significant relaxations up to the fourth atomic layer. Osuch and Verwoerd [19], as well as Ooi and Adams [12], carried out density functional theory (DFT) calculations to determine the thermodynamically preferred cleavage along the 001 and 110 directions, correspondingly. They demonstrated that a $2 \times 2$ bridge reconstructions terminated with N atoms represent the thermodynamically most stable arrangement out of all plausible 001-truncated configurations [19]. Nonetheless, a consistent and comprehensive account of thermodynamic stability of all possible surfaces of $c$-BN remains lacking.

To this end, this contribution aims to report structural and electronic properties, and thermodynamic stability phase diagram for all plausible $c$-BN terminations. Calculated properties herein should shed light on the aforementioned remarkable properties of BN-based materials. For example, if facets of $c$-BN are largely dominated by the inactive surface N sites, this should translate into chemical inertness for $c$-BN surfaces.
4.3. Methodology

4.3.1. Structural optimisation of c-BN

VASP [20] code performs all structural optimisation and energy calculations based on the PAW-GGA functional [21]. c-BN low index surfaces along the (100), (110) and (111) directions were constructed from $2 \times 2$ supercells. Each surface consists of 12-15 layers that form a symmetric slab containing about 100 atoms. The vacuum of 10 Å separates surface images in the $z$-direction. During optimisations, all atoms were allowed to relax until the final energy and the forces on each atom converge to $10^{-5}$ eV and $10^{-2}$ eV/Å, in that order. In the optimisation of surfaces, we deploy an energy cutoff of 400 eV and an automatic $\kappa$-points samplings of $4 \times 4 \times 1$.

Bulk unit cells of c-BN were optimised using an energy cutoff of 500 eV and a $5 \times 5 \times 5$ $\kappa$-points. A test using 600 eV and an $8 \times 8 \times 8$ $\kappa$-points has yielded essentially the same unitcell volume and final energy. We calculate the enthalpy of formation ($E^f$) of bulk c-BN according to:

$$E^f = E_{BN}^{bulk} - E_B^{bulk} - \frac{n}{2} E_{N_2}$$

(4.1)

where $E_{BN}^{bulk}$ and $E_B^{bulk}$ correspond to the bulk c-BN and bulk boron energies per unit formula, respectively. $E_B^{Bulk}$ was calculated by averaging the energy of bulk boron in its three experimentally recognised stable forms, $\alpha$, $\beta$ and $\gamma$. While optimising unit cells of these three forms, we found $\alpha$-B$_{36}$ to be more stable than $\beta$-B$_{105}$ and $\gamma$-B$_{28}$ by 25.3 meV and 28.1 meV, respectively, at 0 K. This finding agrees with previous experimental [22] and theoretical [23] studies indicating that, $\alpha$-B$_{36}$ constitutes the thermodynamically most stable form of elemental boron under ambient conditions. Finally, $E_{N_2}$ signifies the energy of a nitrogen molecule.
4.3.2. **Quasi-harmonic approximation (QHA) calculations**

We estimate thermo-elastic properties of bulk $c$-BN by utilising the quasi-harmonic approximation (QHA) approach as implemented in the PHONOPY code [24]. PHONOPY utilises VASP interface to calculate force constants. In these calculations, we utilise $2 \times 2 \times 2$ supercell of $c$-BN (64 atoms) with $5 \times 5 \times 5$ $k$-point grid meshes for integration of the Brillouin zone were used. In all pressure-temperature dependent properties, we elect to deploy the Vinet’s equation of state for the fitting of energy-volume curves [25]. Detailed descriptions of the underlying equations in the QHA can be found elsewhere[24]. Basically, the QHA approach treats vibrational frequencies of crystal to depend on solely on volume; i.e., the intrinsic phonon interactions are independent of temperature [24]. As such, Gibbs free energy $G(T,P)$ is minimized at each volume [26], [27] from Helmholtz free energy $F(V,T)$ through:

$$G(T, P) = \min_{V}[F(V, T) + PV] \quad (4.2)$$

where $V$, $P$ and $T$ stand for cell volume, pressure and temperature, respectively. In this equation, $F(V, T)$ was approximated with the summation of electronic internal energy $U(V)$ and phonon Helmholtz free energy $F_{ph}(V, T)$ [24].

4.3.3. **Ab initio atomistic thermodynamics**

The energy phase diagram (vide infra) incorporates all plausible faces of $c$-BN surfaces based on the approach of ab initio atomistic thermodynamics. Literature provides detailed descriptions of this formalism [28]. In a nutshell, equation 4.3 expresses the dependency of surface free energies, $\gamma(T, P)$, on temperature ($T$) and pressure ($P$):

$$\gamma(T, P) = \frac{1}{2A} [G^{\text{Surf}}(T, P) - N_b G^{\text{Bulk}}(T, P) - (N_N - nN_b) \mu_N(T, P)]$$

\[(4.3)\]
in which $G_{\text{Surf}}^{\text{Bulk}}(T, P)$ and $G_{\text{BN}}^{\text{Bulk}}(T, P)$ denote the Gibbs free energies of $c$-BN surfaces and bulk $c$-BN, respectively, at the temperature and pressure of interest. $N_B$ and $N_N$ correspond to the number of boron and nitrogen atoms in the slab, and $\mu_N(T, P)$ is the chemical potential of nitrogen:

$$\mu_N(T, P) = \Delta \mu_N(T, P) + \frac{1}{2} E_{N_2}$$

(4.4)

The change in the chemical potential of nitrogen ($\Delta \mu_N(T, P)$) was extracted from the standard thermodynamic tables [29]. Therefore, the chemical potential of nitrogen can be written as [29]:

$$\mu(T, P) = -4.86 - 0.967 \times \frac{T}{1000} - 0.1013 \times \left(\frac{T}{1000}\right)^2 + 0.0173 \times \left(\frac{T}{1000}\right)^3 + \frac{k_B T}{2} \ln(P_{N_2})$$

(4.5)

4.4. Results and Discussions

4.4.1. Properties of Bulk $c$-BN at 0 K

The unit cell of bulk $c$-BN can be considered as a diamond-like structure with a space group of $T_d^2$. In this structure, alternately linked boron and nitrogen atoms form a tetrahedral bond network as shown in Figure 4.1(a). Figure 4.1(b) illustrates the variation of the total energy of $c$-BN unit cell with respect to the volume of the unit cell. Our computed equilibrium lattice parameter (3.609 Å) is in a relatively good agreement with corresponding experimental measurements of 3.615 Å [14],[30] and other theoretical predictions of 3.59 - 3.606 Å [1]. In comparison to the LDA functional, the GGA consistently predicts a larger lattice constant for metal nitrides, explaining the discrepancy between our calculated lattice constant and the results of previous LDA computations [12]. Kim and Chen [31] used a combination of LDA
and GGA methods to obtain an analogous value of 3.620 Å for lattice constant of c-BN. Using equation (4.1), the enthalpy of formation of c-BN was calculated as -2.816 eV (-271.12 kJ/mol). Calorimetric measurements for the heat of formation of c-BN afford predictions of -266 kJ/mol [32], -266.8 kJ/mol [33] and -254 kJ/mol [34] which are slightly underestimates our value.

Figure 4.1. (a) c-BN unit cell (read and black spheres denote B and N, respectively), (b) energy versus volume curve for bulk c-BN.
Figure 4.2 depicts the density of states (DOS) and the partial density of states (PDOS) of bulk c-BN. The DOS of c-BN exhibits two valance bands. The lowest band extends from -20 eV to -15 eV and corresponds to a combination of B(s) and N(s) orbitals. The second valance band ranges between -10 eV to 0 eV. The DOS plots in Figure 4.2(a) visualises a non-metallic character of bulk c-BN. The calculated indirect band gap of 3.9 eV lies at the lower end of the experimental values of 3.8 - 5.8 eV [30], but is in accord with another theoretically derived estimate of 3.9 eV [30]. Along the same line of enquiry, it is well-documented that plain DFT methods tend to underestimate band gaps [35]. For that reason, we deploy the hybrid DFT method of HSE06 [36] to obtain a band gap of 5.7 eV. This value resides at the upper end of the aforementioned experimental values.
4.4.2. **Thermo-elastic properties of c-BN.**

The practical utilisation of hard coating materials at harsh elevated temperatures and pressures calls for deriving their thermo-elastic properties at these operating conditions. However, it is also intended that contrasting our calculated thermo-elastic properties with analogous estimates in the literature to provide an accuracy benchmark for obtained surface properties conveyed the next section. Table 8.1 enlists our estimated bulk modulus \((B)\) for c-BN at 0 K along with other available experimental and theoretical estimations where a relative satisfactory is attained. Figure 4.3 shows the calculated phonon dispersion for optimised BN structure at zero
pressure and zero temperature. Our calculated phonon dispersion correlates very well with previous analogous estimation by Srivastava et al. as Figure 4.3 portrays. It is very challenging to distinguish between acoustic and optical branches of phonon dispersion [37]. This is primarily due to the fact that B and N atoms share very similar atomic masses. Figure 4.4 portrays the variation of $B$ with $T$ at selected $P$. The obtained $T$-dependent decreasing trends in $B$ values is consistent with the analogous LDA curve by Albe et al. [38] at 0 GPa. Figure 4.5.a contrasts our calculated $C_p(T)$ values with the experimental and theoretical estimates in references [39], [40] and [33]. As Figure 4.5.b depicts, thermal expansion of $c$-BN decreases with the applied pressure. Figure 4.6 shows $V/V_o$ curves with varying temperature and pressure where $V_o$ signifies the equilibrium volume of the $c$-BN unit cell at 300 K and 0 GPa. Analogous experimental values of Grimsditch et al. [41] and Knittle et al. [42] on single crystal $c$-BN are in good agreement with the present results. 3

Table 4.1 Lattice parameter and Bulk modulus of BN compared to other analogous theoretical and experimental results.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$a$ (Å)</th>
<th>$B$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>3.620</td>
<td>366.0</td>
</tr>
<tr>
<td>Albe et al. [38]</td>
<td>3.593</td>
<td>395.0</td>
</tr>
<tr>
<td>Furthmuller et al. [30]</td>
<td>3.576</td>
<td>397.0</td>
</tr>
<tr>
<td>Wentzcovitch et al. [1]</td>
<td>3.606</td>
<td>367.0</td>
</tr>
<tr>
<td>Mosuанг et al. [43] (LDA)</td>
<td>3.567</td>
<td>391.8</td>
</tr>
<tr>
<td>Mosuанг et al. [43] (GGA)</td>
<td>3.631</td>
<td>365.4</td>
</tr>
<tr>
<td>Expterimental [42]</td>
<td>3.615</td>
<td>369.0 −400.0</td>
</tr>
</tbody>
</table>
Chapter 4 – Electronic Properties and Stability Phase Diagrams for Cubic BN Surfaces

Figure 4.3 Phonon density of states for c-BN. Dashed-line responds to theoretical calculations of Srivastava et al. [37].

Figure 4.4 Dependence of Bulk modulus of c-BN on temperature and pressure. Empty squares correspond to theoretical calculations of Albe et al. [38] at 0 K.
Figure 4.5 Heat capacity (a) and thermal expansion (b) of $\epsilon$-BN as a function of temperature. Empty squares, rectangles and circles correspond to the theoretical calculation of Solozhenko et al. [39] and Tohei et al. [40], respectively.
Figure 4.6 (a) Dependence of $V/V_0$ on pressure and (b) temperature. Empty squares, circles and rectangles represent experimental data by Grimsditch et al. [41], Knittle et al. [42] and theoretical by Knittle et al. [42].
4.4.3. Geometry of low index surfaces of cubic BN

Surfaces of c-BN afford three distinct low-index configurations, namely (100), (110) and (111). The c-BN(100) surface offers separate B and N terminations (denoted as c-BN(100)_B and c-BN(100)_N), whereas c-BN(111) and c-BN(110) truncate with a combination of boron and nitrogen atoms (denoted as c-BN(111)_BN and c-BN(110)_BN). Consequently, c-BN permits four distinct surfaces. Figure 4.7 portrays side and top views of optimised structures of c-BN surfaces.

Figure 4.7 Geometries of optimised c-BN slabs (red and black spheres denote B and N, respectively).
The analysis of the relaxed structures indicates that all surfaces experience both reconstructions and relaxations. (110)-BN surface consisted of B and N atoms in ABAB stacking order [12]. In the reconstructed surface layer of (110)\_BN, neighbouring B and N atoms move closer toward each other to satisfy their missing bonds. This reduces the length of covalent B-N bonds from 1.56 to 1.45 Å. Surface relaxation manifests itself in changes in the interlayer distances in the slabs. Figure 4.8(a) elucidates the interlayer spacing between B atoms and N atoms in adjacent layers. The variability in the locations of the topmost layers take the largest values because of the upward displacement of the top layer. This reduces the distance between the first and second layers. The distance between the second and third layer increases due to the enhanced bonding of the second layer with the top layer.

Consequently, this results in the weakening of bonds between second and third layers. These displacements gradually die out for the inner layers, which approximate the bulk phase, as electron densities around atoms reach their default bulk value. According to Figure 4.8(b), expansions and contractions in the BN(100)\_N and BN(100)\_B slabs fall below those of the (110) surface. In addition, N-terminated (100) surface experiences larger displacement in comparison to the B-terminated surface.
Bader’s theory [44] presents an accurate formalism to calculate partial charge density on individual atoms. Table 8.1 lists Bader’s charges on selected B and N atoms belonging to the first three topmost atomic layers in all BN surfaces. B and N atoms hold net charges of 3.0 e and -3.0 e in the bulk c-BN structure. Charge values in Table 8.1 show that, B atoms in surfaces assume similar charges if compared with bulk B atoms, except the topmost layer of the
BN(100)_B surface. N atoms in the topmost layer of BN-terminated (110)/(111) slabs are associated with very similar charges to bulk N atoms. However, N atoms in the topmost layer of c-BN(100)_B configuration carry higher negative charges. On the contrary, Table 8.1 also shows nitrogen atoms, in the topmost layer of the BN(100)_N, carrying significantly lower negative charges when contrasted with the bulk N. Electronegativity of N atoms in the second and third layers of studied slabs remains very close to their corresponding bulk values. Overall, the high positively and negatively charged B and N atoms atomic inferred from Table 8.1 verifies the ionic nature of N-B bonds in c-BN surfaces.

Figure 4.9 to Figure 4.12 plots DOS and PDOS on adjacent B and N atoms for the investigated surfaces. DOS plots illustrate three groups of peaks corresponding to core state, valence band and conduction band, respectively. As evident from the occupied energy states around the Fermi level, the c-BN(100)_B attains metallic character while c-BN(100)_N, c-BN(110)_BN and c-BN(111)_BN surfaces engender band gaps of 2.7, 2.5 eV and 3.9 eV, respectively.
Figure 4.9 DOS of the c-BN(100)_B surface: (a) DOS for entire surface, (b) PDOS on B atoms and (c) PDOS on N atoms.
Figure 4.10 DOS of the c-BN(100)\textsubscript{N} surface: (a) DOS for entire surface, (b) PDOS on B atoms and (c) PDOS on N atoms.
Figure 4.11 DOS of the c-BN(110) BN surface: (a) DOS for entire surface, (b) PDOS on B atoms and (c) PDOS on N atoms.
Figure 4.12 DOS of the c-BN(111)_BN surface: (a) DOS for entire surface, (b) PDOS on B atoms and (c) PDOS on N atoms.
Table 4.2. Bader's charges on B and N atoms. Subscript numbers refer to the first, second and third layers.

<table>
<thead>
<tr>
<th>Bader’s charge (e)</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>N1</th>
<th>N2</th>
<th>N3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk c-BN</td>
<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
<td>-3.01</td>
<td>-3.00</td>
<td>-2.99</td>
</tr>
<tr>
<td>BN(100) B</td>
<td>2.05</td>
<td>3.00</td>
<td>3.00</td>
<td>-3.54</td>
<td>-3.10</td>
<td>-2.78</td>
</tr>
<tr>
<td>BN(100) N</td>
<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
<td>-1.72</td>
<td>-2.91</td>
<td>-2.88</td>
</tr>
<tr>
<td>BN(110) BN</td>
<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
<td>-3.09</td>
<td>-3.01</td>
<td>-3.01</td>
</tr>
<tr>
<td>BN(111) BN</td>
<td>2.99</td>
<td>3.00</td>
<td>2.64</td>
<td>-3.00</td>
<td>-3.00</td>
<td>-3.00</td>
</tr>
</tbody>
</table>

4.4.4. Stability phase diagrams for c-BN surfaces

Value of $\Delta \mu_N(T,P)$ vary between N-lean and N-rich limits. These limits symbolise the practical conditions of the chemical potential of nitrogen. The N-lean boundary refers to the value of $\Delta \mu_N(T,P)$ when bulk c-BN starts to form from adsorption of nitrogen molecules on bulk boron. The N-rich limit characterises the onset of decomposition of nitrogen gas into N atoms. Appropriate and well-defined values for the N-rich and N-lean limits can be taken as 0.0 eV and -2.816 eV; the latter is the computed $E^f$ value for c-BN. Figure 4.13 plots the stability phase diagram of c-BN surfaces. At all accessible values of $\Delta \mu_N(T,P)$, BN(100) N surface displays the profound thermodynamic stability. As conveyed in the introduction, the predominant stability of the N-truncated surface is in line with the chemically inert nature of BN. In a recent study [45], we have demonstrated that the thermodynamic stability ordering might stem from the combined effect of surface relaxation, charge distribution and band gaps. These combined factors may have contributed to the profound stability of the BN(100) N termination.
Figure 4.13 Stability phase diagram of c-BN surfaces.

4.5. Conclusions

This contribution documented the geometric and electronic properties of bulk c-BN and its surfaces along the three low-Miller indices. We found the nitrogen-terminated surface along the 100 direction to be the most thermodynamically stable configuration over all physically accessible values of the chemical potential of nitrogen. This finding explains the inert nature of BN. While it was not the main focus of the current investigation, we have found that \( \alpha\)-B\(_{36}\) dictates the stability phase diagram of bulk boron at 0 K, in agreement with the recent experimental measurements. Analysis of Bader’s charges indicates that, all surfaces of c-BN largely retain the ionic character of the bulk c-BN.
Chapter 4 – Electronic Properties and Stability Phase Diagrams for Cubic BN Surfaces

4.6. References


Chapter 4 – Electronic Properties and Stability Phase Diagrams for Cubic BN Surfaces


Chapter 5

Paper II: Thermo-Mechanical Properties of Titanium Nitride


This chapter describes the thermo-elastic properties of TiN thin films as functions of temperatures up to 3100K and pressures up to 60 GPa.
5.1. Abstract

The equilibrium structure, elastic constants $C_{ij}$ and thermodynamic functions of cubic titanium nitride (TiN) were calculated within the temperature range of 0-3100 K and under a pressure range 0-60 GPa. Properties were computed using the generalised gradient approximations (GGA) exchange-correlation functional. Calculated mechanical properties (Elastic constants, Young’s modulus, shear modulus), and phonon spectra of TiN obtained via robust DFT-QHA algorithm, were generally in a good agreement with available experimental and theoretical analogous values. In particular, a well-examined quasi-harmonic approximation method implemented in the Gibbs2 code is utilised herein to provide an accurate estimation of thermal expansion coefficients, entropies, heat capacity values (at different combinations of temperature/volume/pressure), and Debye’s temperature. Parameters calculated herein shall be useful to elucidate the superior performance of TiN at harsh operational conditions encompassing elevated temperatures and pressures pertinent to cutting machinery and surface coatings.
5.2. Introduction

Owing to a wide array of remarkable mechanical and thermal properties, titanium nitride (TiN) finds direct applications pertinent to surface protections and metal cutting machinery [1,2]. TiN exhibits extreme hardness, corrosion resistance (stable below 800 °C), good adhesion to the substrate, high fraction toughness and high melting point (2950 °C) [3]. Due to these unique applications, many contributions report characterisations of TiN-based coatings [4]–[7] and its derivatives such as ternary combinations (TiAlN [8]) and superlattice coatings (TiN/CrN [9], [10]).

Kress et al. [11] compared the experimentally obtained phonon dispersion curves of TiN with calculations obtained via a double-shell model. They reported an acoustical section of the phonon spectra. A theoretical study by Wolf et al. [12] documented elastic properties and thermal expansion of TiN. Kim et al. [13] utilised line-focus acoustic microscopy to determine mechanical properties of single-crystal TiN from its surface acoustic wave dispersion curves. Their measurements confirmed the previous theoretical values of elastic constants and modulus properties of TiN low-index surfaces calculated by Marlo et al. [14] based on the DFT-GGA formalism. They illustrated a stability surface diagram of TiN surfaces; an important parameter in understanding the competing mechanisms encountered during the thin film growth and preferential growth orientations.

The theoretical predictions of relative volume and bulk modulus of TiN were studied by Chen et al. [15] as a function of pressures (0-6 GPa) and temperatures (0-2000K). Wang et al. [16] theoretically compared the structural stability and elastic constants of TiN in rocksalt and Wurtzite forms. Similarly, Brik et al. [17] studied the electronic structure and elastic properties of TiN using different flavours of density functional theory functions (DFT). Zhu et al. [2]
studied the phase transition of TiN at ground state establishing a relationship between enthalpy and pressure. They predicted a transition from cubic B1-TiN (NaCl-type) to B2-TiN (CsCl-type) around 342 GPa. Gupta et al. [18] studied the phonon and thermodynamical properties of TiN within the DFT framework of Generalised Gradient Approximation (GGA) coupled with the Quasi-Harmonic Approximation (QHA) approach. However, their calculations for thermodynamic properties were limited to a zero pressure. Mehmood et al. [19] calculated the electronic and optical properties of low index surfaces of TiN employing both DFT and many-body GW methods. More recently, Yu et al. [20] explored the structural stabilities of several Ti$_{n+1}$N$_n$ compounds (TiN, Ti$_2$N, Ti$_3$N$_2$, Ti$_4$N$_3$, Ti$_5$N$_5$, TiN$_2$) by first-principle structure predictions under ambient conditions and at pressures up to 60 GPa. It was concluded that the TiN$_2$ configuration displays the largest hardness of 27.2 GPa, and at high pressure, new phases were formed (Ti$_2$N and TiN$_2$). All investigated phases were found to be mechanically and dynamically stable under ambient conditions.

Knowing the pressure- and temperature-dependent crystal properties enable us to model extreme conditions that are not easily attainable by experimental means. QHA calculations have been considered as one of the mainstream methodologies of incorporating temperature effect in the DFT calculations, commonly obtaining results at 0 K [21]. This method operates in the framework of harmonic approximation and widely considered to be accurate at temperatures of the order or below the Debye constant [22] and is generally proved to provide satisfactory results up to the melting point of materials [23]. These properties are vital in the design process of advanced engineering materials. This study aims to deploy first-principle calculations and the QHA formalism to attain a detailed insight on the thermo-elastic properties of TiN at high pressure and temperature conditions relevant to the harsh operational conditions commonly encountered in their real life applications, i.e. in cutting machinery. As mentioned
above, there are a few theoretical studies on the thermodynamic properties of TiN as a function of temperature up to 2000K. Accurate determination of mechanical properties at conditions encountered in real applications requires incorporating the pressure effect on all pertinent properties, not only the temperature effect. Herein, we present the first-ever reported pressure- and temperature- dependent thermodynamic and mechanical properties of rocksalt-structured TiN. The effect of pressure on the thermodynamic behaviour of TiN over a large temperature range has not been elucidated theoretically. To the best of our knowledge, literature provides no theoretical validation of the analogous thermo-elastic experimental data for TiN. Therefore, the main contribution of this work is to determine the pressure dependency of thermodynamic and mechanical properties for rocksalt-structured TiN in the very wide pressure range of 0 - 60 GPa and temperature range of 0 – 3100K.

5.3. Theoretical Method

A plane-wave basis projector augmented wave method [21] is utilised herein in all structural and electronic calculations, as implemented in the Vienna ab initio simulation package (VASP) code [24]. The exchange and correlation functional were described within the GGA formalism. A plane-wave cut-off energy and energy convergence criteria of 600 eV and 10^{-8} eV were employed, respectively. A Monkhorst pack \( \kappa \)-points sampling of 15x15x15 was used in structural calculations. TiN adopts a NaCl-type structure with space group Fm-3m (#225). In this structure, the Ti and N atoms occupy the 1a (0, 0, 0) and 1b (0, 0.5, 0) sites, respectively.

The enthalpy of formation (\( E^f \)) for TiN was calculated according to:

\[
E^f = E_{TiN}^{Bulk} - E_{Ti}^{Bulk} - \frac{n}{2} E_{N_2}
\]

(5.1)
where $E_{\text{TiN}}^{\text{Bulk}}$, $E_{\text{Ti}}^{\text{Bulk}}$ and $E_{\text{N}_2}$ denote the ground state per-formula energies of bulk TiN (cubic), Ti (hcp) and nitrogen molecule, respectively.

In order to apply the QHA method within the Gibbs2 code, results from VASP and Phonopy programs were deployed as input to Gibbs2 to calculate all thermodynamic values [25]. An important input in QHA calculations is the phonon density of states (phDOS) obtained at each of the calculated crystal volumes. Phonon frequencies were computed using the open source Phonopy code [26] whereas force constants were calculated from VASP outputs. For the phonon calculations, a 2x2x2 supercell of the conventional primitive cell was utilized with eight atoms at each volume grid. In calculations of force constants, atomic displacement distances vary within 0.01 Å.

5.4. Results and Discussions

5.4.1. Bulk TiN

Figure 5.1 shows the unit cell of TiN in NaCl-type structure (Fm-3m space group) where both Ti and N occupy an octahedral arrangement with identical Ti-N distances of 2.13 Å. Our calculated lattice constant for c-TiN attains a value of 4.255 Å; and coincides very well with experimental and theoretical data as listed in Table 5.1. According to Equation (5.1), the computed enthalpy of formation for TiN is estimated to be -3.77 eV (-363.8 kJ/mol); and reasonably agrees (within ~ 7%) with the corresponding experimental value of -337.8 kJ/mol [27].
Chapter 5 – Thermo-mechanical properties of Titanium nitride

5.4.2. Mechanical properties

Elastic properties are important due to their close relationship to various fundamental properties including; interatomic bonding, equations of state, phonon dispersion. It is also possible to associate them with thermodynamic properties such as specific heat, thermal expansion, etc [2] as well as to a wide array of fundamental properties encompassing load

Table 5.1 Calculated lattice constant (a), elastic constants (C_{ij}), bulk modulus (B), shear modulus (G), elastic modulus (E), Zener anisotropy factor (A) and Poisson ratio (\nu).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>4.255</td>
<td>4.202</td>
<td>4.18</td>
<td>4.18-4.25</td>
<td></td>
</tr>
<tr>
<td>C_{11} (GPa)</td>
<td>611</td>
<td>625</td>
<td>778</td>
<td>590</td>
<td>535-649</td>
</tr>
<tr>
<td>C_{12} (GPa)</td>
<td>138</td>
<td>165</td>
<td>139</td>
<td>145</td>
<td>118-129</td>
</tr>
<tr>
<td>C_{44} (GPa)</td>
<td>159</td>
<td>163</td>
<td>169</td>
<td>169</td>
<td>175-194</td>
</tr>
<tr>
<td>B (GPa)</td>
<td>296</td>
<td>352</td>
<td>294</td>
<td>257-302</td>
<td></td>
</tr>
<tr>
<td>G (GPa)</td>
<td>190</td>
<td>216</td>
<td>189</td>
<td>187-188</td>
<td></td>
</tr>
<tr>
<td>E (GPa)</td>
<td>469</td>
<td>418-556</td>
<td>499-530</td>
<td>466</td>
<td>492-429</td>
</tr>
<tr>
<td>A (GPa)</td>
<td>0.671</td>
<td>0.527</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>\nu</td>
<td>0.23</td>
<td></td>
<td></td>
<td>0.235</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.1. Crystal structure of TiN (Blue and grey spheres denote Ti and N atoms, respectively).
deflection, thermo-elastic stress, internal strain, sound velocities, and fracture toughness. For instance, high internal stress in the coating may result in poor coating/substrate adhesion.

Elastic constants were calculated from stress–strain relationships. Variations in stress tensor due to crystal strain were used to compute the elastic constants ($C_{ij}$) matrix and its inverse matrix $S_{ij}$. The Young’s modulus ($E$), Shear modulus ($G$), Zener anisotropy factor ($A$) and bulk modulus ($B$) of a polycrystalline cubic system were estimated by Voigt, Reuss and Hill formulae [28]. Voigt approximations exhibit the higher limits:

$$B_V = \frac{1}{9} (C_{11} + C_{22} + C_{33}) + \frac{2}{9} (C_{12} + C_{13} + C_{23})$$

(5.2)

$$G_V = \frac{1}{15} (C_{11} + C_{22} + C_{33} - C_{12} - C_{13} - C_{23}) + \frac{1}{5} (C_{44} + C_{55} + C_{66})$$

(5.3)

On the other hand, Reuss approximations assume equations for lower limits:

$$B_R = \frac{1}{(S_{11}+S_{22}+S_{33})+2(S_{12}+S_{13}+S_{23})}$$

(5.4)

$$G_R = \frac{15}{4(S_{11}+S_{22}+S_{33})-4(S_{12}+S_{13}+S_{23})+3(S_{44}+S_{55}+S_{66})}$$

(5.5)

Hill formulas express the arithmetic mean values as:

$$B_H = \frac{B_R + B_V}{2}$$

(5.6)

$$G_H = \frac{G_R + G_V}{2}$$

(5.7)

Finally, the polycrystalline Young’s modulus and Poisson ratio can be obtained using:

$$E = \frac{(9B_HG_H)}{(B_H+G_H)}$$

(5.8)

$$v = \frac{(3B_H-2G_H)}{2(3B_H+G_H)}$$

(5.9)

The Zener anisotropy factor ($A$) is estimated according to [29]

$$A = \frac{2C_{44}}{C_{11}-C_{12}}$$

(5.10)
For a cubic structure, the following mechanical stability conditions should be satisfied [29]:

\[ C_{11} - C_{12} > 0, \quad C_{11} > 0, \quad C_{44} > 0, \quad C_{11} + 2C_{12} > 0, \quad C_{12} < B < C_{11} \]  

(5.11)

The optimised lattice parameter \((a)\), elastic constants \((C_{ij})\), bulk modulus \((B)\), shear modulus, Young’s modulus \((E)\), Zener anisotropy factor \((A)\) and Poisson ratio \((\nu)\) for cubic TiN are listed in Table 5.1 at the ground state; 0 K. As shown in Table 5.1, the calculated elastic constants satisfy all of the above mentioned conditions of Equation 5.10. As Table 5.1 portrays, our estimated values agree well with experimental and other theoretical values. The large \(C_{11}\) value indicates low compressibility along the \(c\)-axis. The shear modulus reflects the resistance of the material to changes in shape at a constant volume. Knowing the bulk modulus and shear modulus of a material, enables one to predict its hardness using developed formulas by Chen et al. [30] and Jiang et al. [31]. It was shown, by Jiang et al., that there is a clear linear correlation between shear modulus and hardness based on experimental data for several covalent crystals [31]. Poisson’s ratio displays the level of the directionality of covalent bonding. Strong directional covalent bonds lead to a Poisson’s ratio close to 0.2, while the value for metals is about 0.4 [20]. Our calculated bulk modulus in Table 5.1 of 295 GPa is in good agreement with analogous experimental values of 318 and 292 GPa obtained by Wolf et al. [12].

### 5.4.3. Electronic properties

In this section, the changes in total electron density of state due to pressures (0, 33 and 60 GPa) is discussed. It can be seen that, the TiN structure is metallic in the entire pressure range which is in good agreement with the analogous literature values depicted in [14], [18]–[20]. The total and partial density of state (PDOS) in range of -20 to 10 eV for \(c\)-TiN are presented in Figure
5.2. These plots were used to evaluate the pressure dependency of the electronic structure of TiN.
Figure 5.2. DOS and PDOS of c-TiN under pressures of (a) 60 GPa, (b) 33 GPa and (c) 0 GPa. Fermi level is located at 0 eV.

The non-zero values of DOS at the Fermi level observed at different pressures indicate that, TiN maintained its metallic behaviour. The DOS curves consist of three main sections which are marked as P1, P2 and P3. Peak P1 (located at -15 eV) belongs to N-2s states and separated
by a significant gap from the P2 peak which is the valence band. P2 is a combination of N-2p and Ti-3d with some contribution from Ti-3p. It can be observed that, the valence band at P2 is primarily dominated by the hybridisation of Ti-3d and N-2p with some contribution of Ti-3p state. The strong hybridisation of N-2p and Ti-3d shows the formation of covalent bond between Ti and N atoms, similar to the theoretical results of Gupta et al. [18]. One can see that P3 around Fermi level is dominated by Ti-3d states hybridized by N-2p anti-bonding states. These peaks are observed to shift toward the higher negative energy as the pressure increases from 0 to 60 GPa, i.e., the P1 shifts from -14.85 eV to -15.6 eV. Overall, no significant broadening is observed in the DOS curve under the influence of pressure.

5.4.4. Phonon spectra

The normalised phonon density of states \( g(\omega) \) for \( N \) number of unit cells is defined as

\[
g(\omega) = \frac{1}{N} \sum_{qj} \delta(\omega - \omega_{qj})
\]

where \( q \) and \( j \) are wave vector and band index, respectively. The phonon density of states (PDOS) of the TiN crystal shown in Figure 5.3 is in good agreement with experimentally obtained neutron scattering values [32]. The present acoustic and optical phonon calculations are in reasonable agreement with theoretical values for the acoustic phonons by Kress et al. [11] and both acoustic and optical phonons by Gupta et al. [18]. Our calculations clearly show that there is a gap of almost 6 THz between the phonon branches of optical and acoustical. This is due to the considerable mass ratio of Ti and N atoms. All positive PDOS dispersion curves indicate the dynamical stability of TiN in the NaCl-type structure (the rock salt form).
Figure 5.3. Calculated phonon DOS for TiN and experimental phonon dispersion obtained from neutron diffraction of bulk TiN [32]

5.4.5. Thermodynamic properties

Thermal behaviour of any given material can be obtained by exploring the combined temperature-pressure effects on its thermodynamic properties. Since TiN is a promising material in the coating technology, it is crucial to understand its thermal properties under high pressure and temperature conditions. At a constant volume, a number of thermodynamic properties can be derived from non-equilibrium vibrational Helmholtz free energy ($F'$) including entropy ($S$), Gibbs free energy ($G$), heat capacity at constant volume ($C_v$) and isothermal bulk modulus [22], [33]

$$ F = F'(V(p, T), T) $$

$$ S = \Sigma_j -k_B \ln(1 - \exp \frac{\omega_j}{k_B T}) + \frac{\omega_j}{T} \exp \left( \frac{\omega_j}{k_B T} \right) - 1 $$

$$ G = \text{Gibbs Energy} = U + pV - TS $$
Chapter 5 – Thermo-mechanical properties of Titanium nitride

\[
C_v = \sum_j k_B \left( \frac{\omega_j}{k_BT} \right)^2 \frac{\exp\left(\frac{-\omega_j}{k_BT}\right)}{\exp\left(\frac{-\omega_j}{k_BT}\right) - 1} \quad (5.16)
\]

\[
B_T = V \left( \frac{\partial^2 E}{\partial V^2} \right)_T \quad (5.17)
\]

where \( k_B \), \( \omega_j \) and \( V \) are the Boltzmann constant, volume independent frequencies and volume of the unit cell, respectively. Phonon properties are sensitive to the changes in volume of unit cell because the crystal potential signifies an anharmonic function of volume. Our results demonstrate that phonon frequency tends to decrease when the volume increases. Typically, changes in volume lead to variation of the phonon properties because the potential of the crystal is an anharmonic function of crystal volume. Togo et al. [26] examined phonon frequencies for a unit cell with several different volumes. Their calculations showed that, changes in volume slightly affect the slope of phonon modes. However, phonon frequencies tend to shrink constantly as the volume of the unit cell gets larger. As mentioned above, phonon energy is measured based on the frequency of phonons and displays a profound sensitivity as volume varies. Therefore, one can transform the thermodynamic properties at constant volume to constant pressure based on the following governing relationships:

The thermal expansion coefficient (\( \alpha \)), constant-heat capacity (\( C_p \)) can be calculated from

\[
\alpha = \frac{\gamma th C_v}{V B_T} \quad (5.18)
\]

\[
C_p = C_v (1 + \gamma th \alpha T) \quad (5.19)
\]

where \( \gamma \) signifies the thermodynamic Grüneisen ratio [22].

The Debye temperature (\( \Theta_D \)) also can be obtained from the implemented Debye-Slater model in Gibbs2:

\[
\Theta_D = \frac{\omega_D}{k_B} = \frac{1}{k_B} \left( \frac{6\pi^2 n}{V} \right)^{1/3} v_0 \quad (5.20)
\]
where \( n \) and \( v_0 \) are the number of vibrational states and static equilibrium frequency of the phonon, respectively. Figure 5.4(a) depicts the changes in total heat capacity (\( C \)), of TiN, at a constant pressure (1 atm) and constant volume between 0 K to 3100 K. The experimental results of Chase et al [27] and Lengaurer et al [34] are also included in the plot. It can be seen that calculated heat capacity, using the Debye-Slater model, agrees very well with the experimental data. For example, the calculated \( C_p \) at room temperature amounts to 34.4 J/mol/K; very close to the experimental value of 33.74 J/mol/K [3]. The changes in heat capacity at constant volume (\( C_v \)) of TiN are shown in Figure 5.4 (b and c) as functions of pressure (at fixed temperature values) and temperature (at fixed pressure values); respectively. The plots reveal that, when the pressure increases from 0 to 60 GPa at 300 K, the \( C_v \) is reduced by 28.6 % from 32 to 24 J/mol/K. However, this tendency in the reduction of \( C_v \) is less profound at elevated temperatures. The \( C_v \) approaches constant values at higher temperatures due to the suppression of anharmonic effects as it gets closer to the Dulong-Pettit limit of \( 3nR = 50 \) KJ/mol/K (where \( n \) and \( R \) are the number of atoms per formula and the universal gas constant, respectively) [35]. Figure 5.4d presents the changes in \( C_p \) with respect to temperature between 0 K to 3100 K, at fixed pressure values.
Chapter 5 – Thermo-mechanical properties of Titanium nitride

(a) Heat capacity, \( C_v \), 1 atm
\( C_p \), 1 atm
Expt. [27]
Expt. [35]

(b) Heat capacity, \( C_v \), J/mol/K
0K
300K
500K
1000K
2000K
3000K

Pressure (GPa)
Figure 5.4. Heat capacities (Total heat capacity $C$, $C_v$ and $C_p$) for TiN with respect to various temperatures and pressures: (a) $C$ versus $T$ at 1 atm, (b) $C_v$ versus $P$ at a constant $T$ (isotherms), (c) $C_v$ versus $T$ at constant $P$ (isobars) and (d) $C_p$ versus $T$ at constant $P$ (isobars).

Figure 5.5(a) shows the $V/V_0$ ratio as a function of temperature up to 3100 K at fixed equidistance pressures (in range 0 - 60 GPa). Here, $V_0$ is the volume of primitive cell of TiN at
300 K (i.e., 19.27 Å³). Experimental results by Aigner et al. [34] from XRD at 1 atm are also included for comparison. Results suggest that, TiN cell volume is a nonlinear function of pressure. The cell compression due to pressure is more distinct at higher temperatures. This, in turn, indicates that, pressure reduces the thermal expansion of TiN at high temperatures. Figure 5.5b also shows changes in $V/V_0$ ratio as a function of pressure at fixed temperatures (in range of 0 - 3100 K). It is observed that unit cell volume expands as the temperature increases.
Following the aforementioned points regarding the effect of pressure on thermal expansion, it can be observed in Figure 5.6(a and b) that pressure reduces the volumetric thermal expansion of TiN progressively (based on Equation (5.16)). Reduction in thermal expansion of TiN does not obey a linear relation while the pressure increases from 0 to 60 GPa. The thermal expansion tends to drop more sharply at pressures below 40 GPa revealing that, the TiN is rather uncompressible under very high pressures. The calculated entropy ($S$) based on Equation (5.12) for TiN are plotted in Figure 5.7a and 4.7b as functions of temperature (isobar) and pressure (isotherms) respectively. The experimental data from Chase et al. [27] at 1 atm in Figure 5.7a, display good agreement with our calculations. Changes in entropy proved to be more sensitive to temperature than pressure.
Figure 5.6. Volume thermal expansion for TiN as a function of (a) T at different fixed P (isobars) and (b) P at different fixed T (isotherms).
According to Equation (5.16), the isothermal bulk modulus ($B$) was calculated as the second derivative of the isothermal Helmholtz free energy against volume. Bulk modulus values are
illustrated as a continue function of temperature and pressure in Figure 5.8(a and b), respectively. The calculated bulk modulus at 0 K and 0 pressure gives a value of 286.8 GPa; correspond very well with analogous values by Chen et al. [15] at 280.1 GPa (represented by empty circles). It is inferred herein that pressure increases the bulk modulus systematically. Variation of bulk modulus when $T < 100$ K is relatively small which is in connection with the relatively constant volume of the unit cell at this temperature range. As the temperature increases, the volume of the cell expands and at the same time, bulk modulus declines. However, bulk modulus reduces as the temperature increased at any given pressure. The combined effect of temperature and pressure on bulk modulus of TiN is comparable to the calculation of Erba et al. [23] for $\gamma$-Al$_2$O$_3$ crystal and Ma et al. [36] for Cr$_2$N using QHA and quasi-harmonic Debye methods, respectively. In both cases, the bulk modulus starts to decline at about 200 K at constant pressures.
Debye temperature is a sign of thermal stability and hardness of solids [18]. It is also closely related to the thermal vibration of atoms, specific heat and thermal coefficient. Figure 5.9 (a and b) show the computed Debye temperature for TiN crystal in a wide pressure and temperature ranges obtained based on Equation (5.19). The experimental data for pure TiN obtained from X-ray diffraction is shown with empty circles in Figure 5.9a [37]. The calculations reveal that, the Debye temperature is 870 K at 300 K; a value that is very comparable to 754K and 809K calculated by Gupta et al. [18] and Jacob et al. [38]. Nonetheless, all these theoretically obtained values somehow deviate from the average reported experimental values for TiN; 671 K [37] and 580 ± 20 K [39]. A plausible explanation for this deviation may stem from the choice in the deployed methodology. For example, metals with d-orbitals are better to be described by the DFT + U methodology rather than via plain DFT.
The effect of the $U$ values in the DFT + $U$ treatment on thermo-elastic properties of transitional metal nitrides will be investigated in due course.

Figure 5.9. Debye temperature of TiN as a function of (a): T at different fixed P (isobars). and (b): P at different fixed T (isotherms)
5.5. Conclusions

In summary, using first principle calculations, the electronic structure, phonon spectra and thermodynamic properties of TiN in rocksalt form were thoroughly investigated based on a DFT-QHA approach. The lattice constant, elastic constants and bulk modulus values are in good agreement with previous literature values. The electronic density and band structure curves show that TiN exhibits a metallic character. One can see that Ti-3d hybridised with N-2p anti-bonding orbitals dominate the states around the Fermi level. The PDOS spectra showed that, the TiN is dynamically stable. The temperature and pressure dependency of several mechanical and thermal properties of TiN were thoroughly investigated and discussed in the context of their physical significance.

5.6. References


Chapter 5 – Thermo-mechanical properties of Titanium nitride


Chapter 5 – Thermo-mechanical properties of Titanium nitride


Chapter 6

Paper III: Influence of Bias Voltage on The Thermal Stability and Mechanical Properties of TiSiN Coatings

Mohammadpour, E., Jiang, Z-T, Altarawneh, M., H. Taha, M. M. Rahman, B. Z., Dlugogorski, manuscript under preparation

This chapter describes the influence of sputtering parameters and Si alloying on the microstructure and mechanical properties of TiSiN coatings
6.1. Abstract

In the present study, the influence of substrate bias voltage on the material properties of the TiSiN coating was investigated. The bias voltage used during the magnetron sputtering process ranged from -30V to -80V. Thermal stability, microstructure (crystallite size, microstrain, lattice constant), and mechanical properties of the deposited TiSiN coatings were investigated using synchrotron powered x-ray diffraction beamline (SR-XRD), x-ray photoelectron spectroscopy (XPS), field emission scanning electron microscope (FESEM), and nanoindentation techniques. The SR-XRD were carried out within the temperature range of 25 to 800 °C. Rietveld analysis of SR-XRD data showed that coatings consist of cubic TiN in the form of (Ti,Si)N solid solutions. TiO$_2$ and Ti$_2$O$_3$ were identified in the high temperature experiment results for the samples deposited at lower bias voltages. Si content within the coatings decreases with increased bias voltage. Experimental results showed that increasing substrate bias voltage up to -80 V during Ti–Si–N deposition resulted in significant smoothening of surface morphology. At the same time, this also changed the phase composition and microstructure. Oxidation resistance and thermal stability of the TiSiN coatings were improved as the bias voltage increased from -30 to -50V and beyond. As the substrate bias voltage increases from -30V to -80V, Both the hardness and Young's modulus of the coatings constantly improved from 23 GPa to 33 GPa and 310 GPa to 450 GPa, respectively, corresponding to almost 50% increase.
6.2. Introduction

One of the major causes for the high cost of modern machining processes is the damage of different types of machining tools, such as cutting tools, drills, hobs, mills, and machining inserts. These damages are normally caused by wear, fatigue or crack propagations. Hard coatings can be applied to machining tools to improve the efficiency of engineering tools. Transition metal nitride hard coatings have greatly improved machining performance including high-speed cutting, stamping and moulding tools. Among them, TiSiN coatings exhibited outstanding properties such as high hardness, good wear resistance [1], and good thermal and chemical stability [2] thanks to its nanocomposite microstructure consisting of TiN nanocrystals (nc-) TiN embedded in an amorphous (a-) Si$_3$N$_4$ matrix (nc-TiN/a-Si$_3$N$_4$) [3]. The maximum improvement in mechanical properties of TiSiN systems is expected when the extremely fine nc-TiN crystals (∼3 nm) are surrounded in a-Si$_3$N$_4$ at a Si content of ∼7at.% [4].

Sophisticated metal nitride coatings can only be achieved by an appropriate choice and precise control over the parameters governing the deposition process. Deposition parameters such as Si targets current, substrate negative bias voltage, temperature, pressure and nitrogen flowrates [5],[6],[7] are the most important factors that determine the Si content, microstructure, bonding and crystalline structure, deposition rate, surface roughness, and mechanical properties of the sputtered coatings [8]. Substrate bias voltage has a significant influence on the atom mobility on the coating surface and ion bombardment during sputtering [9],[10].

Benegra et al. [11] showed that TiN coating exhibited higher compressive residual stress and lower average grain sizes when the negative bias voltage increases from 0 to -100 V. Early studies of Vaz et al. [12] confirmed the formation of TiN nanocrystals and substitution of Ti
atoms by smaller Si atoms in TiSiN coating during ion-bombardment. It was shown that the mechanical properties of coating films could be optimised by adjusting the negative bias voltage [13],[14],[15]. Applying a proper bias voltage to the substrate can significantly improve the ionisation and energy of the sputtered particles and enhance the films crystallisation [16],[11]. The decrease in deposition rate with an increase of the substrate bias voltage would be related to resputtering phenomena and densification of the coating due to strong collision energy of ions. Choi et al. [9] showed that in Ti-Si-N coating system the deposition rate and Si contents decrease as the substrate bias voltage increases from 0 to -500V and significantly influenced mechanical properties of the coatings. Chang et al. [17] showed that in TiSiN coatings, the combination of ion-bombardment, Si alloying and re-sputtering at higher bias voltages formed nanocomposite structure and increased the coating hardness and elastic modulus up to 35 and 360 GPa, respectively. Cheng et al. [8] showed that the increasing Si content of the TiSiN coating to 7 at.% progressively reduces the TiN crystallite size and at the same time increases the coating internal stresses. Wo et al. [7] studied the mechanical properties of multilayered TiN/TiSiN coatings and concluded that the relative thickness of layers determines the hardness and deformation mechanisms of the coatings. Coatings with thicker TiSiN layers showed higher hardness and deformed by crack prorogation mechanism. Yazdi et al. [2] studied the TiSiN coatings with various Si content before and after annealing in air and showed that it is possible to reduce the nc-TiN crystal sizes to ~ 6 nm by adjusting the Si content and enhance the hardness to 40 GPa. Although his results suggest that adding Si improved the oxidation resistance at 700 °C, the hardness of the coatings almost reduced by half after 2 hours annealing. Greczynski et al. [18] showed that the deposition technique has decisive influences on the nanostructure, nanochemistry and mechanical properties of TiSiN coatings deposited by hybrid high-power pulsed/dc magnetron (HIPIMS/DCMS) co-sputtering system.
Chapter 6 – Thermal stability of TiSiN coatings

Although there are comprehensive studies on the nanostructure and mechanical properties of TiSiN coatings, studies on the thermal stability and oxidation resistance of these coatings are rather scarce. In this study, the influence of substrate bias voltage on the structure and mechanical properties of TiSiN nanocomposites was investigated firstly using high-resolution SR-XRD beamline in the temperature range 25 to 800 °C. The results provide precise microstructural and phase composition data to help understand the effect of Si dopants on the thermal stability of TiSiN coatings. First principle calculations (DFT) was employed to study the effect of bias voltage and Si content on the thermal expansion of TiSiN coatings. Combination of Rietveld refinement analysis, nanoindentation data, x-ray photoelectron spectroscopy, and Field-emission electron microscopy imaging showed that optimised bias voltage could enhance the mechanical properties of the TiSiN coatings significantly.

6.3. Experimental

6.3.1. Thin film coating preparation

The TiSiN hard coatings (9 samples) were deposited onto AISI M42 tool steel substrates (hardened to HRC 62) by using a closed-field unbalanced magnetron sputtering system with a four-target configuration. The steel substrates were finely polished ($R_a \sim 0.02 \, \mu m$), degreased, ultrasonically cleaned, and subsequently blown dry in flowing nitrogen gas. The magnetron sputtering system comprised three Ti targets (purity > 99.7 at%) and one Si target (purity > 99.9 at%). The size of the targets was 380 mm × 175 mm × 8 mm. The coating equipment was furnished with a rotating substrate holder at a speed of 10 rpm to permit a homogeneous composition of the coatings, and the target-to-substrate distance was 17 cm. The vacuum chamber was pumped down to a background pressure less than $2 \times 10^{-6}$ Torr before deposition.
After that, the Ar working gas (purity 99.995 at %) pressure was set at ~1.3×10^{-3} Torr by controlling the flow rate (50 sccm) of Ar via an MKS mass flow controller. The DC current applied to each Ti target was fixed at 8.0 A (~2.3 kW for each Ti target), while the target current to the Si target was 2.5 A (sputtering power ~0.8 kW). The nitrogen content in the coatings was controlled using a closed-loop optical emission monitor (OEM) with a setting at 60 %, which regulated dynamically the flow of N\textsubscript{2} reactive gas (purity 99.995 at %) via a fast-responding piezoelectric valve. The pressure of Ar/N\textsubscript{2} mixed gases was 2×10^{-3} Torr. The deposition process of the hard coatings comprised three major steps: plasma ion cleaning, Ti adhesive layer (0.2 \textmu m), TiN buffer layer (0.4 \textmu m), TiSi\textsubscript{x}N compositional gradient layer (0.3 \textmu m), and TiSiN top layer (2 \textmu m). The Si content in the compositional gradient layer was increased linearly in the thickness direction in order to accommodate the internal stress. The substrate holder was heated by a radiation heater (5 kW) located in the centre of the vacuum chamber, and the substrate temperature was maintained at 550 °C during deposition. The ion etching to the steel substrates at the first stage (at a bias of -600 V) was employed for 30 min to remove the oxide layers on the substrate surface. For the sputter deposition of Ti (10 min), TiN (30 min), and TiSi\textsubscript{x}N (20 min) layers, the bias voltage was reduced to -60 V. The top TiSiN layer was deposited for 120 min. The substrate bias was operated in a pulsed mode at a frequency of 250 kHz. In this case, in order to study the effect of bias voltage, different bias voltages (from -30 V to -80 V) were applied to the substrate holder when the TiSiN top layer (2 \textmu m) was coated. The bias voltage mainly determined the energy of ions, bombarding the growing surface. For comparison, a binary TiN coating of similar total thickness was prepared at a bias voltage of -50 V (Sample No. 532A).
6.3.2. **In situ SR-XRD characterisations**

*In situ* SR-XRD experiments were performed on the Powder Diffraction beamline at the Australian Synchrotron with monochromatic X-rays, $\lambda = 0.827 \text{ Å}$, verified by standard reference material (LaB6 660b) as supplied by the USA National Institute of Standards and Technology (NIST). The incidence angles of the X-ray beam ($\omega$) were in the range of 4.1 to 5.9°. The diffraction data were collected by a Mythen microstrip detector over the range of $10^\circ \leq 2\theta \leq 89^\circ$ in flat-plate asymmetric reflection geometry. The coated substrates were mounted on a Pt heating stage in an Anton Paar HTK-2000 high temperature furnace and aligned to the centre of rotation on the diffractometer. The heating rate was 10 °C/min from ambient temperature up to 700 °C in air atmosphere. The temperature difference between the sample surface and Anton Parr furnace was calibrated manually before the *in situ* experiments carried out. Diffraction patterns of 6 samples (bias voltages of -30, -40, -50, -60, -70 and -80) were obtained at three temperatures (25, 200 and 500 °C) below, and three temperatures (600, 700 and 800 °C) above the deposition temperature of 550 °C due to time constraints at the synchrotron facilities. Each data acquisition at designated temperature was 120 s.

The diffraction patterns were analysed with the TOPAS v5 academic software [19] using the Rietveld method [20]. The atomic positions for the structural models, based on the main identified phases of the coating, were extracted from the Crystallography Open Database [21]. Modelled peak shapes were used to determine the volume-weighted mean crystallite sizes ($L_{vol}$) and microstrain ($\varepsilon_0$). An accurate description of the peak shapes, in all of the diffraction patterns, was obtained by applying correctional functions for a flat plate in fixed incident beam geometry [22]–[24]. The initial parameters for the refinement, as well as phase determination, were obtained from the JCPDS cards. All the diffraction patterns shown in Figure 11.2 to Figure 11.7 of the supplementary section were analysed by Rietveld refinement method. Figure
6.1 shows the refinement results for diffraction pattern of TiN sample at 800 °C containing peaks originated from the substrate (Fe and FeWC) and coating (TiN, TiO₂) phases.

Figure 6.1 Experimental SR-XRD and Rietveld refinement profile of TiN coating at 800 °C. The \( hkl \) values for each phase are indicated by the small vertical bars.

### 6.3.3. Surface analysis

Surface morphology of the thin film coatings was inspected using a field emission scanning electron microscope (FESEM) (Zeiss Neon 40EsB) coupled with Energy-dispersive X-ray spectroscopy (EDS). FESEM images were obtained using InLens detectors at various
magnifications at 5 kV and a working distance of ~2.4 mm. X-ray photoelectron spectroscopy (XPS) analysis provides comprehensive information on the chemical state, bonding structure and elemental composition of the outermost layers of surfaces. XPS data of all thin films was acquired using a Kratos Axis Ultra XPS spectrometer (Kratos, Manchester, UK) with Al-Kα monochromatic radiation (hν = 1486.6 eV) source and at an operating current of ~10 mA and voltage of ~15 kV. The XPS machine is also equipped with a cold stage, and an Ar ion gun for etching and depth profiling. The samples were mounted on a steel sample holder. The chamber pressure was reduced to 2.9 × 10⁻⁹ Torr and maintained at that level during the analysis. XPS survey spectra were acquired from both etched (6 minutes of ion sputtering) and unetched samples. High resolution XPS spectra were recorded immediately after 6 minutes of Ar⁺ sputtering. Etching was done to remove any surface oxide layers and to reduce the Ti⁴⁺ ions in order to lower oxidation states. Pass energy of 20 eV was used for high resolution Si₂p and N₁s photoelectron lines measurement. CASA XPS (Version 2.3.18) software was used for processing and fitting the peaks of the XPS spectra.

6.3.4. Nanoindentation measurements

Nanoindentation data were collected to study the mechanical properties of the samples under study. An Ultra-Micro Indentation System 2000 workstation (CSIRO, Sydney, Australia) was used, together with a diamond Berkovich indenter. The calibration of the area function of the indenter tip is carried out using a standard fused silica specimen. Load control method was employed, in which the loading was increased in 20 steps to reach the pre-defined maximum loading, then it was decreased in 15 steps to zero. For each of the steps, the displacement was recorded. The maximum loading is defined as 8 mN, which was based on the considerations that the maximum displacement during indentation should be no higher than 10% of the coating
thickness, and that high loading may result in micro-cracks in the coating which is thought to be relatively brittle, compared with metal coatings.

6.3.5. DFT computational simulations

All structural optimisations and calculations were performed with the generalised gradient approximations (GGA) using the PW91 functional [25] as implemented in the VASP package [26]. Energy cut-off for plane waves included in the expansion of wave functions was 500 eV. Pseudo-atomic calculations were performed for Ti: $3d^54s^1$ and N $2s^22p^3$. $k$-point sampling for reciprocal space integration was optimised, and a $21 \times 21 \times 21$ Gamma scheme for cubic structures was adopted. The thermodynamic properties of TiN phase were explored using the quasi-harmonic Debye–Slater model as implemented in Gibbs2 code [27]. In all temperature dependent property calculations, the Vinet’s equation of state was adopted to fit the energy–volume curves [28]. To calculate the elastic constants and determine the second derivatives, we used a finite differences method as implemented in VASP package (IBRION=6).

6.4. Results and Discussions

6.4.1. Microstructure and chemistry

Elemental concentrations in the TiSiN coatings were measured using XPS and listed as a function of substrate bias voltage in Table 6.1. XPS results show that the Si content of the coatings decreases as the bias voltage increases from -30 to -80 V. The changes in Si content can be attributed to the different acceleration effects of the bias voltage on the Si ions which are lighter than Ti ions. Si ions accelerate faster than Ti ions when the bias voltage and energy level is relatively low. As the bias voltage increases to -70 and -80 V, Si content of the coatings
drops to zero which could be caused by two main reasons: (1) After Ti ions reach a sufficiently high energy level during accelerating toward the substrate at higher substrate voltages, the Ti concentration will suppress Si content within the coatings, (2) heavy Ti ions with high kinetic energy may re-sputter the lighter Si adatoms near the surface of the substrate, as reported in similar studies on TiSiN and TiAlN systems.

Table 6.1 Elemental compositions of TiN and TiSiN unbalanced magnetron sputtered coatings, deposited at different bias voltages, acquired via XPS survey scans.

<table>
<thead>
<tr>
<th>Sample’s name</th>
<th>Atomic percentages of the elements</th>
<th>Bias voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
<td>Si</td>
</tr>
<tr>
<td>TiN</td>
<td>-</td>
<td>41.73</td>
</tr>
<tr>
<td>TiSiN</td>
<td>-30</td>
<td>31.40</td>
</tr>
<tr>
<td></td>
<td>-40</td>
<td>34.43</td>
</tr>
<tr>
<td></td>
<td>-50</td>
<td>36.53</td>
</tr>
<tr>
<td></td>
<td>-60</td>
<td>39.40</td>
</tr>
<tr>
<td></td>
<td>-70</td>
<td>40.89</td>
</tr>
<tr>
<td></td>
<td>-80</td>
<td>41.83</td>
</tr>
</tbody>
</table>

Figure 6.2 shows the SR-XRD patterns as a function of the substrate bias voltage for as-deposited samples. Diffraction patterns show that the TiN and TiSiN coatings consist of TiN phase in B1 type (fcc crystal) structure with space group fm-3m. List of detected diffraction peaks of TiN and diffraction angles are shown in Table 11.1 at supplementary information. The SR-XRD data of the samples in the studied temperature range are shown in (11.17-11.25) in the supplementary information. All of the coatings exhibited strong texture along TiN(111) which is more pronounced in TiSiN-60V. TiN (200) is convoluted by the peak caused by the substrate. Rietveld Refinement results suggest that TiSiN-30V and TiSiN-40V coatings consist of two TiN phases: a nanocrystal TiN phase with a lattice constant of 4.24 Å and a TiN phase with very coarse grains which has a slightly smaller lattice constant of 4.23 Å. SR-XRD data shows no evidence of crystalline Si$_3$N$_4$ or Ti-silicide phases.
Figure 6.2 SR-XRD patterns of the as-deposited TiSiN coatings at varying bias voltages at room temperature. The dashed vertical lines indicate substrate peaks.

Figure 6.3 shows the XPS spectra of Si 2p and N 1s for Ti-Si-N coatings. The Si 2p showed two peaks with binding energies of 99 and 101.4 eV corresponding to the Si and Si$_3$N$_4$ phase, respectively. N 1s spectrum can be fitted by two peaks located at 397 (main peak) and 399.48 eV (satellite peak) corresponding to TiN and Si$_3$N$_4$ phases. The absence of Si$_3$N$_4$ diffraction peaks in SR-XRD results suggests that this phase exists in amorphous form. The combination of these evidences support the finding from the structural analysis that the TiSiN coating films consist of crystals TiN embedded in an amorphous Si$_3$N$_4$ matrix which was observed in TEM studies on Ti-Si-N systems [17].
Figure 6.3 (a) Si 2p and (b) N 1s XPS diffractograms of sputtered TiSiN coatings deposited at various bias voltages.

Figure 6.4 shows the SR-XRD patterns of TiSiN coatings at 800 °C. Crystalline tetragonal TiO₂ in P42/mnm space group was detected in TiN, TiSiN-30 and TiSiN-40 coatings. The lattice constant of TiO₂ was measured as \( a=4.623\pm 5\% \) Å and \( c=2.983\pm 5\% \) Å. Rhombohedra Ti₂O₃ (space group R-3c) was only identified in TiSiN-40 above 700 °C with lattice constants of \( a=5.14\pm 10\% \) Å and \( c=13.65\pm 10\% \) Å. The evolution of TiO₂ and Ti₂O₃ phases in different samples during the in situ experiments are illustrated in Figure 11.2 to Figure 11.7 of the
supplementary section. TiO$_2$ peaks were observed in the SR-XRD pattern of TiN sample at 600 °C while the coatings with Si dopants only showed TiO$_2$ at 700 °C. The observed formation of TiO$_2$ layer on top of TiN coatings could be resulted from outward diffusion and oxidation of Ti due to poor oxidation resistance of pure TiN coatings at high temperatures. It is interesting to note that the quantitative SR-XRD study showed that the TiO$_2$ amount detected in TiSiN coatings is lower than that in the TiN sample. These results suggest that Si dopants improved oxidation resistance of TiSiN coatings and reduced the oxidation rate, with the threshold of the oxidation temperature increased by about 100 °C. Coatings deposited at bias voltages above 40V are consisted of TiN phase up to 800 °C. Between 700 and 800 °C, a major phase transition in the steel substrate takes place where Fe (Im-3m) transforms to Fe (Fm-3m).

![Figure 6.4 SR-XRD patterns of TiSiN coatings deposited at various bias voltages, measured at 800 °C. The dashed vertical lines indicate substrate peaks](image-url)

Figure 6.4 SR-XRD patterns of TiSiN coatings deposited at various bias voltages, measured at 800 °C. The dashed vertical lines indicate substrate peaks.
Figure 6.5 shows the TiN lattice constant as a function of temperature, with the data being obtained from Rietveld refinement results. The lattice constant of TiN at room temperature ranged from 4.25 to 4.27 Å which is slightly smaller than the reported value from Tkadletz experiment [29] and present QHA modelling predictions. Comprehensive studies on the changes in TiN lattice constant in Ti-Si-N coating systems showed that incorporation of smaller Si atoms in the position of Ti leads to the formation of solid solutions in the form of (Ti,Si)N. TiSiN-30V shows the smallest lattice constant amongst all the samples in this study, suggesting the highest Si incorporation into the TiN lattice, which is in agreement with the higher Si content of this coating concluded from Table 6.1. TiN lattice constant constantly increased as the Si content of the coatings decreased, and the TiSiN-80V sample showed the largest lattice constant. These evidences confirm the formation of (Ti,Si)N solid solutions with various Si content in TiSiN coatings. TiN lattice constant measurement based on SR-XRD data shows gradual expansion of the lattice constants with the increase of the negative bias voltage. Thermal expansion during annealing also leads to expansion of lattice constants, as confirmed by the experimental results on TiN powers, conducted by Tkadletz et al. and Bartosik et al. [30]. The accuracy of the QHA modelling for bulk TiN could be estimated when it is compared to experimental results of Bartosik et al. [30] on powdered TiN. There is a small mismatch (< 2%) between QHA predictions and results from SR-XRD data, especially at higher temperatures. This mismatch could be due to: (1) differences in thermal expansion coefficient of M2 steel and thin film coatings, and (2) Si dopants incorporated in TiN lattice. The TiN lattice constant measured for samples deposited with the bias voltage of -80V is very close to the modelling results, which could be due to the absence of Si (Table 6.1).
Chapter 6 – Thermal stability of TiSiN coatings

Figure 6.5 TiN lattice constants in TiSiN coatings deposited at various bias voltages, within the experimental temperature range of 25-800 °C

Figure 6.6 schematically summarises the phase evolution in TiSiN coatings during the in situ experiments within the temperature range 25 to 800 °C. Ti oxides such as TiO$_2$ and Ti$_2$O$_3$ were observed only in coatings deposited at low bias voltages, while coatings deposited at higher bias voltages (>40V) consist of only cubic (c-) (Ti,Si)N solid solutions. TiO$_2$ was observed in 3 of the coatings at temperatures higher than 600 °C, and Ti$_2$O$_3$ only detected in TiSiN-40V above 700 °C.
Chapter 6 – Thermal stability of TiSiN coatings

Figure 6.6 Schematic summary of the phase evolution for TiSiN coatings obtained from the \textit{in situ} experiment analysis.

Figure 6.7 shows the effect of measurement temperature on the crystallite size and microstrain of TiN crystals in TiSiN coatings. Results show that as-deposited TiSiN-30V coating possesses the smallest crystallite size of 10 nm in co-existence with coarse TiN phase. The as-deposited TiN crystallite size increased almost monotonously from 10 to 35 nm as the bias voltage increased from -30 to -80V. TiSiN-50V is the only exception, exhibiting 17 nm TiN nanocrystals which is slightly lower than TiN crystals in 20nm crystals in TiSiN-40V coating. These coatings showed excellent resistance to crystallite growth during the \textit{in situ} experiments at lower temperatures ($< 500 \, ^\circ C$). TiN coating showed a sharp increase in crystallite growth rate ($\approx 33\%$) between 600 $^\circ C$ and 800 $^\circ C$. TiSiN-30V showed the highest crystallite growth rate ($\approx 70\%$) starting at 500$^\circ C$ as the crystallite size increased from 10 to 17 nm. The co-existence of two TiN phases featuring fine and coarse grains may lead to unsuccessful nanostructure optimisation of the coating. TiSiN-40, -50 and -60V showed excellent crystal size stability (17-24 nm) within the studied temperature range. It could be due to the successful
formation of a nanocomposite structure of nc-TiN/a-Si$_3$N$_4$ which inhibits the diffusion processes and subsequently stopped the grain growth in these coatings. Coatings deposited with the highest bias voltages, TiSiN-70 and TiSiN-80, showed growth rates of less than 10% between 500 and 800 °C. Figure 6.7(b) illustrates the microstrain evolution of TiN crystals as a function of experimental temperature. The result shows that the coatings deposited at lower bias voltages (TiSiN-40 and TiSiN-30) exhibit higher microstrain. The internal stress in the coatings decreased as the temperature increases in all the coatings with different rates. TiSiN-30 and TiN coating show the highest and lowest microstrain levels at 800 °C, respectively, while internal strain in TiSiN-60 reduced with the lowest rate compared to the rest of the coatings.
Figure 6.7 (a) crystallite size and (b) microstrain of TiN phase as a function of measurement temperature, obtained from the analysis of in situ experiments.

6.4.2. Surface morphology

The surface morphology of TiSiN coatings deposited at various bias voltages is shown in Figure 6.8. The coatings gradually became denser and smoother at high bias voltages which could be attributed to the increasing number of nucleation sites, resulting from the increasing defects caused by high energy impinging ions. The (Ti,Si)N nanocrystalline were formed in island-shaped particles at lower bias voltages (e.g., -30V and -40V) and TiN coatings. TiSiN-30V particularly showed a porous microstructure. These structures could be responsible for the poor resistance of these coatings to oxidation at higher temperatures, which is indicated by the SR-XRD results. As the bias voltage increases, The (Ti,Si)N grains gradually diffuse and linked together (Figure 6.8d-e), and packed densely in TiSiN-50 and TiSiN-60 coatings. It seems that higher bias voltages assisted in producing smooth surfaces and uniform microstructures as observed in TiSiN-60. The surface morphology of TiSiN-70 and TiSiN-80
Chapter 6 – Thermal stability of TiSiN coatings

again shows some features which could be due to two simultaneous phenomena: (1) zero Si content and (2) very high energy ion bombardment during deposition. SR-XRD results confirm that all the coatings deposited at bias voltages > 40V are thermally stable up to 800 °C, regardless of their Si content.

Figure 6.8 FESEM images of TiN and TiSiN coatings deposited at different bias voltages.
6.4.3. Mechanical properties

Nanoindentation results of TiSiN samples deposited at various bias voltage is shown in Figure 6.9. Coating hardness continuously improved from 23 to 33 GPa as the bias voltage increased from -30 to -80V. The elastic modulus of the coatings also increased from 300 to 440 GPa as the bias voltage increases from -30 to -80V. Densification of coatings and the higher residual stress induced by ion bombardment at higher bias voltages due to the higher energy of the ions can contribute to the higher hardness, and Young’s modulus observed. Rietveld refinement and XPS results suggested that TiSiN-50 and TiSiN-60 coatings contain nanostructure c-(Ti,Si)N crystals surrounded by amorphous Si$_3$N$_4$. FESEM images also showed that these samples and TiSiN-70, TiSiN-80 exhibit low roughness surfaces with high density coating thanks to high energy ion bombardment during deposition. Hardness results also suggest that the maximum hardness belongs to TiSiN-60 featuring modified nanocomposite nanostructure. At bias voltages > 60 V, Si content is relatively low suggesting that nanocomposite formation is less favourable. However, at high bias voltages coatings contain a high level of internal stress, and coating density is significantly higher, which can also contribute to high hardness. The crystallite size study based on SR-XRD data in Figure 6.7(a) shows that the TiN crystallite size in coatings deposited at high bias voltages -70 to -80 is not stable. The relatively rapid crystallite growth in these samples (compared to TiSiN-50 and TiSiN-60V) may result in coating softening due to the annihilation of defects and stress-release at high temperatures. As discussed before, TiO$_2$ and Ti$_2$O$_3$ were observed only in coatings deposited at low bias voltages, while coatings deposited at higher bias voltages (>40V) consist of only cubic (c-) (Ti,Si)N solid solutions. These, as well as the observed porous microstructure observed in the TiSiN-30V sample, could also be the factors contributing to the lower hardness and elastic modulus for the coatings deposited at lower bias voltages,
In smarmy, indentation results show an overall trend that the mechanical properties of the coatings under study constantly improved as the bias voltage increases, which could be attributed to densification of coatings, higher residual stress, less Si content, larger crystal size, more smooth and homogeneous surface, and low porosity in the coatings deposited using higher bias voltages.

![Graph showing hardness and elastic modulus as a function of bias voltage](image)

**Figure 6.9** Hardness and Elastic modulus of TiSiN samples as a function of bias voltage, derived from nanoindentation experiments.

Figure 6.10 shows the influence of bias voltage and silicon content on internal stress ($\sigma$) embedded in dominant TiN(111) orientation in TiSiN coatings. These measurements are based on equation (6.1) in which the changes in d-spacing along TiN(111) in TiSiN coatings ($d$) deposited at various bias voltages compared to d-spacing in TiN coating ($d_0$) at each temperature.
\[ \sigma = \frac{E}{(1-\nu)} \times \frac{d-d_0}{d_0} \]  

(6.1)

where \( E \) (Elastic modulus) and \( \nu \) (Poisson ratio) are assumed for TiN as 300 GPa and 0.23, respectively. For as-deposited coating, residual stress constantly changes with bias voltage increments from the maximum tensile stress of \( \sim 6 \) GPa in TiSiN-30V to minimum compressive stress of \( \sim -4 \) GPa in TiSiN-80V. The compressive residual stresses in the coating film were shown to promote the coating mechanical properties and resist crack propagation [31]. The gradual changes in internal stress from tensile to compressive stresses could be an effective parameter in constant hardness increases in TiSiN coating as shown in Figure 6.10.

![Figure 6.10 The residual stress for TiN(111) in TiSiN coatings as a function of bias voltage compared to TiN coating at various temperatures](image)

It can be seen that the internal stress is strongly sensitive to deposition parameters such as temperature, pressure and substrate bias voltages [8],[32]. The measured residual stress values for TiSiN-50V matched almost perfectly with the reference sample (TiN coating) which deposited at bias voltage of -50V. The residual internal stress for TiSiN-50V coating is close
to zero in as-deposited state and during in situ experiment and eventually reaches zero at 800 °C.

Internal stresses are stable up to 600 °C in TiSiN coatings and then significantly changes in some of the coatings at temperatures up to 800 °C which could be due to the microstructure instability at high temperatures. Coatings deposited at bias voltages of -30, -40 and -80V showed various levels of stress-release during the in situ experiments above 600 °C which reveal degrees of ineffective microstructural refinement and nanocomposite formation. Although TiSiN-70V and 80V coating exhibit a high level of compressive stresses, the internal stresses are unstable above 600 °C and may lead to coating softening at high temperatures. TiSiN-60V is the only coating that shows significant hardness, internal compressive stress and stability during the in situ test.

6.5. Conclusions

In the present study, the influence of deposition bias voltage (-30 to -80V) on TiSiN coatings deposited by magnetron sputtering was investigated using a number of experimental techniques. The results showed that coatings deposited at bias voltage of -50 V and above showed stable phase composition in the temperature range of 25 to 800 °C consisted of nc-(Ti,Si)N embedded in a- Si3N4 and smooth surface and enhanced hardness (33GPa). Higher negative bias voltage significantly changes the phase composition, stability, microstructure and surface morphology of the coatings, which, in turn, resulted in desirable improvement in the oxidation resistance, thermal stability, and mechanical properties. Both the hardness and Young's modulus of the coatings constantly improved from 23 GPa to 33 GPa and 310 GPa to 450 GPa, respectively, as the substrate bias voltage increases from -30V to -80V, representing almost 50% increase.
6.6. References


This chapter presents a systematic approach of investigating the microstructure, phase composition and thermal stability of CrAlN hard coating systems.
7.1. Abstract

This contribution investigates the phase composition of CrN and CrAlN coatings by in-situ high temperature synchrotron radiation (SR-XRD), with the coatings deposited on steel substrates using closed field unbalanced magnetron sputtering. Rietveld refinement on the SR-XRD diffraction patterns indicated CrN as the major phase, over the temperature range of 25 °C – 700 °C, for both coatings. At the high temperature of 700 °C, a Cr$_2$N phase was observed in the CrN coating while the CrAlN coating also had a Cr phase. Williamson-Hall plots, from the refined data, afforded estimating variations of the strain and crystallite size of the major phase, up to 700 °C. The crystallite size (10 nm) for the CrAlN coating, at 25 °C, agrees very well with previous GI-XRD and TEM results obtained at room temperature [1].
Chapter 7 – Thermal Stability of CrN thin films

7.2. Introduction

Magnetron-sputtered hard-surface coatings composed of transition metal nitride have been utilised to improve the productivity of cutting machinery in a wide range of applications such as drills, mills and cutting tools [2][3][4]. The main merit of magnetron sputtering is the attainment of robust control of the composition and microstructure of hard films and other nanostructured composite materials [5].

Due to their exceptionally high hardness characteristics and outstanding wear resistance, TiN coatings are a major component in cutting machinery. However, TiN coatings exhibit only moderate resistance to oxidation and corrosion lessening their duration of use. In contrast, CrN coatings display enhanced performance under oxidative and corrosive conditions that is primarily derived from the formation of an isolating adhesive chromium oxide layer on the coated surface [6]. In some applications, the thickness of the coating is an important parameter in deciding the type of coating to use. The maximum thickness of TiN coatings is typically limited to 10 μm, while CrN coatings can be made with thicknesses of more than 40 μm [7]. However, CrN coatings are associated with significantly lower hardness (i.e. 12.0 – 18.0 GPa), compared with TiN coatings (> 20 GPa). The demand for improved properties has resulted in the development of ternary and quaternary coatings such as CrAlN, CrAlYN, CrSiN, CrAlSiN and CrAlTiN [8].

Incorporating (alloying) Al in the cubic lattice of c-CrN coatings forms a metastable phase that considerably improves the hardness of the coating. Since c-CrN exhibits high solubility for c-AlN, ternary CrAlN nanocomposite coatings are promising pseudo binary nitrides in which Al and Cr sesquioxides provide effective resistance against oxygen diffusion through the coating [9]. Outward diffusion of Cr and Al ions, to the surface in CrAlN coatings, results in the
formation of complex surface oxides which enhance the thermal properties of CrAlN by acting as barriers against further oxidation [5]. Additionally, the hardness and thermal stability of CrAlN is enhanced by Al substitution of Cr atoms in the face-centred cubic structure of c-CrN [8]. The solute atoms are believed to hinder slip by diffusing to and segregating around dislocations [10]. These two hardness-enhancing mechanisms in coatings are determined by the Al content and are characterised by the formation of a metastable solid solution that produces internal lattice strains. Properties of such coating are highly sensitive to Al content where the excessive addition of Al beyond 64 at. % alters the structure from rock-salt (NaCl) crystal structure (Fm3m) to wurtzite structure (P-31m) resulting in deterioration of hardness and anti-oxidation properties with alteration of preferred growth orientation [11]. Formation of hexagonal h-AlN structures significantly decreases the hardness and thermal stability of CrN coatings reducing the benefit of Al alloying [12].

High temperature properties of hard coatings primarily depend on their crystalline-phase structures. Alloying elements, present in the phase formed during the deposition stage, exert a noticeable influence on the durability and the expected service life of hard coatings [13]–[19]. Any significant variations in coating grain size may affect their thermal stability [20]. Therefore, any unforeseen changes in the microstructure and phase composition of coating material can potentially reduce the thermal resistance and hardness [21] of the coatings. Since coatings deposited by the sputtering techniques are in a non-equilibrium condition [22], it is of vital importance to study the microstructure of the coatings at elevated temperatures.

Literature articles and reviews discuss overall mechanical and thermal properties including various preparation techniques of CrAlN coatings, in terms of their microstructure [23], effects of atomic ratio (i.e. Al/Cr ratios) on their phase composition [2][24], deposition control parameters [25], [26], and high temperature oxidation properties [18], [19].
Tribological properties of CrN coatings with Al and Si dopants deposited by cathodic arc, studied by Polcar et al. [27], showed high hardness, excellent oxidation resistance and thermal stability up to 800 °C. X-ray analysis showed that, the dominant structure in Al and Si-doped coating material was cubic structured solid solutions of Al and Si in CrN. However, hexagonal AlN was also detected in the AlCrSiN coating. Sánchez-López et al. [12] studied the tribological behaviour of CrAl(Y,Zr)N coatings at 300, 500 and 650 °C, and concluded that the CrAlN coating had lower film wear due to high hardness and presence of Al₂O₃ on the coating surface. Forsen et al. [28] reported improved hardness of CrAlN coating by addition of Ti which improves the formation of h-AlN at annealing temperatures up to 1100 °C. The enhanced hardness was due to spinodal decomposition into coherent TiCr and Al-rich structures of the coating material, causing age hardening that stabilised the significantly improved hardness.

Wang et al. [18] deposited CrN and CrAlN using single electron beam plasma assisted physical vapour deposition (PAPVD) system, annealed them at 500 °C-1000 °C and then cooled down to 25 °C for characterisation. Their analysis showed orthorhombic CrN structure in the CrN coating, CrN was converted to β-Cr₂N at about 500 °C and Cr₂O₃ was detected above 700 °C. A solid solution of (Cr,Al)N was detected in the CrAlN coating and was stable up to 900 °C. The hardness of the CrN coating dropped from 24.8 GPa to 16 GPa at 600 °C. On the other hand, the original hardness of CrAlN amounted to 30 GPa which decreased to 21.6 GPa after annealing at 600 °C. CrAlN solid solutions can be deposited with up to 66.0 at.% of Al input [29][15], which precipitates into a more stable h-AlN phase with low mechanical properties, above 800 °C, as a result of a spinodal reaction [30].

Kirchlechner et al. [31] studied the deposition of CrN coating by reactive magnetron sputtering at temperatures of 25 °C – 850 °C. They employed high intensity synchrotron radiation beamline to obtain diffraction patterns from both coating and steel substrate simultaneously.
Rivadulla et al. [32] used synchrotron radiation ($\lambda = 0.44397$ Å) in combination with *ab initio* calculations to identify the cubic to orthorhombic transformation of CrN at pressures of about 1 GPa. This transformation reduces the bulk modulus of the coatings.

The promising properties of CrAlN coatings highly depend on their complex phase behaviour and more detailed studies on their nanostructure could lead to fabrication of improved hard coatings. In our previous studies [2][1], we employed multiple surface and subsurface analysis characterisation techniques to investigate $\text{Cr}_x\text{Al}_{1-x}\text{N}$ coatings on various substrates. Results revealed the formation of CrAlN solid solution, with amorphous AlN present at columnar CrN grain boundaries. The next step necessitates an accurate investigation of the role of Al on the change of crystal structure phases of CrN coatings at temperatures up to 700 °C. We explore the phase composition and crystal structure of the aforementioned coating in the temperature range of 25 °C to 700 °C using *in-situ* SR-XRD measurements. Finally, we analysed the SR-XRD measurements to derive the crystallite size and strain of the main phases up to 700 °C.

### 7.3. Experimental Procedure

CrN and CrAlN coatings were deposited on M2 high speed steel substrates using closed field unbalanced magnetron sputtering system (Teer Coatings Ltd, UK) with four-target configuration. The coating process has been described in detail elsewhere [1][33]. To observe a phase formation in the CrAlN coatings, *in-situ* SR-XRD measurements were carried out as a function of temperature. Synchrotron radiation has a number of advantages including the ability to tune the wavelength to avoid the formation of sample fluorescence, superior energy bandpass and significantly higher signal/noise (S/N) compared to a laboratory instrument. The experiment was performed on the Powder Diffraction beamline at the Australian Synchrotron.
with monochromated X-rays of wavelength 0.82647 Å. The X-ray diffraction data were collected on a Mythen microstrip detector and the wavelength was determined by Rietveld refinement of a Standard Reference Material, LaB6 660b, as supplied by the National Institute of Standards and Technology (USA). The coated substrates were mounted on a Pt heating strip in an Anton Paar HTK-2000 high temperature furnace and aligned to the centre of rotation on the diffractometer. The samples were heated from ambient temperature up to 700 °C with a heating rate of 10 °C/min and X-ray diffraction data were collected over the angular range 10° ≤ 2θ ≤ 89°. The sample surface temperature was calibrated before the experiment.

Samples made with CrN coating on M2 steel will be denoted as CrN-M2ST and samples made with Cr$_x$Al$_{1-x}$N coating on M2 steel will be denoted as CrAlN-M2ST.

### 7.4. Theoretical Procedure

In the present study, assuming Bragg-Brentano geometry, phase analysis of SR-XRD data was performed by the Rietveld method using the GSASII software package [34]. Initially, refinement was applied to the unit cell parameter while all other structural parameters were fixed to the original standard values of the JCPDF data files listed in the results and discussion section. The crystal strain, atomic position, atomic isotropic temperature, zero shift, background as Chebyshev polynomial of fifth degree, peak profile, sample displacement and texture were then successively refined. The fittings were performed using analytic Hessian refinement derivatives. These corrections help to obtain physically realistic intensities, displacement and peak width models when analysing diffraction patterns in non-standard geometries.
7.5. Results and Discussions

The coating composition was analysed at room temperature by X-ray Photoelectron Spectroscopy (XPS) [1] and the results are listed in Table 7.1.

### Table 7.1. Contents of coating sample obtained from XPS measurements

<table>
<thead>
<tr>
<th>Samples</th>
<th>Cr</th>
<th>Al</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrAlN-M2ST</td>
<td>27.5</td>
<td>14.2</td>
<td>31.8</td>
<td>26.6</td>
</tr>
<tr>
<td>CrN-M2ST</td>
<td>49.6</td>
<td>-</td>
<td>30.3</td>
<td>20.1</td>
</tr>
</tbody>
</table>

The phases found in the coatings, from SR-XRD, are: CrN (JCPDF 011-0065), AlN (JCPDS 046-1200), Al (JCPDS 004-0787), Cr$_2$N (JCPDS 00-035-0803), Cr (JCPDS 00-900-8467) and AlO$_2$ (JCPDS 00-901-1413) on a substrate of Fe (JCPDS 006-0696) dominated M2 steel. For clarity, only the Miller indices of appropriate phases are indicated in the SR-XRD plots of Figure 7.1 to Figure 7.3. Peaks without Miller indices are due to the M2 steel substrate.

Figure 7.1(a) and (b) shows the SR-XRD patterns for CrN coating (18° – 30° $\theta$ range) and CrAlN coatings (18° – 27° $\theta$ range) respectively, at 25, 200, 500, 600 and 700 °C. The emphasis is on the CrN, AlN, Al, Cr$_2$N and Cr phases.
Chapter 7 – Thermal Stability of CrN thin films

Figure 7.1. SR-XRD patterns of (a) CrN-M2ST and (b) CrAlN-M2ST samples at different temperatures

For the CrN-M2ST samples, CrN is the main phase over the entire temperature range with a Cr$_2$N phase produced above 600 °C. For the CrAlN-M2ST samples, CrN is a major phase over the entire temperature range. A cubic AlN phase is observed up to 500 °C. From 600 °C the c-
AlN phase disappears. Due to the similar crystal structure of CrN and c-AlN phases, it is possible that they form a solid solution, as there is a shift of peaks in the diffraction pattern of CrN with increasing temperature. It is also possible that, the grain size of AlN has become very small and undetectable by XRD. Above 600 °C, a significant Cr phase and a very small amount of AlO₂ phase appear. Lu et al. [39] have investigated Aluminium peroxide (AlO₂) formation in the interfacial region of Pt-Al₂O₃ (sapphire) couple (≈ 1mm plates). It’s interesting that the authors state that the formation of AlO₂ occurs in the range of 1200 °C to 1400 °C but not below 1100 °C.

The room temperature XPS results indicate the appearance of oxygen for both samples. The Cr2p3/2 and Cr2p1/2 bonding states of CrAlN-M2ST sample indicate a combination of CrN and Cr₂O₃ on the surface. The Al2p peak indicated a combination of AlN and Al₂O₃ on the surface. The N1s spectra consisted of a CrN component (strong peak) and a Cr-O-N component (weak peak). The binding energy characteristic of Al₂O₃ and Cr₂O₃ oxides in the very top atomic layers of the surface can explain most of the detected oxygen [35]. Oxidation of CrN at high temperatures is understood to occur through outward diffusion of chromium, aluminium and nitrogen while oxygen diffuses inwardly and forms oxides inside coating layers [36], [37]. The formation of Cr-O-N was discussed by Minami et al. [38] which crystalised in the similar cubic structure of CrN with strong diffraction in (111) and (200) directions. CrN coating material exhibits remarkable oxidation resistance due to its fine and dense equiaxial crystal structure which reduces the oxygen diffusion rate significantly. Formation of adhesive aluminium and chromium oxides on the surface also hinder oxygen diffusion. Combination of these effects can restrict the formation of oxides only on very top surface layers which can be detected by XPS. There were no signs of Al₂O₃ and Cr₂O₃ phases in the SR-XRD results of CrAlN-M2ST samples below 600°C presumably due to only a very small amount of oxides.
Chapter 7 – Thermal Stability of CrN thin films

presented on the surface. However, the presence of AlO$_2$ ($\approx$2.8\%) was detected between 600 °C and 700 °C, due to the increase in temperature.

CrN phase, with a rock-salt (NaCl) like unit cell, dominated the structure of the coating film. The crystallographic characteristic of the coating was determined from refined synchrotron data. Results showed a significant change of the CrN lattice parameter in the CrAlN coating. The lattice parameter value of reference for the CrN phase was 4.145 Å (JCPDF 011-0065). Refinement of the lattice parameter resulted in a value of 4.209 Å at room temperature (25 °C) continuously decreasing to 4.167 Å at 600 °C and then abruptly increasing to 4.176 Å at 700 °C. The initial decrease of the lattice parameter, from room temperature value, can be attributed to the formation of a solid solution of Al/CrN from the diffusion of Al (from the cubic AlN and amorphous Al that is in the grain boundaries) into the CrN structure substituting the Cr atoms. The smaller size of Al atoms effectively reduces the lattice constant of the dominant phase in CrAlN. The TEM images of similar coating, discussed by Munroe et al. [1] and Rahman et al. [2], generated from cross section of the columnar CrN grains confirmed the presence of amorphous AlN phase between CrN grains, at room temperature. The continuous decline of unit cell value may indicate two simultaneous phenomena: (1) the higher amount of Al dissolution in the structure and (2) strain release due to temperature increment. CrN showed high solubility of Al which improves the mechanical properties of coating material through the formation of a solid solution [9].

A major change in the microstructure of CrAlN-M2ST samples occurred at the temperature range above 600 °C with the appearance of Cr diffraction peaks of substantial intensity and AlO$_2$ diffraction peaks of very low intensity. Results suggest that, the CrAlN coating (CrN/AlN grains and amorphous boundaries) produced a CrN-Cr/AlN-Cr multi-phase grain composition by crystallisation of Cr from the boundary into the grain due to thermal activation and Al from
the amorphous boundary forming AlO$_2$. It should be noted that, there is much less Al/AlN within the grains than in the amorphous boundaries.

Figure 7.2 depicts the refined SR-XRD pattern of the CrAlN-M2ST sample at 700 °C with emphasis on the main Cr, AlO$_2$ diffraction peaks. Main differences between experimental and fitted plots were due to the substrate peaks are identified as a combination of Fe and Fe$_3$W$_3$C phases. Formation of metallic Cr and AlO$_2$ in the nanocomposites coating at 700 °C may underline the initiation of changes in mechanical properties of the film coating. Protective nanocomposite coatings can only preserve their hardness and mechanical properties provided the nanostructure remains stable and unchanged.

Figure 7.2 Refined SR-XRD pattern of CrAlN coating at 700 °C

Careful analysis of diffraction patterns in Figure 7.1 and Figure 7.2 reveals changes in peak positions and widths as the temperature increased to 700 °C. Such shifts in peak positions and
widths usually indicate change in lattice parameter and/or strain in the crystal structure. The high resolution refined SR-XRD data of the CrN and (Cr,Al)N phases are analysed to give some indication of the domain/crystallite sizes and strains in both the CrN-M2ST and CrAlN-M2ST samples, respectively, over the 25 °C – 700 °C temperature range. The same analysis is performed for the Cr phase at 700 °C.

The crystallite domain size and lattice strain are deduced from the Williamson-Hall equation [36]:

Williamson-Hall equation:

$$\beta \cos \theta = 4\varepsilon \sin \theta + \frac{K\lambda}{D}$$

(7.1)

Where $\beta$, $\varepsilon$, $D$ are the full width at half maximum, microstrain and domain/crystallite size, respectively. $K$ is a constant which equals to 0.89 and $\lambda$ is the X-ray wavelength [32]. GSAS refinement produced data of (hkl), d, 2$\theta$ and FWH values for all of the identified phases in the samples. This data is used to make plot of $\beta \cdot \cos \theta$ and $4\sin \theta$ (see Figure 7.3).

According to equation 7.1, the strain component ($\varepsilon$) is calculated from the slope and the crystallite domain size ($D$) from the intercept ($K\lambda/D$) at each temperature. The strain and domain/crystallite size of the CrN phase in CrN-M2ST and CrAlN-M2ST samples were estimated up to 700 °C and results shown in Table 7.2 and Figure 7.4.

Similar estimates of the strain and crystallite size for the Cr phase at 700 °C indicate crystallite size $\approx$ 11 nm and strain $\approx$ 0.0024.
Figure 7.3 Williamson-Hall plots for CrN phase in (a) CrN-M2ST and (b) CrAlN-M2ST samples at different temperatures.
Table 7.2. Calculated strain and crystallite size of CrN phase in the CrN-M2ST and CrAlN-M2ST samples at different temperatures (T)

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Strain CrN-M2ST</th>
<th>Strain CrAlN-M2ST</th>
<th>Crystallite size (nm) CrN-M2ST</th>
<th>Crystallite size (nm) CrAlN-M2ST</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.853</td>
<td>0.779</td>
<td>40.1</td>
<td>9.8</td>
</tr>
<tr>
<td>200</td>
<td>0.807</td>
<td>0.556</td>
<td>42.0</td>
<td>10.5</td>
</tr>
<tr>
<td>500</td>
<td>0.469</td>
<td>0.423</td>
<td>54.7</td>
<td>45.1</td>
</tr>
<tr>
<td>600</td>
<td>0.263</td>
<td>0.323</td>
<td>56.5</td>
<td>55.4</td>
</tr>
<tr>
<td>700</td>
<td>0.180</td>
<td>0.180</td>
<td>61.8</td>
<td>56.8</td>
</tr>
</tbody>
</table>

The plots of Figure 7.4(b) indicate that, the crystallite sizes of the CrN phase are smaller in the CrAlN-M2ST samples than in the CrN-M2ST samples at all temperature. Furthermore, sizes increase as temperatures approach 700 °C, for both coatings. Previous room temperature GI-XRD and TEM studies of the same CrAlN-M2ST samples showed the size of crystallite domains of approximately 10 nm, in good agreement with the current SR-XRD result at 25 °C [4]. Interestingly, the size of crystallites corresponds to about 11 nm at the high temperature of 700 °C, which is about the same size of the CrN crystallites in CrAlN-M2ST sample up to 200 °C.

The plots of Figure 7.4(a) indicate the strain for the CrN phase follows a similar pattern with the crystallite size variation. The strains are less in the CrAlN-M2ST samples than in the CrN-M2ST samples. Similarly, the strain decreases as the temperature increases up to 700 °C for both sample coatings. Since the Cr phase occurs above 600 °C, its strain value is unimportant.
Figure 7.4. Calculated (a) strains vs. $T$ and (b) crystallite size vs. $T$ for CrN phase in the CrN-M2ST and CrAlN-M2ST samples

The solid solution of AlN into CrN generally increases the strains of the lattice in bulk sized material. However thin films synthesised using plasma technology may not follow the general
trend due to the complicated plasma effects. These include very fast reaction and grain growth of the thin films at very short time periods. The direction of plasma and resulting non-equilibrium interactions add to the complication of the thin film growth mechanism. The higher strain results of CrN phase in the CrN-M2ST samples than in the CrAlN-M2ST samples are most probably due to the differing plasma interactions occurring at film synthesis. Interestingly at 600 °C and above the values for strain and crystallite size for the CrN phase in both samples are the same (within experimental errors). It could be due to the AlO$_2$ and Cr formation within that temperature range.

The calculated strain and size values imply that, the mechanical properties (such as hardness, elastic modulus) of the coatings deteriorate as the temperature increases from 25 °C – 700 °C. However measuring strains, hardness and grain sizes at very high temperatures is very challenging and in some cases probably impossible.

7.6. Conclusions

Rietveld analysis of in-situ high temperature synchrotron radiation X-ray diffraction (SR-XRD) of CrN and CrAlN coatings, deposited on M2 steel substrate by closed field unbalanced magnetron sputtering, revealed CrN, Cr$_2$N, AlN, Al and Cr phases in the coatings. Analysis indicated that CrN is the major phase in both coatings at all temperatures. At the high temperature of 700 °C, the formation of CrN, Cr and AlO$_2$ (~2.8%) phases in the CrAlN coatings were detected. Similarly, Cr$_2$N phase was detected in the CrN coating.

Williamson-Hall plots were used to estimate the crystallite size and strains of the CrN phase for temperatures up to 700 °C. Analysis indicates a decrease in crystallite size and strains of the major phase, in both coatings, over the temperature range. The strains and crystallite size of the CrN phase in the CrAlN coating are less than those in the CrN coating for temperatures
below 600 °C while they are equal above 600 °C. An estimate for the Cr phase indicated very small crystallites of ~ 11 nm at 700 °C. The estimate crystallite size of ~ 10 nm at 25 °C, of CrN phase, for the CrAlN coating agrees well with previous TEM results.

Acknowledgment

This study has been supported by School of Engineering and Information Technology at Murdoch University. The authors gratefully acknowledge the support provided by the Australian Synchrotron beam time award AS141/PD/7582. E. M greatly appreciates Murdoch University for the award of a postgraduate scholarship.

7.7. References


Chapter 7 – Thermal Stability of CrN thin films


This chapter presents a systematic approach of investigating the microstructure, phase composition and thermal stability of CrAlN hard coating systems.
8.1. Abstract

Cr$_{1-x}$Al$_x$N coatings, synthesised by unbalanced magnetic sputtering system, showed improved microstructure and mechanical properties for ~14-21 % Al content. In situ SR-XRD analysis indicated various crystalline phases in the coatings that included: CrN, AlN, $\alpha$-Cr with a small amount of AlO$_2$ and Al$_2$O$_3$ over 25 – 700 °C range. Al doping improves resistance to crystal growth, stress release and oxidation resistance of the coatings. Al doping also enhances the coating hardness ($H$) from 29 to 42 GPa, elastic modulus ($E$) from 378 to 438 GPa and increased resistance to deformation. First-principles and quasi-harmonic approximations (QHA) studies on bulk CrN and AlN were incorporated to predict the thermo-elastic properties of Cr$_{1-x}$Al$_x$N thin film coating in the temperature range of 0 - 1500 °C. The simulated results at T= 1500 °C give a predicted hardness of $H = \sim 41.5$ GPa for a ~ 21% Al doped Cr$_{1-x}$Al$_x$N coating.
8.2. Introduction

3-d transition metal nitrides, such as CrN and TiN, combine attractive physico-chemical, electronic, optical, magnetic, mechanical and thermal properties [1]. These composite materials have shown a wide range of technical applications in various key industry areas. For example, due to its extreme hardness, high melting point and superior chemical stabilities, nitride-based ceramic coatings have been used for high-speed machining [2], cold forming, moulding dies[3], sliding parts and rocket nozzles [4]. It is noted that CrN has significant superiority over TiN in wear, corrosion resistance [5], and anti-oxidative properties in temperatures up to 700 °C [6]. Vacuum sputtering technique is an outstanding method for synthesising high quality CrN ceramic thin film coatings with superior structural, mechanical and tribological properties [3,4]. These studies have been extended to ternary combinations of CrN with doping of other elements, e.g., Al [7], Si [8], [9], Ti [10], V [11], Nb [12] or Cu [13]. The doping elements mainly distribute in the amorphous layers which surrounds the columnar structured nanocrystalline (nc-) CrN grains. These amorphous layers can effectively enhance many mechanical properties of such thin film coatings. In particular, Al has shown great potential in improving the hardness [14] as well as corrosion and oxidation resistance[15], [16]. This Cr–Al–N framework is of particular interest as they can form aluminium oxides on the top surface layers which suppress the diffusion of oxygen into the coating film. Analysis indicated the thin film coatings have enhanced chemical stability, good mechanical properties, good tribiological properties, high temperature stability (up to 1000 °C) and exhibit excellent oxidation resistance [3],[ 11], [17].

Characterisation at room temperature indicated that Al significantly affected the preferred grain orientation of the thin films. TEM and XPS studies indicated that amorphous AlN existed at
Chapter 8 – Thermal Stability of CrAlN thin films

the columnar CrN grain boundaries. The incorporation of Al introduced compressive residual stress to the coating material lattice. Moreover, the mechanical properties such as hardness, elastic strain and plastic deformation resistance of the coatings showed significant improvement over non doped CrN coating. These clearly indicated the crucial role of Al in producing a combination of superior hardness and excellent damage resistance in nc-CrN frameworks [18].

In the present work, in-situ synchrotron radiation powder diffraction (SR-XRD) beamline was employed to quantitatively investigate the changes in phase composition and microstructure of Cr$_{1-x}$Al$_x$N thin film coatings as a function of Al content at different measurement temperatures in an atmospheric environment. Rietveld analysis of high resolution SR-XRD data and nanoindentation measurements will provide quantitative results, hence making a connection between microstate phases and mechanical properties of the coating. Density Functional Theory (DFT) calculations and Quasi-harmonic approximation (QHA) are employed to estimate the cell-volume, thermal expansion and hardness of Cr$_{1-x}$Al$_x$N system at temperatures up to 1500 °C.

8.3. Experimental

8.3.1. Thin film coatings preparation

Cr$_{1-x}$Al$_x$N coatings with a total film thickness of 2 µm were deposited on M2 high speed steel substrates at 550 °C using a closed field unbalanced magnetron sputtering system (Teer Coatings Ltd, UK) with a four-target configuration. The coating process were described in detail by Li et al. [18] and Wo et al. [19].
8.3.2. \textit{In situ} SR-XRD characterisations

\textit{In-situ} SR-XRD experiments were performed on the Powder Diffraction beamline at the Australian Synchrotron with monochromatic X-rays, $\lambda = 0.827$ Å, verified by standard reference material (LaB6 660b) as supplied by the USA National Institute of Standards and Technology (NIST). The incidence angles of the X-ray beam ($\omega$) were in the range of 4.1 to 5.9°. The diffraction data were collected by a Mythen microstrip detector over the range of $10^\circ \leq 2\theta \leq 89^\circ$ in flat-plate asymmetric reflection geometry. The coated substrates were mounted on a Pt heating stage in an Anton Paar HTK-2000 high temperature furnace and aligned to the centre of rotation on the diffractometer. The heating rate was 10 °C/min from ambient temperature up to 700 °C in air atmosphere [20]. The temperature difference between the sample surface and Anton Parr furnace was calibrated manually before the \textit{in-situ} experiments carried out. Diffraction patterns were obtained at three temperatures (25, 200 and 500 °C) below and two temperatures (600 and 700°C) above the deposition temperature of 550 °C due to time constrains at the synchrotron facilities. Each data acquisition at designated temperature was 120 s.

The diffraction patterns were analysed with the TOPAS v5 academic software [21] using the Rietveld method [22]. The atomic positions for the structural models, based on the main identified phases of the coating, were extracted from the Crystallography Open Database [23]. Modelled peak shapes were used to determine the volume-weighted mean crystallite sizes ($L_{\text{vol}}$) and microstrain ($e_0$). An accurate description of the peak shapes, in all of the diffraction patterns, was obtained by applying correctional functions for a flat plate in fixed incident beam geometry [24]–[26]. The initial parameters for the refinement, as well as phase determination, were obtained from the JCPDS cards.
8.3.3. Nanoindentation measurements

Young's modulus and hardness of the coatings were measured, at room temperature (~25 °C), by a calibrated Ultra-Micro Indentation System, UMIS-2000 equipped with a Berkovich indenter. A maximum load of 20 mN was applied in 10 increments. The loading rate used was 2.5 mN/s and represented the static response of the materials. The area function of the indenter tip was calibrated using a standard fused silica specimen. Load control method with a maximum loading of 5 mN was employed for calibration. The peak loading is based on the considerations that the maximum displacement during indentation should be no more than 10% of the coating thickness. For better resolutions, the number of test points were 20 for loading and 20 for unloading.

8.3.4. DFT computational simulations

All structural optimisations and calculations were performed with the generalised gradient approximations (GGA) using the PW91 functional [27] as implemented in the VASP package [28]. Energy cut-off for plane waves included in the expansion of wave functions was 500 eV. Pseudo-atomic calculations were performed for Cr: 3d⁵4s¹, Al 3s²3p¹ and N 2s²2p³. \( k \)-point sampling for reciprocal space integration was optimised and adopted a \( 21 \times 21 \times 21 \) Gamma scheme for cubic structures. CrN in contrast to other early transition metal (Ti, Sc, V, ...) nitrides, needed additional effort due to the local magnetic moments of the Cr atoms in CrN structure. The calculations for bulk CrN was carried out for both paramagnetic (CrN-m) and non-magnetic (CrN-nm) structures.

The thermodynamic properties of cubic phases were explored using the quasi-harmonic Debye–Slater model as implemented in Gibbs2 code [29]. In all temperature dependent
property calculations, the Vinet’s equation of state was adopted to fit the energy–volume curves [30]:

\[ P = 3B_0 \left( \frac{1-\eta}{\eta^2} \right) e^{\frac{2}{3}(B_0' - 1)(1-\eta)} \]  

(8.1)

where \( P, B_0 \) and \( \eta \) are pressure, isothermal bulk modulus and cube root of the specific volume respectively. To calculate the elastic constants and determine the second derivatives, we used a finite differences method as implemented in VASP package (IBRION=6).

8.4. Results and Discussions

8.4.1. Structural analysis via in situ SR-XRD data

The surface elemental composition and chemical bonding state, obtained from previous XPS analysis and full discussion of the coatings by Li et al. [18] indicated the existence of CrN, Cr\(_2\)O\(_3\), AlN and Al\(_2\)O\(_3\) phases in the coating surface region, are summarised in Table 8.1.

Table 8.1. Elemental composition of the Cr\(_{1-x}\)Al\(_x\)N coatings determined by XPS.

<table>
<thead>
<tr>
<th>Coating Notation</th>
<th>Cr</th>
<th>Al</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>33.4</td>
<td>0</td>
<td>34.9</td>
<td>31.7</td>
</tr>
<tr>
<td>C2-14%Al</td>
<td>27.5</td>
<td>14.2</td>
<td>31.8</td>
<td>26.6</td>
</tr>
<tr>
<td>C3-17%Al</td>
<td>16.6</td>
<td>17.2</td>
<td>29.4</td>
<td>36.8</td>
</tr>
<tr>
<td>C4-21%Al</td>
<td>19.1</td>
<td>21.4</td>
<td>30.4</td>
<td>29.0</td>
</tr>
</tbody>
</table>

The JCPDS cards used for phase identification in the SR-XRD diffraction patterns: 00-076-2494 (CrN), 00-025-1495 (AlN), 00-901-4565 (Al\(_2\)O\(_3\)), 00-900-9676 (Al\(_2\)O\(_3\)), 00-035-0803 (Cr\(_2\)N), 00-901-3484 (\(\alpha\)-Fe) and 00-041-1351 (Fe\(_3\)W\(_3\)C). The atomic positions for Fe\(_3\)W\(_3\)C
were taken from [31]. The full in-situ patterns of all samples, for all temperatures, are included in the Supplementary section (Figure 11.8 to Figure 11.11). For clarity, the diffraction pattern for each temperature are combined in one plot for each sample.

The Rietveld refinement of the diffraction patterns resulted in R-weighted pattern \((R_{wp})\) values in the range of 15-20. The largest errors in the refinement models are mainly due to the incomplete crystallographic data for the substrate. An example of a typically fitted spectrum is indicated in Figure 8.1, which shows the Rietveld refinement for the C1 sample at 700°C with \(R_{wp} = 15\). The allowed hkl values for each phase are indicated by the small vertical bars. The difference between experimental and modelled results is indicated by the difference plot above the \(hkl\) bars.

All 20 diffraction patterns shown in Figure 11.8 to Figure 11.11 of the supplementary section were analysed by Rietveld analysis with similar plots as Figure 8.1 producing data used for further analysis as indicated in Figure 8.2 to Figure 8.6. The phases of the C1 sample at different temperatures was similar to the sample (denoted as CrN-M2ST) recorded in Mohammadpour \textit{et al.}[20].
Figure 8.1 Experimental SR-XRD and Rietveld refinement profile of C1 coating at 700°C. The allowed hkl values for each phase are indicated by the small vertical bars.

SR-XRD diffraction patterns at ~ 25 °C of as-deposited Cr$_{1-x}$Al$_x$N coatings are depicted in Figure 8.2. For clarity, the 2θ range in Figure 8.2 is from 18° to 35° 2θ consisting of the main peaks for each phase.
Figure 8.2 SR-XRD diffraction patterns at ~25 °C of as-deposited Cr$_{1-x}$Al$_x$N coatings with various Al contents. The dashed vertical lines indicate substrate peaks. The high intensity peak at 2θ = 23.5 which belongs to Steel substrate was omitted to avoid overlapping with above diffraction patterns.

The compositions of the main phase in as-deposited CrAlN thin film coatings were determined to be CrN and AlN phases. Thin film coating C1 showed strong intensity in (200), (220) directions at ~22.8° and ~32.4° 2θ, respectively for the CrN phase. In the Al doped samples, the dominant orientations of the CrN phase are in the (200) and (111) planes. These diffraction peaks became broader and of lower intensity as the Al content increased (C3-17%Al and C4-21%Al) indicating a combination of small grain size and high concentration of possible amorphous nature. The peaks at 20.2°, 23.4° and 33.3° 2θ in the C4-21%Al sample are identified as diffractions from c-AlN (111), (200) and (220) planes, with some overlap with substrate (α-Fe) diffraction peaks. The confirmation of the AlN phase in SR-XRD pattern agrees with the NEXAFS results by Mahbubur et al [32] and XPS analysis by Li et al [13] from similar coatings. All samples in as-deposited condition (~25 °) had Al$_2$O$_3$ and Cr$_2$O$_3$ phases.
detected by XPS but SR-XRD did not show any noticeable peaks related to those oxides. It could be due to (i) most of the oxygen accumulate in the top surface layers of thin films, and (ii) possible amorphous state of the oxide phases. However, at temperatures > 500 °C minor amounts of Al₂O₃ and metastable AlO₂ were observed from the diffraction patterns (Figure 8.7).

Figure 8.3 indicates the main phases of these coatings at 700 °C. Diffraction patterns of CrAlN coatings at 700 °C show α-Cr, AlO₂ and Al₂O₃ phases. Peaks at 22.60°, 26.16° and 37.33° can be determined as α-Cr (111), (200) and (220), respectively. Agouram et al. [33] concluded that the phase content of CrNₓ-based coatings is strongly influenced by deposition processes. The presence of α-Cr in CrNₓ coatings can reduce the hardness; however, it may improve the coating toughness or as a metallic source which diffuses outward and contributes to the formation of surface oxidation layers. Although hexagonal-structured Cr₂N (h-Cr₂N) exhibits higher hardness than cubic CrN, it is more susceptible to oxidation which can deteriorate the thermal stability of the C1 thin film with considerable h-Cr₂N content especially at high temperatures [20]. It seems Al doping successfully prevents the formation of h-Cr₂N in the CrAlN coatings even at lowest Al percentage (C2-14%Al) in the temperature range of study. Our observations did not confirm any possible existence of Cr₂O₃ crystalline phases in the column structure of coatings; that may indicate (i) small amorphous structures distributing in grain boundary regions, and (ii) either amorphous or crystalline phase structure in the very top surface layers of thin films where normal XRD cannot fully determine the phases (Grazing incidence SR-XRD would be able to provide more precise surface crystalline information). The shifts of diffraction peaks from the substrate, especially for Fe (111) at 23.8 ° is probably due to the thermal expansion of the unit cells at elevated temperatures. Peaks related to CrN and AlN phases exhibited some sharpening with increasing temperature [21].
Chapter 8 – Thermal Stability of CrAlN thin films

Figure 8.3 SR-XRD diffraction patterns at 700 °C of Cr$_{1-x}$Al$_x$N coatings with various Al contents. The dashed vertical lines indicate substrate peaks.

From the Rietveld refined SR-XRD data, the lattice constants of the CrN and c-AlN phases in the Cr$_{1-x}$Al$_x$N coatings were calculated and plotted as a function of temperature in Figure 8.4. The lattice constant of CrN decreases continuously from 4.21 Å to 4.17 Å for C1 and to 4.19 Å for the Al doped samples. The overall changes of the lattice constant for the CrN phase are slightly smaller in the samples with Al doping than without doping. Overall, the lattice parameter values agree with the experimental values from other sources, such as Barshilia et al. [34] (4.09 to 4.16 Å) and Elangovan et al. [35] (4.15 to 4.17 Å). Lattice constants of c-AlN (in sample C4-21%Al) increased steadily from approximately 4.09 Å at room temperature to 4.1 Å at 700 °C indicating unit cell expansion by 0.5%. The lattice constant of α-Cr phase, in all samples at 700 °C, was 3.65 Å ± 10 %. 

199
Figure 8.4 CrN and c-AlN lattice constants, from Rietveld analysis, in Cr$_{1-x}$Al$_x$N coatings as a function of the in-situ experiment temperature.

The crystallite size and microstrain as a function of temperature, from Rietveld analysis for the CrN phase, are shown in Figure 8.5. The Effect of adding Al onto the microstructure of the as-deposited coatings is more pronounced in C3-17%Al and C4-21%Al coatings exhibiting about 30% smaller crystallite sizes compared to Al free and C2-14%Al samples. The crystallite sizes in all samples gradually increased in the temperature range 25 to 600 °C and then abruptly increased from 600 to 700 °C. C1 and C2-14%Al show the highest crystallite size growth by ~100% and ~67%, respectively. The higher Al content in C3-17%Al and C4-21%Al effectively prevented the crystallite growth of CrN during heating below 700 °C. Above, 600°C the CrN crystallite size in C4-21%Al increases by ~34%. The most stable crystallite size for CrN is exhibited by C3-17%Al with an 8% crystallite growth. The crystallite sizes of the α-Cr phase...
are 1832 (C2-14%Al), 1780 (C3-17%Al) and 828 (C4-21%Al) nm in the 700 °C \( \text{Cr}_{1-x}\text{Al}_x\text{N} \) samples.

Our observations showed that microstrain in C1 sample decreased by \(~ 67\%\) during heating which is almost \(~ 1.7\times\) of the microstrain release in samples with Al contents. The residual stress in these types of coatings could be due to two mechanisms (1) thermal stress and/or (2) accumulation of defects (dislocations, vacancies, etc.) in the coating layer. Thermal stress is a resultant of the difference in the coefficient of thermal expansion (CTE) value for coating and substrate. The decline of internal stress in the coatings could be a result of absorption and annihilation of defects during annealing. It allows the defects to diffuse through the lattice and to be absorbed in grain boundaries and dislocation cores. It seems to be more pronounced in the binary CrN coating case. The presence of amorphous content in \( \text{Cr}_{1-x}\text{Al}_x\text{N} \) coatings at grain boundaries hinders stress release in the coatings which resist against coating softening.
Chapter 8 – Thermal Stability of CrAlN thin films

Figure 8.5 Effect of temperature on the CrN phase in the Cr\(_{1-x}\)Al\(_x\)N coatings, from Rietveld analysis: (a) crystallite size (b) microstrain.

The stress in the coating structure, from the changes in \(d\) space for CrN (220), is shown in Figure 8.6. Similar plots for the (111), (200) and (311) planes of CrN phase are included in Figure 11.12 to Figure 11.14 of the supplementary section. The stress (\(\sigma\)) in the coating was calculated based on equation (8.1) using the elastic properties of CrN (Elastic modulus, \(E = 300\) GPa and Poison ratio, \(\nu = 0.28\)) [36].

\[
\sigma = \frac{E}{(1-\nu)} \times \frac{d-d_0}{d_0}
\]

(8.2)

where \(d\) and \(d_0\) are from the experimental diffraction patterns and JCPDS card of CrN, respectively. Refinement data show that there is a considerable amount of residual stress in the as-deposited coating structure. Stress values in Al free coating decrease progressively as
temperature increases from 25 to 700 °C by ~56%. The stress release in samples containing Al is slower as Al content increases and reduced to only ~11% in C4-21%Al coating. Based on observations in Figure 8.5(b) and Figure 8.6, there is a direct correlation between residual strain, stress and Al at% in the coating composition.

![Graph showing the effect of temperature on the residual stress for CrN (200) orientation in Cr\(_{1-x}\)Al\(_x\)N coating.](image)

Figure 8.6 Effect of temperature on the residual stress, from equation (8.2), for CrN (200) orientation in Cr\(_{1-x}\)Al\(_x\)N coating

### 8.4.1. Experimental mechanical properties of CrAlN coatings

Nano-indentation tests, for Cr\(_{1-x}\)Al\(_x\)N coatings at as-deposited conditions and after the completion of the in-situ SR-XRD experiment (heated samples), were undertaken at room temperature. The hardness (\(H\)) and elastic modulus (\(E\)) for these coatings are set out in Table...
Chapter 8 – Thermal Stability of CrAlN thin films

8.2 and Figure 11.15 to Figure 11.16 of the supplementary section. Analysis of Table 8.2 and the plots clearly indicate that there is no difference in $H$ and $E$, within the experimental errors, between the as-deposited and heated sample. The resistance to deformation is indicated by $H^3/E^2$ and plotted in Figure 11.17 of the supplementary section. The coatings with smaller crystallite size/higher microstrain present greater hardness (C3-17\%Al and C4-21\%Al samples) in as deposited condition. Improvement in coating hardness confirms the microstructure refining effect of Al dopants.

These findings are consistent with the quantitative SR-XRD measurements of crystallite size and microstrains in the Al doped coatings that exhibited very little hardness drop after heating. The calculated ratio of $H^3/E^2$ improved significantly in samples containing Al compared to the reference sample (C1). However, there is no change in resistance to deformation between as deposited and heated conditions of the samples. The combination of microstructure and nanoindentation studies indicate that the hardness of the as-deposited nanocrystalline coatings can be controlled by several parameters such as phase composition, crystallographic directions, crystallite size and residual stress/microstrain [37].

Table 8.2. Nanoindentation, at 25\^C, of Cr$_{1-x}$Al$_x$N coatings: as-deposited and heated samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>As-deposited H (GPa)</th>
<th>E (GPa)</th>
<th>Heated H (GPa)</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>29 ± 2</td>
<td>378 ± 21</td>
<td>28 ± 2</td>
<td>376 ± 22</td>
</tr>
<tr>
<td>C2-14%Al</td>
<td>35 ±3</td>
<td>401 ± 27</td>
<td>35 ± 3</td>
<td>396 ± 25</td>
</tr>
<tr>
<td>C3-17%Al</td>
<td>39 ± 3</td>
<td>421 ± 38</td>
<td>39± 3</td>
<td>421 ± 30</td>
</tr>
<tr>
<td>C4-21%Al</td>
<td>42 ± 3</td>
<td>438 ± 32</td>
<td>42 ± 3</td>
<td>436 ± 32</td>
</tr>
</tbody>
</table>
8.4.2. Density functional theory modelling

8.4.3. Structural optimisation

The energy and lattice constant of bulk CrN-nm, CrN-m and c-AlN were optimised to find the most stable ground state. Figure 8.7 shows changes in energy of the unit cell ($\Delta E = E - E_0$) versus primitive unit cell volumes for each structure used for predictions of thermodynamic properties.

![Figure 8.7 The change in energy of primitive unit cells for bulk CrN-NM, CrN-M and AlN as a function of cell volume](image)

Table 8.3 lists experimental lattice parameter values from SR-XRD data and DFT calculations from present work and available literature. The calculated lattice parameter for CrN-m (spin-polarised) is closer to SR-XRD results. The magnetic moment for each Cr atoms in CrN-m structure converged to 2.044 $\mu_B$ which is within range of 1.9 to 2.28$\mu_B$ from calculations of Filippetti et al. [38].
Chapter 8 – Thermal Stability of CrAlN thin films

Table 8.3. Lattice constant from experimental SR-XRD and DFT calculations.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Lattice constant, a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>experimental</td>
</tr>
<tr>
<td>CrN-nm</td>
<td>4.17 - 4.20</td>
</tr>
<tr>
<td></td>
<td>4.18 [40]</td>
</tr>
<tr>
<td></td>
<td>4.145 [41]</td>
</tr>
<tr>
<td>CrN-m</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>c-AlN</td>
<td>4.07</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The QHA method (Debye model) was used to predict the thermal expansion of the studied bulk structures as a function of temperatures. Figure 8.8(a) and 4.8(b) are plots of the experimental and theoretical lattice parameters, with respect to temperature, for bulk CrN and c-AlN phases in the temperature range 0 - 1500 °C, respectively. Figure 8.8(a) also includes lattice constant calculated from the experimental thermal expansion coefficient, α(T), of Zhou et al. [46] with a₀ = 4.14 Å (standard CrN phase) at room temperature. Figure 8.8(a) clearly shows the CrN-m model is highly compatible with the experimentally obtained data. The CrN lattice constants at room temperature for all samples differ from the simulation values within ~1.6%. Interestingly these converge to the simulated results with increasing temperature resulting in a ~0.4% difference at 700 °C. The most significant drop in lattice constant values of CrN occurs to C1 sample which is very close to the QHA model at 700 °C.

Quasi-binary systems like Cr₁₋ₓAlₓN coatings with a mixture of NaCl-structured CrN/AlN phases can form (Cr,Al)N solid solutions up to x = 0.75 [47]. Phase segregation during deposition results in a mixture of fcc-structured Cr-rich (Cr,Al)N and AlN [28], [48] which will increase the coating hardness due to activation of solid-solution hardening mechanism.
Theoretical [49] and experimental [47], [50] studies show that substitution of Cr atoms (r=1.4 Å) with Al atoms (r=1.25 Å) can progressively decrease lattice constant of CrN phase as Al content increases. However, smaller Al atoms can incorporate into interstitial positions in CrN structure which can expand the lattice constant as observed for CrSiN coating [19], [51].

The c-AlN lattice parameters in C4-21%Al are in good agreement with experimental data from Tkadletz et al. [52] as indicated in Figure 8.8b. The experimental results are within ~±0.3 %, of the simulated QHA results up to 700 °C.

Overall the differences between the simulated and experimental results is due to the use of the pure homogeneous bulk material in the Debye (QHA) model calculations, and the solid solution of different nitride phases of the thin film coatings.
8.4.4. Prediction of elastic constants and hardness

Three independent elastic constants are needed to describe the behaviour of cubic-structured materials to stress and can be used to describe the nature of the bonds between atoms in the crystals. These constants \((C_{11}, C_{12} \text{ and } C_{44})\) were calculated for CrN-nm, CrN-m and c-AlN at zero K and zero pressure and listed in Table 8.4. The mechanical stability of these phases can be ascertained by using the following criterion for cubic systems [53]:

\[
C_{11} + 2C_{12} > 0, \quad C_{11} \cdot C_{12} > 0, \quad C_{44} > 0, \quad C_{11} > 0, \quad C_{11} > B > C_{12}
\]  

(8.3)

All these conditions were satisfied by the CrN and c-AlN phases indicating the mechanical stability of these structures. The overview of available literature as shown in Table 8.4 indicates that the reported calculated values for elastic constants and modulus are widely scattered and
depend on the choice of $k$-points, cut-off energies, functional(s) and simulation packages. As an example, Yan et al. [42] and Brik et al. [54] used the CASTEP module of Materials Studio package with different settings of $k$ points grids and cut off energies for CrN-nm analysis. With $8 \times 8 \times 8$ (400 eV) and $10 \times 10 \times 10$ (320 eV) $k$ points grids the authors calculated $C_{11}$ values of 526 and 546 GPa, respectively.

Supplementary section Table 11.3 and Table 11.4 show the influence of $k$-points grids selection on the elastic constants of CrN-m and CrN-nm for the present project. To calculate the elastic constants for CrN-m and CrN-nm, $k$-point grids of $21 \times 21 \times 21$ and $31 \times 31 \times 31$ were chosen for the simulations. The results of these analyses are tabulated in Table 8.4. The calculated elastic constants for CrN-nm in the present study are comparable (~ 2%) with calculations of Zhou [46] who used similar approach via VASP package and projector-augmented wave (PAW) method. The values of $C_{11}$ and $C_{12}$ for c-AlN underestimate by ~9% the calculations of Wang et al. [45] carried out by VASP package and PAW method.

The positive difference between $C_{11}$ and $C_{44}$ ($C_{11}-C_{44}=582$ for CrN-nm), known as Cauchy pressure, indicates the metallic bonding nature of Cr-N structure[55] which is comparable to much smaller difference for AlN ($C_{11}-C_{44}=83$). Cauchy pressure is also a sign of the ductility of materials, since it indicates the angular character of atomic bonding in metals. A positive Cauchy pressure reveals ductility of crystal, while a brittle material exhibits a negative value[56]. Bulk modulus ($B$), shear modulus ($G$) and Young’s modulus ($E$) for each phase were estimated by applying Voigt-Reuss equations [57] and compared with available literature.
Chapter 8 – Thermal Stability of CrAlN thin films

Table 8.4. Calculated elastic constants ($C_{ij}$), bulk modulus ($B$), Young's modulus ($E$), Poisson ratio ($\nu$) of CrN (non-magnetic and spin-polarized) and c-AlN phases. Calculated and experimental data from the literature are denoted by $c$ and $e$, respectively.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$C_{11}$ ($\text{GPa}$)</th>
<th>$C_{12}$ ($\text{GPa}$)</th>
<th>$C_{44}$ ($\text{GPa}$)</th>
<th>$B$ ($\text{GPa}$)</th>
<th>$G$ ($\text{GPa}$)</th>
<th>$E$ ($\text{GPa}$)</th>
<th>$\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrN-nm</td>
<td>588.0</td>
<td>215.1</td>
<td>5.9</td>
<td>340</td>
<td>126</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td></td>
<td>526 c, [42]</td>
<td>226 c, [42]</td>
<td>5 c, [42]</td>
<td>326 c, [42]</td>
<td>101 c, [42]</td>
<td>0.43 c, [42]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>502 c, [54]</td>
<td>214 c, [54]</td>
<td>4.1 c, [54]</td>
<td>410 c, [54]</td>
<td>163 c, [58]</td>
<td>0.41 c, [58]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>580 c, [46]</td>
<td>210 c, [46]</td>
<td>8 c, [46]</td>
<td>327 c, [58]</td>
<td>100-250 e, [36]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>546 c, [58]</td>
<td>184 c, [58]</td>
<td>20 c, [58]</td>
<td>340 c, [59]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrN-m</td>
<td>352</td>
<td>88.7</td>
<td>61.0</td>
<td>176.4</td>
<td>93.9</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>369 c, [42]</td>
<td>125 c, [42]</td>
<td>114 c, [42]</td>
<td>192 c [42]</td>
<td>239.0</td>
<td>0.25 c, [42]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>348 c, [46]</td>
<td>117 c, [46]</td>
<td>74 c, [46]</td>
<td></td>
<td>279 c, [42]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c-AlN</td>
<td>387</td>
<td>149</td>
<td>305</td>
<td>254.3</td>
<td>209</td>
<td>0.2788</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>221 e, [60]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The calculated results, at 0 K, from Table 8.4 are spread out but have similar magnitudes including the 2 experimental values at ~25 °C. The $k$-point grids that optimised the calculation of the elastic constants and unit cell volumes will be used in the DFT and QHA simulations.

QHA method for CrN and c-AlN are used to predict the hardness of two binary compounds (CrN and c-AlN) in a wide temperature range (25 - 1500 °C). The method for calculating the hardness of materials is based on atomic potentials and bond strength developed by Simunek and Vackar [61] for single crystals and then extended to binary compounds. The hardness of a crystal can be calculated by introducing its bond strength ($S_{ij}$):

$$S_{ij} = \sqrt{\varepsilon_i \varepsilon_j / (d_{ij} n_{ij})} \quad (8.4)$$
where $e_i$ and $e_j$ are atomic potentials of $i$ and $j$ atoms, respectively, and are defined as the valence electron number divided by the radius of the atom; $d_{ij}$ is the distance of the nearest atom $j$ to atom $i$ and $n_{ij}$ is the number of bonds between atom $i$ and its neighbouring atoms $j$.

For binary compounds, the difference between atomic potentials is:

$$f_e = \left[ \frac{e_i - e_j}{e_i + e_j} \right]^2$$  \hspace{1cm} (8.5)

The hardness of such a system with volume ($V \Omega$) is defined as:

$$H = \left( \frac{C}{d_{ij}^4} \right) \sqrt{e_i e_j / (d_{ij} n_{ij}) e^{-\sigma f_e}}$$  \hspace{1cm} (8.6)

where $C$ and $\sigma$ are constants ($C = 1450$ and $\sigma = 2.8$) [61]. The DFT results (at T = 25 °C) for $c$-CrN and $c$-AlN are listed in Table 8.5. The difference between the calculated value and the experimental value for the CrN phase in C1 sample is ~15%. This difference can be explained by considering the columnar orientation of the coating which is completely different from an ideal single crystal.

Table 8.5 DFT calculated hardness, at T = 25 °C, of bulk CrN, AlN based on $d_{ij}$. Current project and literature experimental data included for comparison.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$d_{ij}$</th>
<th>$e_i$</th>
<th>$e_j$</th>
<th>$f_e$</th>
<th>$H_{DFT}$</th>
<th>$H_{EXPT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrN-nm</td>
<td>2.028</td>
<td>3.125</td>
<td>4.904</td>
<td>0.0490</td>
<td>24.1</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>19 - 28.6 [36]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>24 - 25 [62]</td>
<td></td>
</tr>
<tr>
<td>CrN-m</td>
<td>2.071</td>
<td>22.4</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>$c$-AlN</td>
<td>2.034</td>
<td>2.793</td>
<td>4.545</td>
<td>0.056</td>
<td>21.1</td>
<td>-</td>
</tr>
</tbody>
</table>
Chapter 8 – Thermal Stability of CrAlN thin films

Temperature dependent variations in unit cell volume for each structure were obtained from QHA modelling up to 1500 °C (Figure 8.8). Subsequently, the bond length, $d_{ij}$, as a function of temperature was deduced from the cell volumes and by use of equation 5 the hardness values for CrN (CrN-nm and CrN-m) and $c$-AlN phases. The results of hardness over a wide range of temperatures are shown in Figure 8.9. Also plotted in Figure 8.9 are the high temperature (25-500 °C) in-situ nanoindentation data for commercially available $\text{Al}_{0.7}\text{Cr}_{0.3}\text{N}$ coatings studied by Fox-Rabinovich et al. [63] and Beake et al. [64]. Room temperature nanoindentation results for the current projects’ $\text{Cr}_{1-x}\text{Al}_x\text{N}$ coatings are also incorporated in Figure 8.9.

Based on predicted material behaviours, hardness values for both phases constantly reduced at elevated temperatures. However, there are considerable differences in the reduction slopes depending on the phase type. Hardness values for CrN-nm structure showed the highest resistance to temperature while AlN was more susceptible to temperature. Experimental hardness in Table 8.2 of $\text{Cr}_{1-x}\text{Al}_x\text{N}$ samples showed that nanocomposites of CrN in amorphous AlN matrix can effectively improve the resistance to grain boundary sliding [65] which makes these samples harder than C1 sample. In addition, the deposition process and doping significantly distort the lattice of CrN/AlN mixture, as is evident in microstrain and residual stress plots, which can also contribute to improve the deformation resistance of doped samples.

According to Simunek and Vackar [61], the hardness of multicomponent compound systems is expected to be a geometrical sum of the values of the hardness of all binary systems in the solid (given by their equation 6). Interestingly for the current multicomponent system (at 25 °C), consisting of CrN and AlN phases, $H = H_1 + H_2 = 22.5 + 21 = 43.5$ GPa ($H_1$ for CrN-m and $H_2$ for AlN) compares remarkably well with the experimental value of 42 GPa for the C4 sample. Here the values correspond to a numerical sum of equation 5 as opposed to a geometric sum.
To show this point more clearly, the simulated data for CrN-m and AlN are added and the plot included in Figure 7.9.

The experimental results of Fox-Rabinovich et al. [63], are in some agreement with the simulated CrN-m, CrN-nm and AlN results for temperatures up to ~150°C while they deviate significantly for higher temperatures up to ~500°C, whilst Beake et al. [64] results are in agreement over the same temperature range. It should be noted that the materials in Beake’s investigation have a high percentage Al content (~70%) whilst our materials have a maximum of ~21% Al content (C4). The hardness of the experimental result from C4 and computational modelling from the summation of the CrN-m and AlN components are very similar at room temperature, see Figure 8.9. If this is a real relationship, then the magnetic properties of the Cr are important for the formation of stable and hard Cr$_{1-x}$Al$_x$N coatings.

Based on the results from both experiments and computational calculation, the temperature dependent hardness of the synthesised CrN/AlN thin film nanocomposites can be predicted in the temperature range from 20 °C to 1500 °C, refer to Figure 8.9. Furthermore, a numeric sum for the hardness of the 2 components, at T= 1500 °C give a predicted hardness $H \approx 41.5$ GPa. Only real experimental measurements at the 200 - 1500 °C range will show if the hardness of the CrN/AlN multicomponent thin film has the predicted direct sum values.
Figure 8.9 Simulated hardness values as a function of temperature for bulk CrN-m, CrN-nm and c-AlN. Nanoindentation hardness data, at high temperature for Al<sub>0.7</sub>Cr<sub>0.3</sub>N thin film coatings and room temperature for current Cr<sub>1-x</sub>Al<sub>x</sub>N coatings.

8.5. Conclusions

Synthesised Cr<sub>1-x</sub>Al<sub>x</sub>N coatings, with a maximum Al content of ~21 %, by unbalanced magnetic sputtering system, showed improved microstructure and mechanical properties compared to undoped CrN coating. Analysis of in situ synchrotron X-ray diffraction at temperatures range of 200 – 700 °C established: (i) remarkable resistance to crystal growth and stress release up to 700 °C for coatings with Al doping greater than ~14%. (ii) Al-dopants improve oxidation resistance of the coatings by preventing the formation of Cr<sub>2</sub>N at high temperatures.
Nano indentation results at ~ 25 °C show: (i) Al doping improved the coating hardness ($H$) and elastic modulus ($E$) from 29 to 42 GPa and 378 to 438 GPa respectively, and (ii) resistance to deformation increased as the Al content increased.

First-principles and quasi-harmonic approximations (QHA) studies for bulk magnetic and non-magnetic CrN (CrN-m and CrN-nm) and AlN over the temperature range of 0 – 1500 °C were undertaken to calculate elastic constants ($C_{ij}$) and hardness ($H$). Comparison of DFT-QHA models and the nanoindentation results indicate that hardness of Cr$_{1-x}$Al$_x$N coating with ~ 21% Al content may be the sum of values from CrN-m and AlN phase. Our computational modelling predicts that the hardness ($H$) of Cr$_{1-x}$Al$_x$N coating with the Al content of ~21% can reach to about 41.5 GPa at $T = 1500$ °C.

8.6. References


Chapter 8 – Thermal Stability of CrAlN thin films


Chapter 9

Paper VI: Phase Structure and Hardness Prediction of CrSiN and CrNiN Coatings at High Temperature using Synchrotron Radiation and DFT Simulation


This chapter describes the influences of Si and Ni content on the thermal stability of CrN coatings using experimental and modelling techniques.
9.1. Abstract

Microstructure, phase transformation, microstrain, hardness, elastic modulus, and resistance to deformation of magnetron sputtered CrSiN (5 < Si at.% < 18) and CrNiN (13 < Ni at. % < 40) thin film coatings were explored via *in situ* synchrotron diffraction X-ray diffraction (*in situ* SR-XRD) in the temperature range of 300 - 970 K. Nanoindentation measurements made at room temperature on the as-deposited and after *in situ* heating cycle thin film coatings. Thermoelastic properties were predicted, up to 1500K, by employing density functional theory with quasi-harmonic approximation methods. Hardness estimates of the CrN and Ni phases up to 1200 K done by correlating hardness with bulk and shear modulus of these phases. Results indicate incorporating Si improves hardness of CrN coatings from 29 to 36 GPa. Formation of (Cr, Si)N and Ni(Cr) solid solutions are also postulated by studying the changes in lattice constants of CrN. The simulated hardness results predict hardness of $H \approx 20$ and $\approx 6$ for CrN (1200 K) and Ni (600 K), respectively.
Chapter 9 – Thermal Stability of CrSiN and CrNiN thin films

9.2. Introduction

Transition metal nitrides have been used as protective surfaces owing to their superior hardness, high cathodic stability (corrosion resistance) [1], wear resistance, and thermal stability [2]. CrN- and TiN-based coatings have been widely used in the cutting and formation industries as bearing and mechanical parts, dies, and moulds [3],[4]. Several deposition techniques, such as magnetron sputtering, plasma-enhanced chemical vapour deposition, and arc ion plating have been used to apply nanocomposite coatings with various combinations of nano crystalline (nc-) metal nitrides embedded in an amorphous matrix (a-), with significant improvements in mechanical properties. The characterisation of such coatings indicates the addition of Al [5], [6], Si [7], [8] or Ni [9] in binary nitride structures can substantially improve their mechanical properties and corrosion resistance. TiSiN coating systems exhibited excellent mechanical properties, which were attributed to the existence of hard amorphous Si₃N₄ at the TiN grain boundaries [10], [11]. Several studies have successfully produced nc-CrN/a-Si₃N₄ coatings with enhanced mechanical properties,[11], [12] and the hardening mechanisms in the CrSiN system were explored by studying the microstructure and mechanical properties of the CrSiN coating while varying the Si content over the range 0 - 9 at.% [13]. Cross-sectional transmission electron microscope (XTEM) imaging has shown that Si can effectively modify the coating microstructure from packed columnar CrN grains to a refined nc-CrN/a-Si₃N₄ nanocomposite, depending on Si atomic percentage [8]. Previous studies have also shown that coating microstructure is tuneable by control of sputtering conditions during depositions such as bias voltage and sputtering current [14]. In addition, we have previously investigated the deformation mechanism and macrostructure variation in CrSiN coatings by studying the microstructure and mechanical properties of CrSiN coatings with Si content varying from 5 to 18.5 at.% [8].
Incorporation of ductile metals, e.g., Ni, Cu, and Y into hard coatings enhanced their toughness [15]. An increased toughness promotes their applications in medical devices, engine components, and high-speed cutting tools, where sudden failures due to brittle coatings or poor adhesion are unacceptable. Microstructure and mechanical properties of sputtered CrNiN coatings are significantly affected by Ni content; with Ni content < 10 at.% improving the coating hardness [2], while higher Ni content (15 - 40 at.%) resulted in lower hardness, improved toughness due to changes in dominant deformation mechanism from grain boundary sliding to plastic deformation [9].

Our TEM studies on the CrSiN [8] and CrNiN [9] coatings revealed that various atomic percentages of Si and Ni could reduce crystallite sizes in as-deposited coatings by forming nanocomposites of nc-CrN in an amorphous matrix depending on dopant atomic concentration. However, studies on the microstructure and mechanical properties of these coatings are challenging due to the harsh operational conditions at high temperatures. The present study aims to evaluate the compositional changes in phase and microstructure evolutions of the coatings at variable temperatures from 300 to 970 K using in situ SR-XRD. Nanoindentation at room temperature, of as-deposited samples and after the in situ heating cycle, studied the relationship between the microstructure and mechanical properties of the coatings. Evaluating changes in lattice constant, crystallite size and strain of included phases from refined analysis of synchrotron diffraction patterns, combined with estimated thermodynamic properties derived from quasi-harmonic approximations calculations, will shed light on the changes in mechanical properties of the coatings at high temperatures.
9.3. Experimental

9.3.1. Sample preparation

CrN, CrSiN, and CrNiN coatings with thicknesses of 1-2 µm were deposited onto M2 steel substrates using a closed-field unbalanced magnetron sputtering system (Teer Coatings Ltd, UK) with a four-target configuration. Pure chromium (Cr), silicon (Si) and nickel-chromium alloy (Ni:Cr=80:20 at.%) targets (99.9% purity; 345×145×8 mm size) were used to synthesise the nitride coatings. In this experiment, two Cr, one Si, and one NiCr targets installed in the coating system for deposition. High purity (99.999%) Ar and N$_2$ gases were used as the working and reactive gas, respectively. MKS mass flow controllers controlled flow rates of these gases. The vacuum chamber was pumped down to a background pressure of 4×10$^{-4}$ Pa prior to coating deposition. The working gas pressure, during the sputtering process, maintained at ~0.3 Pa. The target-to-substrate distance was set to 17 cm, and substrate rotation speed was 10 rpm. In the first stage, the substrate was sputter cleaned by Ar plasma at a bias of -450 V (frequency 250 kHz) for 20 min, in order to remove the surface oxide layer or any surface contaminant. Film deposition began when the bias voltage decreased to -80 V (frequency 250 kHz). The target current applied to each Cr target remained fixed at 4.0 A (sputtering power ~1.2 kW). Adjusting the target current applied to Si or NiCr target controlled the Si or Ni content in the coatings. CrN, CrSiN and CrNiN thin films deposited with various Ar/N$_2$ ratio by adjusting their flow rates. The deposition time was 60 min. No external heating was used to the substrate holder during deposition. XPS survey spectra, on the cleaned sputtered surfaces of CrN, CrSiN and CrNiN, analysing the surface composition and bonding states for the as-deposited coatings, are detailed in previous investigations [8],[9]. Table 9.1 lists specimen designation and surface chemical compositions. A comparatively higher
concentration of O and C in the coatings surfaces are limited to topmost layers (and/or grain boundaries) and caused by exposed of thin surface surfaces to atmospheric air.

Table 9.1 Surface chemical composition of coatings with different Ni and Si content determined by XPS

<table>
<thead>
<tr>
<th>Sample designations</th>
<th>Elemental Composition (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>C1</td>
<td>33.4</td>
</tr>
<tr>
<td>C2#Si</td>
<td>22.2</td>
</tr>
<tr>
<td>C3#Si</td>
<td>18.3</td>
</tr>
<tr>
<td>C4#Si</td>
<td>15.1</td>
</tr>
<tr>
<td>C5#Ni</td>
<td>40.4</td>
</tr>
<tr>
<td>C6#Ni</td>
<td>34.8</td>
</tr>
<tr>
<td>C7#Ni</td>
<td>29.1</td>
</tr>
</tbody>
</table>

9.3.2. *In situ* SR-XRD characterisation

*In situ* SR-XRD measurements on CrSiN and CrNiN coatings, over a temperature range, taken to observe changes in crystalline phase composition, lattice parameter, and crystallite size/strain as a function of *in situ* temperature. The experiments were performed on the Powder Diffraction beamline [16] at the Australian Synchrotron with monochromatic X-ray (\(\lambda = 0.82646\) Å). The instrument was set up in flat plate, fixed incident beam geometry, with the incident fixed between 4.1 to 5.9°. Data were collected over a range of 10° to 89° 20 with a Mythen microstrip [17] in 2 Detector positions for 30sec in each position with movement between positions of 0.5°. The coated substrates mounted on a Pt heating strip in an Anton Paar HTK-2000 high temperature furnace and aligned to the centre of rotation on the diffractometer. The samples, as indicated in Table 9.1, were heated in air from room temperature to 970 K at 10 K/min, see details in [4],[5].
The diffraction patterns were analysed by the Rietveld method [18] as implemented in the TOPAS program. [19] An accurate description of peak shapes in the diffraction patterns obtained by applying correctional functions for flat plate, fixed incident beam geometry. [20]–[22] Modelled peak shapes were used to determine the volume-weighted mean crystallite sizes (Lvol) and microstrain (e0) using the double-Voigt method. [23] Quantitative phase analysis carried out on a relative basis by an approach of Hill & Howard. [24] The initial structural parameters and atomic positions were taken from the Crystallography Open Database (COD) [25], [26] used for phase identification and Rietveld refinements. The JCPDS cards used for phase identification: 00-076-2494 (CrN), 00-004-0850 (Ni), 00-901-3484 (α-Fe) and Fe3W3C. [27] The atomic positions and occupancies were constrained to fixed values due to: (1) complicated phase composition of the coatings containing a mixture of crystalline and amorphous phases and (2) convolution of high intensity substrate peaks. Figure 9.1 illustrates a whole refinement model output, for C7#Ni coating at 970 K, which is typical for all of the refinement outputs. The small vertical bars in Figure 9.1 indicate the positions of allowed hkl diffractions for each phase: CrN (red), Ni (blue), Fe3W3C (black), Fe (orange). The Rietveld refinement parameters for C7#Ni at 970K are Rwp = 14.28, Rexp=5.6, goodness of fit = 2.55, wavelength = 0.82646 nm, Zero error = -0.027 and Sample displacement = 0.08.
Chapter 9 – Thermal Stability of CrSiN and CrNiN thin films

Figure 9.1 Whole pattern profile modelling for C7#Ni coating at 970 K ($R_{wp}$~14.28).

Figure 11.17 to Figure 11.23 (supplementary information) show the diffraction patterns of CrSiN and CrNiN samples as a function of in situ temperature with all major identified phases listed in Table 11.2. There are noticeable peak shifts from sample to sample, which are mainly due to the sample displacement as also the substrate peaks shift as well.

9.3.3. Nanoindentation test

The Young's modulus and hardness of the coatings were determined using a nanoindentation system (Ultra-Micro Indentation System, UMIS-2000, CSIRO, Australia) fitted with a Berkovich indenter program. [10], [28] Indentation tests were performed in a closed-loop under load control with test repeated 20 times for each specimen. The area function of the indenter tip was calibrated using a standard fused silica specimen with a known modulus of 72 GPa. The load control method had a maximum loading of 5 mN. Proper selection of the peak load
ensured maximum displacement during indentation to be no more than 10% of the coating thickness.

9.3.4. DFT computational simulations

Structural optimisations and calculations in this study were carried out using generalised gradient approximations (GGA) and the PW91 functional [29] as implemented in the Vienna Ab initio simulation package (VASP) [30]. The energy cut-off for plane waves included in the expansion of wave functions was 500 eV. Pseudo-atomic calculations made on Cr: 3d⁵4s¹, Ni 3d⁸4s² and N 2s²2p³ atomic configurations. k-point sampling for reciprocal space integration was optimised and adopted as a 21×21×21 Gamma scheme for cubic structures. The structural optimisations were carried out for bulk paramagnetic CrN (CrN-m) and metallic-Ni structures. The thermodynamic properties of cubic phases are studied over a temperature range of 0 K - 1500 K by use of the full quasi-harmonic (QHA) model as implemented in the Gibbs2 code [31]. In all temperature dependent property calculations, the Vinet’s equation of state is adapted to fit the energy–volume curves [32]. To calculate the elastic constants and determine the second derivatives, we used a finite differences method as implemented in the VASP package (IBRION=6).

9.4. Results and Discussion

9.4.1. Microstructural analysis

Figure 9.2(a) shows the SR-XRD patterns of as-deposited C1 and CrSiN specimens at room temperature. The main crystalline phase in C1 is identified as cubic CrN with Fm-3m symmetry, with the highest intensities from (200) and (220) diffractions. TEM images of an
identical CrN coating, published by Wo et al. [8], show well-defined, closely packed columnar grains of CrN parallel to the film growth direction (column width 100 nm). Furthermore the TEM images from the C2#Si coating exhibited refined nc-CrN grains (column width 80nm) surrounded by a-Si$_3$N$_4$ matrix in the columnar structure. A similar microstructure was observed in C3#Si, although the nc-CrN column width was significantly reduced due to increased Si content (8.5 at.%) and a higher percentage of amorphous Si$_3$N$_4$ phases at grain boundaries. In Figure 9.2(a), the broader and low intensity diffraction peaks in SR-XRD patterns from the CrN (111) and (220) reflections confirm the progressively refined microstructure of nc-CrN in C3#Si compared to C2#Si. However, no well-defined diffraction peaks, from the CrN phase, observed for the C4#Si sample. It is possibly due to the extremely fine (< 10 nm width) and randomly oriented CrN crystals in the amorphous matrix, as reported previously [8]. Although, in general, XRD technique may not be able to detect extremely fine microstructures or amorphous phases and their presence can sometimes be inferred by “humps” in the background. Combination of observations from SR-XRD patterns, previously published TEM images of coating cross-sections and XPS analyses (deconvolution of the N 1s and Si 2p spectra) of these coatings [8] suggest that addition of Si to CrN coatings has significant influence on the coating microstructure, by the formation of an amorphous Si$_3$N$_4$ matrix in the CrN grain boundaries. It is not detectable in present SR-XRD or referenced SAD patterns. The previous XPS and TEM study [8], established the Si$_3$N$_4$ content is directly correlated to the Si content, e.g. the lowest and highest amount of Si$_3$N$_4$ is detected in C2#Si and C4#Si samples. 

*In situ* SR-XRD patterns were taken for CrSiN coatings (see supplementary information for whole patterns, Figure 11.18 - Figure 11.20) over the temperature range 300 to 970 K to deduce the influence of Si content on the phase composition and structural behaviour. Figure 9.2(b) shows the diffraction patterns of these samples at 970 K. The phase composition of C1 was
described in our previous work [5] as a combination of cubic CrN and hexagonal h-Cr$_2$N. Noticeable peak sharpening occurred for C2#Si due to crystal growth and strain release. C3#Si and C4#Si exhibited negligible peak sharpening during the in situ experiment and interpreted as having a highly stable microstructure.
Figure 9.2 Diffraction patterns of C1 and CrSiN coatings: (a) as-deposited condition at 300 K and (b) at 970 K. The dash lines indicate main substrate peaks. The peaks marked with ‘x’in fig. 9.2a indicate phase modifications of substrate.

Figure 9.3(a) shows the diffraction patterns of the as-deposited CrNiN coatings at room temperature (see the supplementary section for whole patterns of in situ data, Figure 11.21 - Figure 11.23). Sample C5#Ni shows a highly textured CrN phase in the (200) direction; a direction which possesses the lowest surface energy [33]. Analysis of SAD pattern for C5#Ni sample provided by Wo et al. [9] displayed discrete rings for CrN (111), (200) and (200), which is comparable to its SR-XRD pattern with diffraction from CrN (200), (111) and (220) directions. At higher Ni content, SR-XRD patterns of C6#Ni and C7#Ni only display some humps at CrN (200) position. Wo et al. [9] reported column width reduced dramatically to 116 and 95 nm for C6#Ni and C7#Ni, respectively, compared to C1 (163 nm).
Small amounts of Cr$_2$N were detected in C5#Ni at 870 K verifying the XPS [9] analyses of the existence of hexagonal Cr$_2$N ($h$-Cr$_2$N) in the coating composition the CrNiN coating surfaces. The $h$-Cr$_2$N detected in the SR-XRD pattern of C5#Ni at high temperatures can explain the thick CrN (111) diffraction ring in SAD [9] pattern due to the co-existence of CrN (111) and Cr$_2$N (110) with close d-spacing values. The microstructure of the coatings exhibited a high degree of crystallisation and grain growth at 970 K, as shown in Figure 9.3(b), featuring sharp peaks of CrN and metallic Ni. Diffraction analysis shows only elemental Ni agreeing with the surface XPS [9].
Figure 9.3 Diffraction patterns of CrNiN samples: (a) as-deposited condition at 300 K and (b) at 970 K. The dash lines indicate main substrate peaks.

Table 9.2 lists the Rietveld analysis phase composition of CrN, C5#Ni, C6#Ni and C7#Ni samples from SR-XRD patterns at 970 K. There is a marked similarity between the Ni atomic percentage measured from XPS [9] analysis (Table 9.1) and quantitative SR-XRD measurements. Quantitative analysis also shows the Cr$_2$N content is suppressed as the Ni percentage increases, which could be desirable due to the poor oxidation resistance of h-Cr$_2$N compared to cubic CrN. [34] This table also shows the effect of Ni on the reduction of Cr$_2$N content from C5#Ni (12 at. %) to C7#Ni (1 at %).

Table 9.2 Relative phase composition (wt. %) of CrNiN coatings at 970 K.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Coating</th>
<th>C1</th>
<th>C5#Ni</th>
<th>C6#Ni</th>
<th>C7#Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrN</td>
<td></td>
<td>47</td>
<td>44</td>
<td>42</td>
<td>40</td>
</tr>
<tr>
<td>Cr$_2$N</td>
<td></td>
<td>15</td>
<td>12</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td>0</td>
<td>13</td>
<td>34</td>
<td>41</td>
</tr>
<tr>
<td>substrate</td>
<td></td>
<td>38</td>
<td>30</td>
<td>21</td>
<td>18</td>
</tr>
</tbody>
</table>
9.4.2. **Lattice constants**

Figure 9.4 shows the Rietveld refinement results for the lattice constant of CrN in CrSiN and CrNiN from 300 to 970 K. Experimental measurements on pure CrN lattice constant from studies by Bartosik *et al.* [35], Zhou *et al.* [36] and equilibrium lattice constants predicted from QHA model are also included in Figure 9.4. Dominant amorphous structures in C4#Si, C6#Ni and C7#Ni samples limited the incorporation of this phase in the Rietveld model. Even so, it is seen that adding 8 at.% Si reduces the lattice constant of CrN by 0.76% compared to C1, which is possibly attributed to the substitution of Cr atoms ($r = 1.40 \text{ Å}$) with smaller Si atoms ($r = 1.10 \text{ Å}$ [37]) and formation of (Cr,Si)N solid solution during deposition.

The changes in the CrN lattice constant during the *in situ* heating cycle follow a similar trend for C1 and CrSiN samples with two main stages: (i) shrinkage of the lattice constant up to 870 K and (ii) lattice expansion comparable to predicted QHA model. The CrN lattice constant in C1 decreased from 4.213 Å in as-deposited state to 4.174 Å at 870 K. The unexpected shrinkage of lattice constant during *in situ* cycle is most likely due to the induced microstrain and disordered growth of CrN structure during the deposition process. Microstrain evaluation of CrN phase shown in Figure 9.6(b) indicates that structural relaxation in the coating is active during the *in situ* cycle, which can bring back the CrN structure to equilibrium state [38]. It is seen that the measured lattice constants are getting closer to the estimated QHA model values at high temperatures and shrinkage rate also decreased as the coating structure reached an equilibrium state.

The deviation of experimental lattice constants from equilibrium values above 870 K (see Fig. 4) can be explained as excessive Si atoms move to interstitial sites in CrN phase leading to the distortion and expansion (0.5% increase in lattice constant value) of its unit cell.
The CrN lattice constant in C5#Ni at room temperature was similar to that of C3#Si which can be due to the substitution of Cr atoms with smaller Ni atoms \((r = 1.35 \text{ Å[37]})\) in the CrN structure during the deposition process. During the \textit{in situ} cycle, the shrinkage due to microstructural relaxation is dominant up to 870 K (lattice constant decreased by 0.5 % compared to 300 K). The lattice constant expansion is fairly close to our predictions based on QHA model for CrN. Similar trends for CrN seen in C6#Ni and C7#Ni at the higher temperatures. Figure 8.5 shows the changes in lattice constant for metallic Ni in CrNiN coatings, QHA model results and experimental thermal expansion values of pure Ni from Hwang [39] and Kohlhaas \textit{et al.} [40]. The binary phase diagram of Cr-Ni [41] shows that Cr can dissolve into Ni at up to 30\% and 47\% at room temperature and above 870 K, respectively. Substitution of Ni atoms \((r = 1.35 \text{ Å})\) [37] with Cr atoms \((r = 1.40 \text{ Å})\) can expand the lattice constant of Ni and result in the formation of Ni-Cr solid solution. Substitution of Cr atoms in the Ni structure can explain the minor (0.83 \%) lattice constant expansion of Ni in C5#Ni (40.4 at.\% Cr) sample compared to QHA model values above 770 K. Rietveld analysis of SR-XRD data reveal no noticeable changes in lattice constant of Ni for C5#Ni above 770K. Considering the thermal expansion of the Ni cell, during the \textit{in situ} cycle, it seems that the Cr concentration in the unit cell decreases. Figure 9.5 displays that Ni unit cell approaches the QHA model as Cr content decreases in C6#Ni and C6#Ni compared to C5#Ni (i.e. less Cr exists to incorporate in Ni lattice).
Comparison of the DFT modelling results of equilibrium predictions on the lattice constant of these phases and results from the Rietveld analysis of the SR-XRD diffractograms indicate the formation of interstitial solid solution of Si atoms in the CrN phase in CrSiN coatings and Ni(Cr) solid solutions in CrNiN coatings. Table 9.3 lists the \( h \)-Cr\(_2\)N lattice constants \((a\) and \(c\)) based on Rietveld models in C1 and C5#Ni specimens.

Figure 9.4 Lattice constants of CrN in CrSiN and CrNiN at different temperatures
Chapter 9 – Thermal Stability of CrSiN and CrNiN thin films

Figure 9.5 Effect of Cr content on lattice constants of Ni in CrNiN. Included are data from QHA model.

Table 9.3 \( h \)-Cr\(_2\)N lattice constants \((a\) and \(c)\) based on Rietveld models of C1 and C5#Ni coatings.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>C1 ( a) (Å)</th>
<th>C1 ( c) (Å)</th>
<th>C5#Ni ( a) (Å)</th>
<th>C5#Ni ( c) (Å)</th>
<th>Literature (0 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>870</td>
<td>4.860</td>
<td>4.513</td>
<td>4.841</td>
<td>4.516</td>
<td>4.800(^{e}) [42], 4.472(^{e}) [42],</td>
</tr>
<tr>
<td>970</td>
<td>4.851</td>
<td>4.5199</td>
<td>4.8583</td>
<td>4.518</td>
<td>4.773(^{e}) [43], 4.406(^{e}) [43]</td>
</tr>
</tbody>
</table>

\(^{e}\) \(^{e}\) denote experimental and DFT calculations respectively, from indicated references.

9.4.3. **Crystallite size and microstrain**

Changes in crystallite size at high temperature can affect the mechanical properties of nanocomposite coatings. Changes in deformation mechanism, due to crystallite growth, could increase dislocation density and reduce the defect density and compressive residual stress in
the coatings, resulting in a reduction in hardness of the nanostructured coatings at high temperatures. Figure 9.6(a) shows changes in volume-weighted mean crystallite sizes of CrN. Results show that the initial crystallite size of CrN in as-deposited coatings is below 20 nm. C1 and C2#Si have the largest and smallest, in the as-deposited state, crystallite size respectively. The coatings behaved differently, in the in situ cycle, depending on the incorporated dopants. Measured changes of crystallite size in C2#Si is similar to binary CrN where crystallite size almost doubled at 970 K compared to room temperature. However, the crystallite growth rate for C3#Si was almost zero, indicating the importance of dopant contents on the coating structural behaviour. The highest crystallite growth rate is in the C5#Ni sample, where the crystallite size at 970 K is 8 times that of the as-deposited condition. C6#Ni and C7#Ni samples show similar behaviour with slightly slower crystallite growth rate, which means Ni is not able to stabilise the refined microstructure of the coatings.

Figure 9.6(b) displays the changes in measured microstrain for CrN in the CrNiN and CrSiN coatings, in the in situ cycle. C1 and C2#Si show the lowest microstrain values at room temperature, while C3#Si and C5#Ni exhibited the highest microstrain levels. During the in situ cycle, microstrain gradually decreased in all samples at different rates. Strain level in C1 sample reduced by 170% and coatings containing Si, regardless of the initial strain level; display the lowest strain release during the in situ heat cycle. The strain level at 970 K in C2#Si and C3#Si samples reduced by 87% and 29%, respectively compared to as-deposited values. Microstrain level in CrNiN coatings at 970 K reduced by more than 170% from 870 K value indicating the high rate of stress release in the coatings.
Figure 9.6 Changes in (a) volume-weighted mean crystallite sizes and (b) microstrain for CrN in CrSiN and CrNiN coatings as a function of temperature.

9.4.4. Mechanical properties

Table 9.4 lists the hardness, Young’s modulus and resistance to deformation ($H^2/E^3$ ratio) of the coatings for as-deposited and after in situ cycle for all samples measured by...
nanoindentation at room temperature. The highest hardness was measured for C3#Si as 36 ± 3 GPa; 21% higher than C1. The hardness increase is due partly to the extremely refined crystallite size and high level of lattice strain in CrN grains surrounded with the amorphous Si$_3$N$_4$ matrix in this sample. [44] Moreover, the addition of Si in the CrN structure leads to significant lattice distortion and segregation of dissolved atoms around defects, such as dislocation cores and grain boundaries, which increases resistance to deformation. [45] The values of the lattice constant, crystallite size and microstrain for C3#Si are strong indications that the dominant hardening mechanism is due to the nanocomposite microstructure. The hardness of C2#Si was very close to C1, and predictable from their similar microstructural measurements analysed from SR-XRD data. The high amount of amorphous Si$_3$N$_4$ (with $H$ = 18 GPa [13]) in C4#Si was not as successful as C3#Si in improving the hardness. C5#Ni exhibited the highest hardness (21 ± 2 GPa) among the coatings with Ni content which can be attributed to its partially crystalline structure; as the Ni content and amorphous portion of the coatings increases, hardness reduces significantly. For example, measured hardness of C7#Ni was 60% lower than C1 coating. XTEM observations of similarly nanoindented CrNiN coatings [9] established the reduction in hardness was accompanied by changes in deformation mechanism from grain boundary sliding (binary CrN sample) to plastic deformation (high Ni content). Analysis of Table 9.4 indicates the CrNiN coatings, with major structural transformation, show minor changes in hardness, within the indicated experimental errors, revealing that their microstructure is stable during the in situ cycle.
Table 9.4 Hardness, elastic modulus and resistance to deformation from nanoindentation measurements made at 300 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>As-deposited</th>
<th>After in situ cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H$</td>
<td>$E$</td>
</tr>
<tr>
<td>C1</td>
<td>29±2</td>
<td>368±21</td>
</tr>
<tr>
<td>C2#Si</td>
<td>31±3</td>
<td>368±21</td>
</tr>
<tr>
<td>C3#Si</td>
<td>36±3</td>
<td>398±21</td>
</tr>
<tr>
<td>C4#Si</td>
<td>32±2</td>
<td>348±31</td>
</tr>
<tr>
<td>C5#Ni</td>
<td>21±3</td>
<td>285±6</td>
</tr>
<tr>
<td>C6#Ni</td>
<td>17±3</td>
<td>276±7</td>
</tr>
<tr>
<td>C7#Ni</td>
<td>16±3</td>
<td>260±5</td>
</tr>
</tbody>
</table>

The C3#Si sample had the highest elastic modulus (398 ± 20 GPa) and ≈ 5% higher than C1 sample. Incorporating Ni in the coating leads to a significant reduction in elastic modulus in the as-deposited condition and the minimum reaching 16 ± 3 GPa with the C7#Ni sample.

Elastic modulus is an intrinsic property of the materials and results show that it is almost constant over the in situ cycle. Knowing the hardness and elastic modulus of the coatings, we can calculate $H^3/E^2$ ratio, which is proportional to the resistance to the deformation for a given material [46] and materials with high $H^3/E^2$ ratio exhibit higher resistance to deformation. Results show that Si dopants increase the resistance to deformation in as-deposited condition.

CrNiN coatings had the lowest deformation resistance, probably due to the presence of metallic Ni in the structure.

9.4.5. High temperature hardness calculations

Experimentally, hardness and Young’s modulus are highly complex properties because the applied stress during indentation may be dependent on the crystallographic orientation of the specimen, the loading forces and the indenter specifications. Knowing the elastic constants, it is possible to obtain the directional elastic modulus ($E_{hkl}$) using equation (5.1) [47]:

\[ \frac{H^3}{E^2} \]
Chapter 9 – Thermal Stability of CrSiN and CrNiN thin films

\[
\frac{1}{E_{hk\ell}} = S_{11} + \frac{(2S_{12}-2S_{11}+S_{44})(k^2l^2+h^2l^2+h^2k^2)}{l^2+h^2+k^2}
\]  \hspace{1cm} (9.1)

where \(S_{ij}\) are the elastic compliance constants (GPa\(^{-1}\)) and \((hkl)\) are the Miller indices. The dependences of \(E\) on crystallographic directions for CrN and Ni are calculated and listed in Table 9.5 from their elastic constants \((C_{ij})\). Elastic constants of CrN at room temperature were taken from experimental and numerical studies of Almer \textit{et al.} \cite{47} and Mozafari \textit{et al.} \cite{48}, \cite{49}. The elastic constants for Ni at room temperature were taken from the experiments of Alers \textit{et al.} \cite{50}, Hosford \cite{47} and DFT modelling of Wen \textit{et al.} \cite{51}. Table 9.5 clearly shows the dependency of \(E\) on the crystallographic orientations of CrN and Ni phases. Equation (5.1) implies that extreme values for elastic modulus only occur at \((100)/(200)\) and \((111)\) directions and the ratio of \(E\) in these directions indicates the maximum anisotropy for cubic crystals. CrN shows some anisotropy of \(\approx 0.5\) meaning its elastic properties in the \((200)\) direction is twice of \((111)\). The \(E\) for Ni has a large dependency on the direction, where \(E_{111}\) is \(\approx 2.4\) times bigger than \(E_{200}\). When dealing with sputtered coatings, it seems important to maximize the preferred growth in directions with the highest modulus parallel to coating surface to reach optimised mechanical properties. For instance, C1 coating with measured \(E=368\pm21\) GPa has noticeable texture in the \((220)\) direction, which is not a preferable orientation in terms of maximum elastic modulus from Table 9.5. We can predict that by optimising the deposition process and orienting the coating in \((200)\) direction, higher elastic modulus values are obtainable. However, in coatings with co-existing phases such as C5#Ni, can estimate higher modulus for coatings with textured microstructures in CrN \((200)\) and Ni \((111)\).
Table 9.5 Dependency of elastic modulus on crystallographic directions in CrN and Ni based on experimental (\(x\)) and computed (\(c\)) elastic constants at room temperature.

<table>
<thead>
<tr>
<th>Phase</th>
<th>(E_{111})</th>
<th>(E_{200})</th>
<th>(E_{220})</th>
<th>(E_{311})</th>
<th>(E_{111}/E_{100})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrN(^x), [48]</td>
<td>229.9</td>
<td>537.4</td>
<td>268.3</td>
<td>329.7</td>
<td>0.43</td>
</tr>
<tr>
<td>CrN(^c), [49]</td>
<td>359.3</td>
<td>560.9</td>
<td>394.8</td>
<td>443.6</td>
<td>0.64</td>
</tr>
<tr>
<td>Ni, present DFT</td>
<td>320.5</td>
<td>158.2</td>
<td>255.0</td>
<td>207.7</td>
<td>2.03</td>
</tr>
<tr>
<td>Ni, [47]</td>
<td>304.6</td>
<td>130.0</td>
<td>228.0</td>
<td>178.1</td>
<td>2.34</td>
</tr>
<tr>
<td>Ni(^x), [50]</td>
<td>302.1</td>
<td>137.9</td>
<td>232.8</td>
<td>185.4</td>
<td>2.19</td>
</tr>
<tr>
<td>Ni(^c), [51]</td>
<td>260.6</td>
<td>113.1</td>
<td>196.5</td>
<td>154.2</td>
<td>2.30</td>
</tr>
</tbody>
</table>

Our previous predictions of the hardness of CrN and AlN phases in sputtered CrAlN coatings, over the temperature range 300 - 1500 K, were based on the variation of covalent bonds strengths with temperature [38]. It is also possible to estimate the hardness of materials by finding the correlations between the hardness \(H\) and their shear modulus \(G\) or bulk modulus \(B\). [52] Recently, Chen et al. [53] introduced the following correlation between the \(H\), \(G\) and \(B\) and validated for a wide range of crystalline materials,

\[
H_c = 2\left[\left(\frac{G}{B}\right)^2 \times G\right]^{0.585} - 3 \tag{9.2}
\]

This equation, based on Pugh’s modulus ratio \((k = G/B)\), is closely correlated to the brittleness and ductility of materials [54],[55]. In other words, the materials with a low \(G/B\) ratio are expected to deform in a ductile manner, while brittle materials exhibit higher \(G/B\) ratio.

In this study, equation (5.2) estimates the hardness of CrN and Ni as a function of temperature. Elastic constants, from present calculations and available literature, for CrN and Ni calculate the bulk modulus and shear modulus at each temperature, assuming only temperature and thermal expansion affect the elastic constants [56]. Then, \(G\) and \(B\) for cubic CrN and Ni are calculated using the Voigt-Reuss-Hill averaging method [57]:

\[
B = \frac{C_{11} + 2C_{12}}{3} \tag{9.3}
\]

\[
G = \frac{(C_{11} + C_{12}) + 3C_{44}}{10} + \frac{5}{2} \left[\frac{4}{C_{11} - C_{12}} + \frac{3}{C_{44}}\right]^{-1} \tag{9.4}
\]
Table 9.6 lists the estimated hardness of pure CrN and Ni at 0 and 300 K (room temperature) from equation (5.2). For CrN at room temperature, the estimated hardness are in reasonable agreement with our previous calculations (22.4 GPa) [38], and reports of Cunha et al. [58] (19 - 28.6 GPa) and Ichimura et al. [59] (24 – 25 GPa) on sputtered CrN coatings. However, the predicted values show a considerable difference with the C1 hardness (28 GPa), which could be due to the sputtering process and preferred growth in the coating. The estimated hardness for Ni, \( H_{\text{cal}} \approx 8.8 \) GPa at room temperature, is in close agreement with the experiments of Mirshams et al. [60] on pure Ni with a measured hardness of \( H = 6 \) to 7 GPa.

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( G ) (GPa)</th>
<th>( B ) (GPa)</th>
<th>( H_{\text{cal}} ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CrN}, [49] )</td>
<td>300</td>
<td>176.4</td>
<td>275.2</td>
</tr>
<tr>
<td>( \text{CrN}^x, [48] )</td>
<td>300</td>
<td>137.4</td>
<td>198</td>
</tr>
<tr>
<td>( \text{Ni, present study} )</td>
<td>0</td>
<td>95.6</td>
<td>199.3</td>
</tr>
<tr>
<td>( \text{Ni, present study} )</td>
<td>300</td>
<td>91.8</td>
<td>193.2</td>
</tr>
<tr>
<td>( \text{Ni}^c, [51] )</td>
<td>300</td>
<td>72.5</td>
<td>157.9</td>
</tr>
<tr>
<td>( \text{Ni}^x, [47] )</td>
<td>300</td>
<td>85.9</td>
<td>183.8</td>
</tr>
</tbody>
</table>

(\(^{c}\))-calculated, (\(^{x}\))-experimental results from indicated references.

Plots displayed in Figure 9.7 show the relation between hardness and temperature for CrN and Ni phases calculated by equations (5.2) and (5.5) using elastic constants from references [48], [49] and [50]. The hardness for both phases’ declines as the temperature increases, as was expected, since similar correlations exist between the elastic constants with temperature for these phases. The estimated hardness for CrN based on the computed elastic constants of Mozafari et al. [49] shows some agreement with our modelling for the hardness of paramagnetic CrN using the bond strength model [38]. However, the calculated hardness based on elastic constants exhibited a sharper decline than our model. The hardness of Ni also...
declined at 500 K by about 30% for both models based on Wen et al. [49] and Alers et al. [49] studies that provided the elastic constants.

Assuming the CrNiN coatings are a composite consisting of CrN and Ni phases, it is possible to predict the hardness of CrNiN coatings ($H_m$) by adopting the role of mixture [61] based on the atomic percentage of Ni in the coatings,

$$H_m = (1 - f_{Ni}) H_{c, CrN} + f_{Ni} H_{c, Ni}$$ \hspace{1cm} (9.5)

where $f_{Ni}$ is the atomic percentage of Ni phase in the coating. $H_{c, CrN}$ and $H_{c, Ni}$ are the calculated hardness from Figure 9.7. Hardness for CrNiN coatings were estimated using equation (5.5) and included in Figure 9.7 up to 500 K. Comparison of the nanoindentation results with the estimated hardness at 300K for CrNiN shows that equation (5.5) can predict the hardness with high accuracy. The temperature range in Figure 9.7 for most of the data is limited to 500 K as the elastic constants from the indicated references are up to 500 K.

![Figure 9.7 Calculated hardness for pure CrN and Ni phases [from indicated references], and CrNiN coatings. Included are experimental hardness of CrN samples.](image-url)
9.5. Conclusions

Combination of experimental in situ SR-XRD results, first principle DFT and modelling with computed elastic constants ($C_{ij}$), studied the microstructure of CrSiN and CrNiN coatings at temperatures in the range of 300 K - 970 K and make predictions of hardness in the range 300 K - 1200 K. Microstructure, microstrain, hardness, elastic modulus, and resistance to deformation interpretations are: (1) As-deposited: Si and Ni reduced the size of nc-CrN crystallites and increased the microstrain in the coating microstructure. The addition of Si improved the coating hardness, elastic modulus, and resistance to deformation while addition of Ni reduced these properties. Sample C2#Si [i.e. CrNSi(5% At.)] holds the most stable microstructure and highest hardness. (2) During the in situ heating cycle, the Si incorporation effectively slowed both crystallite growth and strain release while Ni incorporation exhibited the highest crystallite growth rate and micro-strain release. (3) DFT and Rietveld analysis SR-XRD diffractograms give indications of possible interstitial solid solutions of Si atoms in the CrN phase in CrSiN coatings while CrNiN coatings contain Ni(Cr) solid solutions. (4) Nanoindentation results, at room temperature, supplemented the microstructure evaluations for before and after in situ heating cycle. It indicated the effective role of microstructure and phase composition on the mechanical properties of the coatings. (5) The predicted hardness of CrN and Ni phases in CrNiN coatings at 300 K are ±1 GPa of the experimentally derived values.

9.6. References


Chapter 9 – Thermal Stability of CrSiN and CrNiN thin films


1999.


[29] J. P. Perdew and Y. Wang, “Accurate and simple analytic representation of the


[31] A. Otero-de-la-Roza and V. Luaña, “Gibbs2: A new version of the quasi-harmonic
model code. I. Robust treatment of the static data,” *Comput. Phys. Commun.*., vol. 182,

and J. Núñez, “Universal features of the equation of state of solids from a


study of the oxidation behavior of Cr2N and CrN coatings,” *Thin Solid Films*, vol. 544,

[35] M. Bartosik, D. Holec, D. Apel, M. Klaus, C. Genzel, J. Keckes, M. Arndt, P. Polcik,
C. M. Koller, and P. H. Mayrhofer, “Thermal expansion of Ti-Al-N and Cr-Al-N

Mayrhofer, “Structural stability and thermodynamics of CrN magnetic phases from ab

3204, Nov. 1964.

Dlugogorski, “Experimental and predicted mechanical properties of Cr 1–x Al x N
thin films, at high temperatures, incorporating in situ synchrotron radiation X-ray
diffraction and computational modelling,” *RSC Adv.*, vol. 7, no. 36, pp. 22094–22104,
2017.

the lattice parameter of iron at the Curie temperature,” University of Missouri-Rolla,
1972.

[40] N. Kohlhaas, Rudolf; Duenner, Philipp; Schmitz-Pranghe, “Temperature dependence
of lattice parameters of iron, cobalt, and nickel at high temperatures,” *Zeitschrift fuer


precipitates in high-nitrogen austenitic stainless steel. III. Neutron diffraction study on


Chapter 9 – Thermal Stability of CrSiN and CrNiN thin films


Chapter 10

Conclusions and Recommendations

*This chapter summarises and concludes the entire thesis.*
10.1. Conclusions

Industrial tools usually expose to extreme working conditions, such as high temperatures and oxidising/corrosive atmospheres. These conditions accelerate degradation of the machinery, which significantly reduces their mechanical properties and service life. Hard coatings exhibit excellent potential to improve oxidation resistance and wear protection for machining tools and engineering devices. As discussed in chapter 2, there are several ways to improve the thermal stability of hard coatings including coating designing. Adding specific elements to the coating composition, modifying the interface complexity, creating an amorphous matrix has been among the major approaches for designing hard coatings with enhanced thermal stability. It was mentioned that chemical composition and phase transition of the protective hard coatings could play a crucial role on their nanostructure, high temperature mechanical properties and stability. It is essential to find the connections between phase composition and nanostructure of the hard coatings. Therefore, the present research work explored the nanostructure, thermal stability and mechanical properties of magnetron sputtered CrAlN, CrSiN, CrNiN and TiSiN thin film coatings systems using mainly \textit{in situ} synchrotron radiation based XRD experiments up to 800 °C.

To show the capabilities of DFT and QHA techniques in obtaining a deep understanding of metal nitrides hard coatings, electronic and mechanical properties of cubic structured TiN and BN at high temperatures and pressures were explored and compared with available literature. Chapter 4 documented the geometric and electronic properties of bulk c-BN and its surfaces along the three low-Miller indices. We found the nitrogen-terminated surface along the (100) direction to be the most thermodynamically stable configuration over all physically accessible values of the chemical potential of nitrogen. Our results explain the inert nature of BN. We have found that $\alpha$-B$_{36}$ dictates the stability phase diagram of bulk boron at 0 K, in agreement
with the recent experimental measurements. Analysis of Bader’s charges indicates that, all surfaces of c-BN largely retain the ionic character of the bulk c-BN. First principle calculations were used to study the electronic structure, phonon spectra and thermodynamic properties of BN and TiN. The temperature and pressure dependency of several mechanical and thermal properties of TiN were predicted using QHA method and validated with empirical data in the literature.

Magnetron sputtering parameters can significantly change the microstructure and mechanical properties of metal nitride hard coatings. Therefore, chapter 6 describes the influences of various substrate bias voltage (-30 to -80V) on oxidation resistance, mechanical properties and thermal stability of TiSiN coatings. TiSiN Coatings deposited at bias voltages > -50 V showed stable phase composition in the temperature range of 25 to 800 °C consisted of nc-(Ti,Si)N embedded in a-Si3N4 and smooth surface and enhanced hardness (33 GPa). Higher negative bias voltage significantly changes the phase composition, stability, microstructure and surface morphology of the coatings, which, in turn, resulted in desirable improvement in the oxidation resistance, thermal stability, and mechanical properties. Both the hardness and Young’s modulus of the coatings constantly improved from 23 GPa to 33 GPa and 310 GPa to 450 GPa, respectively, as the substrate bias voltage increases from -30V to -80V, representing almost 50% increase.

Cr1-xAlxN coatings with Al contents up to 21 % were deposited using unbalanced magnetic sputtering system. Results showed that Al dopants reduced the lattice constant of cubic CrN phase as the Cr atoms were substituted by smaller Al atoms. Addition of Al to CrN coatings improved microstructure and mechanical properties compared to undoped CrN coating. Combination of nanoindentation measurements and analysis of in situ synchrotron X-ray diffraction at temperatures range of 200 – 700 °C showed that CrAlN coatings possess
remarkable resistance to crystal growth and stress release up to 700 °C when Al content is greater than ~14%. In addition, Al-dopants improved oxidation resistance of the coatings by preventing the formation of Cr₂N at high temperatures. Nanoindentation results showed that Al doping improved the coating hardness and elastic modulus from 29 to 42 GPa and 378 to 438 GPa respectively. Resistance to deformation value also increased as the Al content increased. First-principles and quasi-harmonic approximations methods have been employed to approximate the thermo-elastic properties of bulk c-CrN (both magnetic and non-magnetic configurations), c-AlN phases over the temperature range of 0 – 1500 °C. The combination of experimental observations and first-principle calculations helped us to develop a model to predict the hardness of studied phases as a function of temperature up to 1500 °C. For instance, Comparison of DFT-QHA models and the nanoindentation results indicate that hardness of Cr₁₋ₓAlₓN coating with ~ 21% Al content may be the sum of values from CrN-m and AlN phase. Our computational modelling predicts that the hardness of Cr₁₋ₓAlₓN coating with the Al content of ~21% can reach to about 41.5 GPa at T = 1500 °C.

Rietveld refinement has been used as the main tool to study the microstructure of CrSiN and CrNiN coatings at high temperatures ranging from 25 to 700 °C. In as-deposited state Si and Ni reduced the size of nc-CrN crystallites and increased the microstrain in the coating microstructure. The addition of Si improved the coating hardness, elastic modulus, and resistance to deformation, especially at 8% Si. The addition of Ni progressively reduced the coating hardness, elastic modulus, and resistance to deformation of the coatings as Ni content increased. At higher temperatures, Si effectively slowed both crystallite growth and strain release based on the Rietveld analysis of in situ diffraction data. Coatings containing Ni exhibited the highest crystallite growth rate and microstrain release. First-principle calculations were carried out to predict the thermodynamical properties of bulk CrN and Ni phases.
Comparing Rietveld modelling results and equilibrium predictions on the lattice constant of these phases showed the formation of interstitial solid solutions of Si atoms in the CrN phase in CrSiN coatings and Ni(Cr) solid solutions in CrNiN coatings. Microstructure evaluations during heating and nanoindentation of heated-treated coatings provided some evidence on the effective roles of microstructure and phase composition on the mechanical properties of these coatings. C2-8%Si possesses the most stable microstructure and highest hardness. Computed elastic constants ($C_{ij}$), within the temperature range 0-930 °C, were used to model the hardness of CrN and Ni phases as a function of temperature. Comparisons of predicted hardness and nanoindentation results for CrNiN coatings showed good agreement with an error of ±1 GPa at 25 °C.

The main contribution of the present work is to combine room temperature analysis such as nanoindentation, FESEM and XPS data with high temperature synchrotron in situ powder diffraction method. In addition, DFT and QHA methods have been utilised to shed light on the thermo-mechanical behaviour of hard coatings at high pressure/temperature environments. Presented results showed that a proper combination of imperial tests and computational studies could be used to predict the microstructure and mechanical properties of metal nitride phases and nanocomposite coatings at elevated temperatures. For instance, the experimentally measured lattice constant of TiN in TiSiN coatings showed excellent agreement with theoretical calculations. Calculated hardesses for CrNiN coatings at room temperature agree well with nanoindentation results.

The combination of experimental results and computations predictions suggest that the as-deposited coatings exhibit unstable microstructure with a high level of internal stress and lattice defects. Grain growth and stress release happen during in situ high temperature experiments at various rates depending on the coating composition. The microstructure tends to become more
stable at higher temperatures. For example, the lattice constant of the CrN in CrSiN and CrAlN coatings become closer to equilibrium conditions at T>600 °C, as predicted by computational methods.

Regarding mechanical properties such as hardness and elastic modulus, CrAlN and CrSiN coatings showed the highest improvements. Mechanical properties of CrNiN coatings were lower than the CrN coating. TiSiN coatings compared to pure TiN coating showed improvement in mechanical properties only when optimum Si content was added to the coating system. Observations showed various levels of solid solution and nanocomposite formation in studied coatings depending on the dopant type and deposition parameters. The different behaviour of studied coating systems could be due to this fact that coating composition and sputtering settings can significantly influence the microstructural stability and oxidation resistance of the coatings and alter the hardening mechanism.

Presented results suggest that the optimised coating systems and the sputtering condition can significantly enhance the properties and behaviour of coatings at high temperatures/pressures. Therefore, proper coating design and deposition technique are crucial steps in obtaining a suitable coating for any given engineering application. Improved mechanical properties and microstructure stability can be achieved through careful selection of coating composition and deposition system. In addition, theoretical calculations such as QHA method can contribute to predicting the mechanical and chemical stability of coating systems at severe working conditions.

The main limitation of this study was the limitation in measuring mechanical properties of hard coatings such as hardness at high temperatures due to unavailability of suitable laboratory equipment. The main tool for coating microstructural studies in the present thesis was in situ synchrotron diffraction patterns. However, due to a major phase transition in M2 steel substrate
in the temperature range 600-800 °C, Rietveld refinement of the diffraction patterns involved
technical complications and errors which could be avoided by picking a more stable substrate
in the targeted temperature range.

One of the main focuses of the present study is to show the potentials of computational
techniques such as DFT and QHA in predicting the mechanical properties of coating systems
at high temperature/pressure conditions. Results showed that applying QHA method with
simplified assumptions can provide a reliable estimation of the mechanical properties of
complicated coatings such as CrNiN coating systems. The main assumption for computational
calculation in the present study is that the existing phases are in pure and equilibrium states.
Our results suggest that incorporating a similar methodology with more realistic assumptions
and considering the existence of doping elements (Al, Si, Ni) and defect in deposited coating
systems can significantly improve the accuracy of predictions. Studies of application of DFT
and QHA on unstable systems containing composite phases can greatly improve our
understanding of microstructural evaluation and underlying hardening mechanism for
complicated coating systems which is not experimentally feasible.

10.2. Future Work

1- M2 stainless steel substrate used for current study added several peaks from iron and
various carbides to the background of diffraction patterns. This substrate undergoes a
major phase transition in the temperature range of 600-700 °C and several cases
substrate peaks convolute with the peaks from the coating materials. It is important to
avoid such complications through using a well-defined substrate in term of XRD
diffraction patterns, which is stable throughout the high temperature experiment to gain
a more precise picture of the thermal evolution of the coating materials.
The results of this study showed that the alloying elements such as Al, Si and Ni could effectively modify the thermo-elastic properties of the CrN and TiN coatings at room temperature and high temperatures as well. Therefore, it is vital to employ first principle calculations to study the effect of such elements on the structural and electronic properties of quaternary coating systems such as CrAlN, CrSiN, CrNiN and TiSiN hard coatings. Knowing the thermodynamic properties of these quaternary systems may contribute greatly toward understanding the thermal stability of these coatings at elevated temperatures.

Cubic BN surfaces showed great potentials for inhibiting chemical reactions. It would be significant to study the oxidation of 2-chlorobiphenyl (2-CB) over c-BN surfaces using the proposed setting at Figure 10.1.

Figure 10.1. Proposed laboratory set-up including tubular furnace reactor.
This chapter presents the supplementary data for some of the chapters included in the thesis.
11.1. APPENDIX 1: Fixed Incident Beam Corrections in TOPAS

A macro was used to correct peak intensity and peak shift for thick samples when in flat plate, fixed incident beam geometry as follows:

```c
macro Fixed_Incident_Beam_Thick_Sample_Correction ( FIBTSC )
macro FIBTSC(alpha_v) ( FIBTSC(, alpha_v,,0) )
macro FIBTSC(alpha_v, sd_v) ( FIBTSC(, alpha_v,, sd_v) )
macro FIBTSC(alpha, alpha_v, sd, sd_v)
{
  Fixed_Incident_Beam_Thick_Sample_Intensity_Correction(alpha, alpha_v)
  Fixed_Incident_Beam_Peak_Position_Correction(alpha, alpha_v, sd, sd_v)
}
```

Following macros should be used together to scale the intensity for a thick sample and peak position corrections in fixed incident beam geometry:

```c
macro Fixed_Incident_Beam_Thick_Sample_Intensity_Correction (alpha, alpha_v)
{
  #m_argu alpha "angle of the incident beam to the flat plate in degrees
  If_Prm_Eqn_Rpt(alpha, alpha_v, min 0.0001 max 90)

  scale_pks =
  IF ( (2 Th) < CeV(alpha, alpha_v) Deg THEN
    0
  ELSE
    2 / (1 + (Sin(CeV(alpha, alpha_v) Deg)) / Sin(2 Th - CeV(alpha, alpha_v) Deg))
  ENDIF;
}
```

next macro models sample displacement as required for a flat plate in fixed incident beam geometry:

```c
macro Fixed_Incident_Beam_Peak_Position_Correction (alpha, alpha_v, sd, sd_v)
{
  #m_argu alpha "angle of the incident beam to the flat plate in degrees
  #m_argu sd "displacement of the sample in mm (technically, the same dimension as the radius...)
  If_Prm_Eqn_Rpt(alpha, alpha_v, min 0.0001 max 90)
  If_Prm_Eqn_Rpt(sd, sd_v, min 0 max 2)

  th2_offset =
  IF CeV(sd, sd_v) == 0 THEN
    0
  ELSE
    Rad_CeV(sd, sd_v) Sin(2 Th) / (Rs Sin(CeV(alpha, alpha_v) Deg))
  ENDIF;
}
```
A macro is also needed to correct the peak profile for a flat plate in fixed incident beam geometry. Main assumptions are: (1) A parallel incident beam and (2) No diffracted optics.

```
macro Fixed_Incident_Beam_Footprint_Correction_With_Mixing { FIBFCWM }  
macro FIBFCWM(alpha_v, beam_v, mix_v) { FIBFCWM(/, alpha_v, beam_v, mix_v) }  
macro FIBFCWM(alpha, alpha_v, beam, beam_v, mix, mix_v)  
{  
#m_argu alpha "angle between the incident beam and the flat plate sample (in degrees)  
#m_argu beam "height of the beam in the vertical (in mm)  
#m_argu mix "the mix param between a purely hat and a purely gaussian beam profile > 1 is pure hat  
If_Prm_Eqn_Rpt(alpha, alpha_v, min 0.0001 max 90)  
If_Prm_Eqn_Rpt(beam, beam_v, min 0.0001 max 10)  
If_Prm_Eqn_Rpt(mix, mix_v, min 0 max 1)  

local width_ = (Sin(2 Th - CeV(alpha, alpha_v) Deg) Rad / Rs) (CeV(beam, beam_v) / Sin(CeV(alpha, alpha_v) Deg));  
"" the width of the footprint as seen from 2Th  ""the actual footprint on the sample  
hat = CeV(mix, mix_v) width_;  
gauss_fwhm = (1-CeV(mix, mix_v)) width_;  
}  
```
11.2. **APPENDIX 2: Supporting information for Chapter 6**

Table 11.1 *hlk* values for major phases in SR-XRD diffractograms as shown in Figure 11.1-Figure 11.7.

<table>
<thead>
<tr>
<th>TiN (●)</th>
<th>~2θ</th>
<th>TiO₂ (♦)</th>
<th>~2θ</th>
<th>Ti₂O₃ (○)</th>
<th>~2θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>19.24</td>
<td>(110)</td>
<td>14.52</td>
<td>(012)</td>
<td>12.71</td>
</tr>
<tr>
<td>(002)</td>
<td>22.26</td>
<td>(011)</td>
<td>18.97</td>
<td>(104)</td>
<td>17.35</td>
</tr>
<tr>
<td>(022)</td>
<td>31.68</td>
<td>(020)</td>
<td>20.59</td>
<td>(110)</td>
<td>18.47</td>
</tr>
<tr>
<td>(311)</td>
<td>37.34</td>
<td>(111)</td>
<td>21.61</td>
<td>(113)</td>
<td>21.26</td>
</tr>
<tr>
<td>(222)</td>
<td>39.06</td>
<td>(210)</td>
<td>23.05</td>
<td>(024)</td>
<td>25.58</td>
</tr>
<tr>
<td>(004)</td>
<td>45.42</td>
<td>(211)</td>
<td>28.14</td>
<td>(116)</td>
<td>27.84</td>
</tr>
<tr>
<td>(331)</td>
<td>49.76</td>
<td>(220)</td>
<td>29.28</td>
<td>(214)</td>
<td>31.80</td>
</tr>
<tr>
<td>(042)</td>
<td>51.14</td>
<td>(002)</td>
<td>32.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(422)</td>
<td>56.44</td>
<td>(310)</td>
<td>32.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(333)</td>
<td>60.20</td>
<td>(031)</td>
<td>35.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(511)</td>
<td>60.20</td>
<td>(112)</td>
<td>35.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(044)</td>
<td>66.18</td>
<td>(311)</td>
<td>36.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(531)</td>
<td>69.64</td>
<td>(022)</td>
<td>38.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(442)</td>
<td>70.77</td>
<td>(212)</td>
<td>39.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(321)</td>
<td></td>
<td>(002)</td>
<td>41.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(040)</td>
<td></td>
<td>(002)</td>
<td>41.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(330)</td>
<td></td>
<td>(031)</td>
<td>44.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(411)</td>
<td></td>
<td>(112)</td>
<td>46.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(312)</td>
<td></td>
<td>(022)</td>
<td>46.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(013)</td>
<td></td>
<td>(012)</td>
<td>50.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(113)</td>
<td></td>
<td>(110)</td>
<td>51.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(213)</td>
<td></td>
<td>(012)</td>
<td>54.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(333)</td>
<td></td>
<td>(033)</td>
<td>56.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(033)</td>
<td></td>
<td>(311)</td>
<td>59.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(522)</td>
<td></td>
<td>(212)</td>
<td>67.46</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 11.1 *In situ* SR-XRD data for TiN coating heated from 25 to 800 °C in air

Figure 11.2 *In situ* SR-XRD data for TiSiN-30 coating heated from 25 to 800 °C in air
Figure 11.3 *In situ* SR-XRD data for TiSiN-40 coating heated from 25 to 800 °C in air

Figure 11.4 *In situ* SR-XRD data for TiSiN-50 coating heated from 25 to 800 °C in air
Figure 11.5 *In situ* SR-XRD data for TiSiN-60 coating heated from 25 to 800 °C in air

Figure 11.6 *In situ* SR-XRD data for TiSiN-70 coating heated from 25 to 800 °C in air
Figure 11.7 *In situ* SR-XRD data for TiSiN-80 coating heated from 25 to 800 °C in air
11.3. **APPENDIX 3: Supporting information for Chapter 8**

Table 11.2 *hkl* values for major phases in SR-XRD diffractograms as shown in Figure 11.8-11.11.

<table>
<thead>
<tr>
<th></th>
<th>CrN (A)</th>
<th>Cr₂N (B)</th>
<th>Cr (C)</th>
<th>AlN (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>19.7</td>
<td>19.5</td>
<td>22.6</td>
<td>20.2</td>
</tr>
<tr>
<td>(002)</td>
<td>22.8</td>
<td>22.2</td>
<td>26.2</td>
<td>23.3</td>
</tr>
<tr>
<td>(022)</td>
<td>32.5</td>
<td>28.9</td>
<td>37.3</td>
<td>33.2</td>
</tr>
<tr>
<td>(311)</td>
<td>38.3</td>
<td>33.8</td>
<td>44.1</td>
<td>39.1</td>
</tr>
<tr>
<td>(222)</td>
<td>40.1</td>
<td>35.8</td>
<td>46.2</td>
<td>41.0</td>
</tr>
<tr>
<td>(004)</td>
<td>46.7</td>
<td>37.6</td>
<td>53.8</td>
<td>47.7</td>
</tr>
<tr>
<td>(331)</td>
<td>51.1</td>
<td></td>
<td>59.1</td>
<td></td>
</tr>
<tr>
<td>(042)</td>
<td>52.5</td>
<td></td>
<td>60.8</td>
<td></td>
</tr>
<tr>
<td>(422)</td>
<td>58.0</td>
<td></td>
<td>67.4</td>
<td></td>
</tr>
<tr>
<td>(333)</td>
<td>61.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(044)</td>
<td>68.1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 11.8 *In situ* SR-XRD data for C1 coating heated from 25 to 700 °C in air

Figure 11.9 *In situ* SR-XRD data for C2-14%Al coating heated from 25 to 700 °C in air
Figure 11.10 *In situ* SR-XRD data for C3-17%Al coating heated from 25 to 700 °C in air

Figure 11.11 *In situ* SR-XRD data for C4-21%Al coating heated from 25 to 700 °C in air
Figure 11.12 Stress in CrN structure for (111) orientations as function of temperature

Figure 11.13 Stress in CrN structure for (200) orientations as function of temperature
Figure 11.14 Stress in CrN structure for (311) orientations as function of temperature.
Figure 11.15 The Hardness (H) measured at room temperature for as-deposited and heated samples.
Figure 11.16 The Elastic modulus (E) measured at room temperature for as-deposited and heated samples.

Figure 11.17 The resistance to deformation (H^2/E^2) measured at room temperature for as-deposited and heated samples.
Table 11.3 k-points grids, used in the VASP simulation, for elastic constants of CrN-m.

<table>
<thead>
<tr>
<th>k-points</th>
<th>Elastic constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>3x3x3</td>
<td>C11 514</td>
</tr>
<tr>
<td></td>
<td>C12 201</td>
</tr>
<tr>
<td></td>
<td>C44 118</td>
</tr>
<tr>
<td>9x9x9</td>
<td>C11 311</td>
</tr>
<tr>
<td></td>
<td>C12 38</td>
</tr>
<tr>
<td></td>
<td>C44 60.3</td>
</tr>
<tr>
<td>13x13x13</td>
<td>C11 395</td>
</tr>
<tr>
<td></td>
<td>C12 126</td>
</tr>
<tr>
<td></td>
<td>C44 60.3</td>
</tr>
<tr>
<td>15x15x15</td>
<td>C11 377</td>
</tr>
<tr>
<td></td>
<td>C12 110</td>
</tr>
<tr>
<td></td>
<td>C44 62.0</td>
</tr>
<tr>
<td>21x21x21</td>
<td>C11 376</td>
</tr>
<tr>
<td></td>
<td>C12 115</td>
</tr>
<tr>
<td></td>
<td>C44 61.7</td>
</tr>
</tbody>
</table>

Table 11.4 k-points grids, used in the VASP simulation, for elastic constants of CrN-nm.

<table>
<thead>
<tr>
<th>k-points</th>
<th>Elastic constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>5x5x5</td>
<td>C11 598</td>
</tr>
<tr>
<td></td>
<td>C12 210</td>
</tr>
<tr>
<td></td>
<td>C44 23.8</td>
</tr>
<tr>
<td>9x9x9</td>
<td>C11 519</td>
</tr>
<tr>
<td></td>
<td>C12 249</td>
</tr>
<tr>
<td></td>
<td>C44 3.7</td>
</tr>
<tr>
<td>13x13x13</td>
<td>C11 582</td>
</tr>
<tr>
<td></td>
<td>C12 217</td>
</tr>
<tr>
<td></td>
<td>C44 4.3</td>
</tr>
<tr>
<td>15x15x15</td>
<td>C11 582</td>
</tr>
<tr>
<td></td>
<td>C12 218</td>
</tr>
<tr>
<td></td>
<td>C44 5.7</td>
</tr>
<tr>
<td>21x21x21</td>
<td>C11 590</td>
</tr>
<tr>
<td></td>
<td>C12 215</td>
</tr>
<tr>
<td></td>
<td>C44 6.7</td>
</tr>
<tr>
<td>25x25x25</td>
<td>C11 589</td>
</tr>
<tr>
<td></td>
<td>C12 215</td>
</tr>
<tr>
<td></td>
<td>C44 6.1</td>
</tr>
<tr>
<td>31x31x31</td>
<td>C11 588</td>
</tr>
<tr>
<td></td>
<td>C12 215</td>
</tr>
<tr>
<td></td>
<td>C44 5.9</td>
</tr>
</tbody>
</table>
11.4. APPENDIX 4: Supporting information for Chapter 9

Table 11.5 hkl values for major phases in SR-XRD diffractograms as shown in Figure 11.18- Figure 11.23.

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CrN (A)</td>
<td>~2θ</td>
<td>Cr₂N (B)</td>
<td>~2θ</td>
<td>Cr (C)</td>
<td>~2θ</td>
<td>Ni (D)</td>
</tr>
<tr>
<td>(111)</td>
<td>19.7</td>
<td>(110)</td>
<td>19.5</td>
<td>(111)</td>
<td>22.6</td>
<td>(111)</td>
</tr>
<tr>
<td>(002)</td>
<td>22.8</td>
<td>(111)</td>
<td>22.2</td>
<td>(002)</td>
<td>26.2</td>
<td>(002)</td>
</tr>
<tr>
<td>(022)</td>
<td>32.5</td>
<td>(112)</td>
<td>28.9</td>
<td>(022)</td>
<td>37.3</td>
<td>(022)</td>
</tr>
<tr>
<td>(311)</td>
<td>38.3</td>
<td>(013)</td>
<td>33.8</td>
<td>(311)</td>
<td>44.1</td>
<td>(311)</td>
</tr>
<tr>
<td>(222)</td>
<td>40.1</td>
<td>(031)</td>
<td>35.8</td>
<td>(222)</td>
<td>46.2</td>
<td>(222)</td>
</tr>
<tr>
<td>(004)</td>
<td>46.7</td>
<td>(113)</td>
<td>37.6</td>
<td>(004)</td>
<td>53.8</td>
<td>(004)</td>
</tr>
<tr>
<td>(331)</td>
<td>51.1</td>
<td>(331)</td>
<td>59.1</td>
<td>(331)</td>
<td>60.29</td>
<td></td>
</tr>
<tr>
<td>(042)</td>
<td>52.5</td>
<td>(042)</td>
<td>60.8</td>
<td>(042)</td>
<td>62.03</td>
<td></td>
</tr>
<tr>
<td>(422)</td>
<td>58.0</td>
<td>(422)</td>
<td>67.4</td>
<td>(422)</td>
<td>68.73</td>
<td></td>
</tr>
<tr>
<td>(333)</td>
<td>61.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(044)</td>
<td>68.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 11.18 In situ SR-XRD data for C2#Si coating heated from 300 to 970 K in air
Figure 11.19 *In situ* SR-XRD data for C3#Si coating heated from 300 to 970 K in air

Figure 11.20 *In situ* SR-XRD data for C4#Si coating heated from 300 to 970 K in air
Figure 11.21 *In situ* SR-XRD data for C5#Ni coating heated from 300 to 970 K in air

Figure 11.22 *In situ* SR-XRD data for C6#Ni coating heated from 300 to 970 K in air
Figure 11.23 *In situ* SR-XRD data for C7#Ni coating heated from 300 to 970 K in air
Figure 11.24 (a) Hardness and (b) elastic modulus for CrNiN and CrSiN coatings in as-deposited and annealed conditions.
Figure 11.25 Resistance to deformation for CrNiN and CrSiN coatings in as-deposited and annealed conditions.
Published Papers
Electronic properties and stability phase diagrams for cubic BN surfaces

Ehsan Mohammadpour, Mohammednoor Altarawneh, Zhong-Tao Jiang, Nicholas Mondinos and Bogdan Z. Dlugogorski

School of Engineering and Information Technology, Murdoch University, Murdoch, Australia

ABSTRACT
This contribution investigates structural and electronic properties as well as stability phase diagrams of surfaces of the cubic boron nitride (c-BN). Our calculated parameters for bulk c-BN agree reasonably well with both experimental and computed values available in the literature. Based on the energies of the three experimentally recognised phases of bulk boron, i.e. α-B28, β-B28, and γ-B28, we estimate enthalpy of formation of c-BN to be −2.8 eV. The c-BN(100) surface offers separate B and N terminations (denoted as c-BN(100)_B and c-BN(100)_N), whereas c-BN(111) and c-BN(110) are truncated with combinations of boron and nitrogen atoms (denoted as c-BN(111)_BN and c-BN(110)_BN). Optimised geometries of surfaces display interlayer displacements up to the three topmost layers. Downward displacement of surface boron atoms signifies a common geometric feature of all surfaces. Bulk c-BN and its most stable surface c-BN(100)_N possess no metallic character, with band gaps of 5.46 and 2.7 eV, respectively. We find that, only c-BN(100)_B configuration exhibits a metallic character. c-BN(110)_BN and c-BN(111)_BN surfaces display corresponding band gaps of 2.5 and 3.9 eV and, hence, afford no metallic property.

1. Introduction
Crystalline boron nitride (BN) exists in hexagonal (h-BN), cubic (c-BN) and wurtzite (γ-BN) configurations.[1,2] Its stable structure under standard conditions assumes a hexagonal graphite-like structure.[1] Nearly two decades ago, two-dimensional BN nanosheets were synthesised with a few layered structures of h-BN analogous to graphite.[2,3] Bulk c-BN has also been synthesised under high pressure (>2 GPa) and high temperature (>1000 K) [1] via chemical vapour deposition techniques. BN nanosheets assume promising applications in many areas, including functional nanocomposites,[4] catalysts supports, cutting machineries,[4] electrical and optical nanodevices [5] and capturing of pollutants.[6] These unique applications are derived by the remarkable properties of BN, spanning outstanding mechanical properties (elastic modulus = 0.9 TPa),[7] high thermal conductivity (up to 2000 W/mK),[7] chemical inertness, large surface area, excellent resistance to oxidation (up to 900°C) [2] and a large band gap (4.7–6.0 eV).[8]

In comparison to diamond, c-BN displays some remarkable structural similarities and differences. For example, the diamond structure comprises two face-centred cubic (FCC) carbon cells whereas the c-BN incorporates one boron FCC (B FCC) cell and one nitrogen FCC (N FCC) cell. The bonding between atoms is entirely covalent in the case of diamond, while c-BN holds ionicity between 0.26 and 0.48.[9] c-BN exhibits the largest heteropolar gaps among the III–V compounds. Structural properties of BN highly affect its physical parameters. Measurements by the soft X-ray spectroscopy and UV absorption techniques yielded an indirect band gap of around 6.4 eV.[10] On the other hand, theoretically derived values widely scatter in the range of 3.9–10.5 eV.[1,9,11,12]

Literature offers detailed theoretical and experimental accounts of structural, optical and mechanical properties of bulk c-BN, including lattice constants, bulk moduli, cohesive energies, dielectric constants, and phonon frequencies.[1,13–15] Analogously, surfaces of c-BN have been the subject of many theoretical investigations. These studies have mainly aimed to elucidate the structural relaxations in B- and N-terminated surfaces.[16] For example, Kádas et al. [17,18] found that B- and N-terminated (1 1 1) surfaces of c-BN experience significant relaxations up to the fourth atomic layer. Osuch and Verwoerd [19] as well as Ooi and Adams [12] carried out density functional theory (DFT) calculations to determine the thermodynamically preferred cleavage along the 0 0 1 and 1 1 0 directions, correspondingly. They demonstrated that, a 2 × 2 bridge reconstructions terminated with N atoms represent the thermodynamically most stable arrangement out of all plausible 0 0 1-truncated configurations.[19] Nonetheless, a consistent and comprehensive account of thermodynamic stability of all possible surfaces of c-BN remains lacking.

To this end, this contribution aims to report structural and electronic properties, and thermodynamic stability phase diagram for all plausible c-BN terminations. Calculated properties herein should shed light into the aforementioned remarkable
properties of BN-based materials. For example, if facets of c-BN are largely dominated by the inactive surface N sites, this should translate into chemical inertness for c-BN surfaces.

2. Methodology

2.1. Structural optimisation of c-BN

VASP [20] code performs all structural optimisation and energy calculations based on the PAW-GGA functional.[21] c-BN low index surfaces along the (1 0 0), (1 1 0) and (1 1 1) directions were constructed from 2 × 2 supercells. Each surface consists of 12–15 layers that form a symmetric slab containing about 100 atoms. Vacuum of 10 Å separates surface images in the z-direction. During optimisations, all atoms were allowed to relax until the final energy and the forces on each atom converge to 10−3 eV and 10−2 eV/Å, in that order. In optimisation of surfaces, we deploy an energy cut-off of 400 eV and an automatic κ-points samplings of 4 × 4 × 1.

Bulk unit cells of c-BN were optimised using an energy cut-off of 500 eV and a 5 × 5 × 5 κ-points. A test using 600 eV and an 8 × 8 × 8 κ-points has yielded essentially the same unit cell volume and final energy. We calculate the enthalpy of formation ($E^f$) of bulk c-BN according to:

$$E^f = E_{\text{Bulk}}^{\text{f}} - E_B^{\text{f}} - \frac{N}{2} E_{N_i}$$

where $E_{\text{Bulk}}^{\text{f}}$ and $E_B^{\text{f}}$ correspond to the bulk c-BN and bulk boron energies per unit formula, respectively. $E_{N_i}^{\text{f}}$ was calculated by averaging the energy of bulk boron in its three experimentally recognised stable forms, α, β and γ. While optimising unit cells of these three forms, we found α-B$_{105}$ to be more stable than β-B$_{105}$ and γ-B$_{28}$ by 25.3 and 28.1 meV, respectively, at 0 K. This finding agrees with previous experimental [22] and theoretical [23] studies indicating that, α-B$_{105}$ constitutes the thermodynamically most stable form of elemental boron under ambient conditions. Finally, $E_{N_i}$ signifies the energy of a nitrogen molecule.

2.2. Quasi-harmonic approximation calculations

We estimate thermo-elastic properties of bulk c-BN by utilising the quasi-harmonic approximation (QHA) approach as implemented in the PHONOPY code.[24] PHONOPY utilises VASP interface to calculate force constants. In these calculations, we utilise 2 × 2 × 2 supercell of c-BN (64 atoms) with 5 × 5 × 5 κ-point grid meshes for integration of the Brillouin zone. In all pressure-temperature dependent properties, we elect to deploy the Vinet's equation of state for fitting of energy–volume curves.[25] Detailed descriptions of the underlying equations in the QHA can be found elsewhere.[24] Basically, the QHA approach treats vibrational frequencies of crystal to depend solely on volume; i.e. the intrinsic phonon interactions are independent of temperature.[24] As such, Gibbs free energy $G(T, P)$ is minimised at each volume [26,27] from Helmholtz free energy $F(V, T)$ through:

$$G(T, P) = \min_V [F(V, T) + PV]$$

where $V, P$ and $T$ stand for cell volume, pressure and temperature, respectively. In this equation, $F(V, T)$ was approximated with the summation of electronic internal energy $U(V)$ and phonon Helmholtz free energy $F_{\text{ph}}(V, T)$ [24].

2.3. Ab initio atomistic thermodynamics

The energy phase diagram (vide infra) incorporates all plausible faces of c-BN surfaces based on the approach of ab initio atomistic thermodynamics. Literature provides detailed descriptions of this formalism [28]. In a nutshell, Equation (3) expresses the dependency of surface free energies, $\gamma(T, P)$, on temperature ($T$) and pressure ($P$):

$$\gamma(T, P) = \frac{1}{2A} \left[ G^{\text{surf}}(T, P) - N_B C_{\text{BN-Bulk}}^{\text{Box}}(T, P) - (N_N - nN_B) \mu_N(T, P) \right]$$

in which $G^{\text{surf}}(T, P)$ and $C_{\text{BN-Bulk}}^{\text{Box}}(T, P)$ denote the Gibbs free energies of c-BN surfaces and bulk c-BN, respectively, at the temperature and pressure of interest. $N_B$ and $N_N$ correspond to the number of boron and nitrogen atoms in the slab, and $\mu_N(T, P)$ is the chemical potential of nitrogen:

$$\mu_N(T, P) = \Delta \mu_N(T, P) + \frac{1}{2} E_{N_i}$$

The change in the chemical potential of nitrogen ($\Delta \mu_N(T, P)$) was extracted from standard thermodynamic tables [29]. Therefore, chemical potential of nitrogen can be written as [29]:

$$\mu(T, P) = -4.86 - 0.967 \times \left( \frac{T}{1000} \right) - 0.1013 \times \left( \frac{T}{1000} \right)^2$$

$$+ 0.0173 \times \left( \frac{T}{1000} \right)^3 + \frac{k_B T}{2} \ln(P_{N_2})$$

3. Results and discussion

3.1. Properties of bulk c-BN at 0 K

The unit cell of bulk c-BN can be considered as a diamond-like structure with a space group of T$^3_{\text{d}}$. In this structure, alternately linked boron and nitrogen atoms form a tetrahedral bond network as shown in Figure 1(a). Figure 1(b) illustrates the variation in the total energy of c-BN unit cell with respect to the volume of the unit cell. Our computed equilibrium lattice parameter (3.609 Å) is in a relatively good agreement with corresponding experimental measurements of 3.615 Å [14,30] and other theoretical predictions of 3.59–3.606 Å.[1] In comparison to the LDA functional, the GGA consistently predicts a larger lattice constant for metal nitrides, explaining the discrepancy between our calculated lattice constant and the results of previous LDA computations.[12] Kim and Chen [31] used a combination of LDA and GGA methods to obtain an analogous value of 3.620 Å for lattice constant of c-BN. Using Equation (1), the enthalpy of formation of c-BN was calculated as −2.816 eV (−271.12 kJ/mol). Calorimetric measurements for heat of formation of c-BN were optimised using an energy cut-off of 400 eV and an automatic κ-points samplings of 4 × 4 × 1.

Figure 2 depicts the density of states (DOS) and the partial density of states (PDOS) of bulk c-BN. The DOS of c-BN exhibits two valence bands. The lowest band extends from −20 to −15 eV and corresponds to a combination of B(s) and N(s) orbitals. The second valence band ranges between −10 and 0 eV. The DOS
plots in Figure 2(a) visualises a non-metallic character of bulk c-BN. The calculated indirect band gap of 3.9 eV lies at the lower end of the experimental values of 3.8–5.8 eV,[30] but is in accord with another theoretically derived estimate of 3.9 eV.[30] Along the same line of enquiry, it is well-documented that plain DFT methods tend to underestimate band gaps.[35] For that reason, we deploy the hybrid DFT method of HSE06 [36] to obtain a band gap of 5.7 eV. This value resides at the upper end of the aforementioned experimental values.

3.2. Thermo-elastic properties of c-BN

The practical utilisation of hard coating materials at harsh elevated temperatures and pressures calls for deriving their thermo-elastic properties at these operating conditions. However, it is also intended that contrasting our calculated thermo-elastic properties with analogous estimates in the literature to provide an accuracy benchmark for obtained surface properties conveyed the next section. Table 2 enlists our estimated bulk modulus ($B$) for c-BN at 0 K along with other available experimental and theoretical estimations where a relative satisfactory is attained. Figure 3 shows the calculated phonon dispersion for optimised BN structure at zero pressure and zero temperature. Our calculated phonon dispersion correlates very well with previous analogous estimation by Srivastava et al. as Figure 3 portrays. It is very challenging to distinguish between acoustic and optical
contrasts our calculated $C_p(T)$ values with the experimental and theoretical estimates in Refs. [39,40,33]. As Figure 5(b) depicts, thermal expansion of c-BN decreases with the applied pressure. Figure 6 shows $V/V_o$ curves with varying temperature and pressure where $V_o$ signifies the equilibrium volume of the c-BN branches of phonon dispersion.\[37\] This is primarily due to the fact B and N atoms share very similar atomic masses. Figure 4 portrays the variation in $B$ with $T$ at selected $P$. The obtained $T$-dependent decreasing trends in $B$ values are consistent with the analogous LDA curve by Albe et al. [38] at 0 GPa. Figure 5(a) contrasts our calculated $C_p(T)$ values with the experimental and theoretical estimates in Refs. [39,40,33]. As Figure 5(b) depicts, thermal expansion of c-BN decreases with the applied pressure. Figure 6 shows $V/V_o$ curves with varying temperature and pressure where $V_o$ signifies the equilibrium volume of the c-BN branches of phonon dispersion.\[37\]

Figure 3. Phonon density of states for c-BN. Dashed-line corresponds to theoretical calculations of Srivastava et al. [37].

Figure 4. Dependence of Bulk modulus of c-BN on temperature and pressure. Empty squares correspond to theoretical calculations of Albe et al. [38] at 0 K.

Figure 5. Heat capacity (a) and thermal expansion (b) of c-BN as a function of temperature. Empty squares, rectangles and circles correspond to the theoretical calculation of Solozhenko et al. [39] and Tohei et al. [40], respectively.

Figure 6. (a) Dependence of $V/V_o$ on pressure and (b) temperature. Empty squares, circles and rectangles represent experimental data by Grimsditch et al. [41], Knittle et al. [42] and theoretical by Knittle et al. [42].
unit cell at 300 K and 0 GPa. Analogous experimental values of Grimsditch et al. [41] and Knittle et al. [42] on single crystal c-BN are in good agreement with the present results.

### 3.3. Geometry of low index surfaces of cubic BN

Surfaces of c-BN afford three distinct low-index configurations, namely (100), (110) and (111). The c-BN(100) surface offers separate B and N terminations (denoted as c-BN(100)_B and c-BN(100)_N), whereas c-BN(111) and c-BN(110) truncate with combination of boron and nitrogen atoms (denoted as c-BN(111)_BN and c-BN(110)_BN). Consequently, c-BN permits four distinct surfaces. Figure 7 portrays side and top views of optimised structures of c-BN surfaces.

The analysis of the relaxed structures indicates that all surfaces experience both reconstructions and relaxations. The (110)-BN surface consisted of B and N atoms in ABAB stacking order.\[12\] In the reconstructed surface layer of (110)_BN, neighboring B and N atoms move closer toward each other to satisfy their missing bonds. This reduces the length of covalent B–N bonds from 1.56 to 1.45 Å. Surface relaxation manifests itself in changes in the interlayer distances in the slabs. Figure 8(a) elucidates the interlayer spacing between B atoms and N atoms in adjacent layers. The variability in the locations of the topmost layers take the largest values because of the upward displacement of the top layer. This reduces the distance between the first and second layers. The distance between second and third layer increases due to the enhanced bonding of second layer with top layer. Consequently, this results in weakening of bonds between second and third layers. These displacements gradually die out for the inner layers, which approximate the bulk phase, as electron densities around atoms reach their default bulk value. According to Figure 8(b), expansions and contractions in the BN(100)_N and BN(100)_B slabs fall below those of the (110) surface. In addition, N-terminated (100) surface experiences larger displacement in comparison to the B-terminated surface.

Bader’s theory [43] presents an accurate formalism to calculate partial charge density on individual atoms. Table 1 lists Bader’s charges on selected B and N atoms belonging to the first three topmost atomic layers in all BN surfaces. B and N atoms hold net charges of 3.0 e and −3.0 e in the bulk c-BN structure.

Charge values in Table 1 show that B atoms in surfaces assume similar charges compared to bulk B atoms, except for the topmost layer of the BN(100)_B surface. N atoms in the topmost layer of BN-terminated (110)/(111) slabs are associated with very similar charges to bulk N atoms. However, N atoms in the topmost layer of c-BN(100)_B configuration carry higher negative charges. On the contrary, Table 1 also shows nitrogen atoms in the topmost layer of BN(100)_B surface. N atoms in the topmost layer of BN-terminated (110)/(111) slabs are associated with very similar charges to bulk N atoms. However, N atoms in the topmost layer of c-BN(100)_B configuration carry higher negative charges. On the contrary, Table 1 also shows nitrogen atoms in the topmost layer of BN(100)_N, carrying significantly lower negative charges when contrasted with the bulk N atom. Electronegativity of N atoms in the second and third layers of studied slabs remains very close to their corresponding bulk values. Overall, the high positively and negatively charged B and N atoms atomic inferred from Table 1 verifies the ionic nature of N-B bonds in c-BN surfaces.

Figures 9–12 plot DOS and PDOS on adjacent B and N atoms for the investigated surfaces. DOS plots illustrate three groups of peaks corresponding to core state, valence band and conduction band, respectively. As evident from the occupied energy states around the Fermi level, the c-BN(100)_B attains metallic character while c-BN(100)_N, c-BN(110)_BN and c-BN(111)_BN surfaces engender band gaps of 2.7, 2.5 and 3.9 eV, respectively.
3.4. Stability phase diagrams for c-BN surfaces

Value of $\Delta\mu(T, P)$ vary between N-lean and N-rich limits. These limits symbolise the practical conditions of the chemical potential of nitrogen. The N-lean boundary refers to the value...
of $\Delta \mu_N(T, P)$ when bulk $c$-BN starts to form from adsorption of nitrogen molecules on bulk boron. The N-rich limit characterises the onset of decomposition of nitrogen gas into N atoms. Appropriate and well-defined values for the N-rich and N-lean limits can be taken as 0.0 and $-2.816$ eV; the latter is the computed $E_f$ value for $c$-BN. Figure 13 plots the stability phase diagram of $c$-BN surfaces. At all accessible values of $\Delta \mu_N(T, P)$, $BN(100)_N$ surface displays the profound thermodynamic stability. As conveyed in the introduction, the predominant stability of the N-truncated surface is in line with the chemically inert nature of BN. In a recent study [44], we have demonstrated that the thermodynamic stability
4. Conclusions
This contribution documented the geometric and electronic properties of bulk c-BN and its surfaces along the three low-Miller indices. We found the nitrogen-terminated surface along the 1 0 0 direction to be the most thermodynamically stable configuration over all physically accessible values of the chemical potential of nitrogen. This finding explains the inert nature of BN. While it was not the main focus of the current investigation, we have found that α-B_{36} dictates the stability phase diagram of bulk boron at 0 K, in agreement with the recent experimental measurements. Analysis of Bader’s charges indicates that, all surfaces of c-BN largely retain the ionic character of the bulk c-BN.

Acknowledgments
E.M. thanks Murdoch University for the award of a postgraduate scholarship.

Disclosure statement
No potential conflict of interest was reported by the authors.

Funding
This study has been supported by the Australian Research Council, the School of Engineering and Information Technology SRG-2014, as well as computing time grants from the National Computational Infrastructure (NCI), Australia and Pawsey Supercomputing Centre in Perth.

References
Thermo-mechanical properties of cubic titanium nitride

Ehsan Mohammadpour, Mohammednoor Altarawneh*, Jomana Al-Nuairat, Zhong-Tao Jiang, Nicholas Mondinos and Bogdan Z. Dlugogorski

School of Engineering and Information Technology, Murdoch University, Murdoch, Australia

1. Introduction

Owing to a wide array of remarkable mechanical and thermal properties, titanium nitride (TiN) finds direct applications pertinent to surface protections and metal cutting machineries [1,2]. TiN exhibits extreme hardness, corrosion resistance (stable below 800 °C), good adhesion to substrate, high fraction toughness and high melting point (2950 °C) [3]. Due to these unique applications, many contributions report characterisations of TiN-based coatings [4–7] and its derivatives such as ternary combinations (TiAlN [8]) and superlattice coatings (TiN/CrN [9,10]).

Kress et al. [11] compared the experimentally obtained phonon dispersion curves of TiN with calculations obtained via a double-shell model. They reported an acoustical section of the phonon spectra. A theoretical study by Wolf et al. [12] documented elastic properties and thermal expansion of TiN. Kim et al. [13] utilised line-focus acoustic microscopy to determine mechanical properties of single-crystal TiN from its surface acoustic wave dispersion curves. Their measurements confirmed the previous theoretical values of elastic constants and modulus properties of TiN low-index surfaces calculated by Marlo et al. [14] based on the DFT-GGA formalism. They illustrated a stability surface diagram of TiN surfaces; an important parameter in understanding competing mechanisms encountered during the thin film growth and preferential growth orientations.

The theoretical predictions of relative volume and bulk modulus of TiN were studied by Chen et al. [15] as a function of pressures (0–6 GPa) and temperatures (0–2000 K). Wang et al. [16] theoretically compared the structural stability and elastic constants of TiN in rocksalt and Wurtzite forms. Similarly, Brik et al. [17] studied the electronic structure and elastic properties of TiN using different flavours of density functional theory functions (DFT). Zhu et al. [2] studied the phase transition of TiN at ground state establishing a relationship between enthalpy and pressure. They predicted a transition from cubic B1-TiN (NaCl-type) to B2-TiN (CsCl-type) around 342 GPa. Gupta et al. [18] studied the phonon and thermodynamical properties of TiN within the DFT framework of Generalised Gradient Approximation (GGA) coupled with the Quasi-Harmonic Approximation (QHA) approach. However, their calculations for thermodynamic properties were limited to a zero pressure. Mehmood et al. [19] calculated electronic and optical properties of low index surfaces of TiN employing both DFT and many-body GW methods. More recently, Yu et al. [20] explored the structural stabilities of several Ti_{2+n}N_{n+1} compounds (TiN, Ti_N, Ti,N, Ti,N, Ti,N and TiN) by first-principle structure predictions under ambient conditions and at pressures up to 60 GPa. It was concluded that the TiN configuration displays the largest hardness of 27.2 GPa, and at high pressure, new phases were formed (TiN and TiN). All investigated phases were found to be mechanically and dynamically stable under ambient conditions.

Knowing the pressure- and temperature-dependent crystal properties enables to model extreme conditions that are not easily attainable by experimental means. QHA calculations have been considered as one of mainstream methodologies of incorporating temperature effect in the DFT calculations, commonly obtained results at 0 K [21]. This method operates in the framework of...
harmonic approximation and widely considered to be accurate at temperatures of the order or below the Debye constant [22] and is generally proved to provide satisfactory results up to the melting point of materials [23]. These properties are vital in the design process of advanced engineering materials. The aim of this study is to deploy first-principle calculations and the QHA formalism to attain a detailed insight on the thermo-elastic properties of TiN at high pressure and temperature conditions relevant to the harsh operational conditions commonly encountered in their real life applications, i.e. in cutting machineries. As mentioned above, there are a few theoretical studies on the thermodynamic properties of TiN as a function of temperature up to 2000 K. Accurate determination of mechanical properties at conditions encountered in real applications requires incorporating the pressure effect on all pertinent properties, not only the temperature effect. Herein, we present the first-ever reported pressure-and temperature-dependent thermodynamic and mechanical properties of rocksalt-structured TiN. The effect of pressure on the thermodynamic behaviour of TiN over a large temperature range has not been elucidated theoretically. To the best of our knowledge, literature provides no theoretical validation of the analogous thermo-elastic experimental data for TiN. Therefore, the main contribution of this work is to determine the pressure dependency of thermodynamic and mechanical properties for rocksalt-structured TiN in the very wide pressure range of 0–60 GPa and temperature range of 0–3100 K.

2. Theoretical method

A plane-wave basis projector augmented wave method [21] is utilised herein in all structural and electronic calculations, as implemented in the Vienna ab initio simulation package (VASP) code [24]. The exchange and correlation functional were described within the GGA formalism. A plane-wave cut-off energy and energy convergence criteria of 600 eV and $10^{-8}$ eV were employed, respectively. A Monkhorst pack $k$-points sampling of $15 \times 15 \times 15$ was used in structural calculations. TiN adopts a NaCl-type structure with space group Fm-3 m (#225). In this structure, the Ti and N atoms occupy the 1a (0, 0, 0) and 1b (0, 0.5, 0) sites, respectively.

The enthalpy of formation ($E_f$) for TiN was calculated according to:

$$E_f = E_{\text{bulk}}^{\text{TiN}} - E_{\text{bulk}}^{\text{Ti}} - \frac{n}{2}E_{\text{N}}$$

where $E_{\text{bulk}}^{\text{TiN}}$, $E_{\text{bulk}}^{\text{Ti}}$, and $E_{\text{N}}$ denote the ground state per-formula energies of bulk TiN (cubic), Ti (hcp) and nitrogen molecule, respectively.

In order to apply the QHA method within the Gibbs2 code, results from VASP and Phonopy programs were deployed as input to Gibbs2 to calculate all thermodynamic values [25]. An important input in QHA calculations are the phonon density of states (phDOS) obtained at each of the calculated crystal volumes. Phonon frequencies were computed using the open source Phonopy code [26], whereas force constants were calculated from VASP outputs. For the phonon calculations, a $2 \times 2 \times 2$ supercell of conventional primitive cell was utilised with eight atoms at each volume grid. In calculations of force constants, atomic displacement distances vary within 0.01 Å.

3. Results and discussion

3.1. Bulk TiN

Figure 1 shows the unit cell of TiN in NaCl-type structure (Fm-3 m space group) where both Ti and N occupy an octahedral arrangement with identical Ti-N distances of 2.13 Å. Our calculated lattice constant for c-TiN attains a value of 4.255 Å; and coincides very well with experimental and theoretical data as listed in Table 1. According to Equation (1), the computed enthalpy of formation for TiN is estimated to be $-3.77$ eV ($-363.8$ kJ/mol); and reasonably agrees (within ~7%) with the experimental corresponding value of $-337.8$ kJ/mol [27].

3.2. Mechanical properties

Elastic properties are important due to their close relationship to various fundamental properties, including interatomic bonding, equations of state and phonon dispersion. It is also possible to associate them with thermodynamic properties such as specific heat and thermal expansion [2] as well as to a wide array of fundamental properties encompassing load deflection, thermo-elastic stress, internal strain, sound velocities and fracture toughness. For instance, high internal stress in the coating may result in poor coating/substrate adhesion.

Elastic constants were calculated from stress–strain relationships. Variations in stress tensor due to crystal strain were used to compute the elastic constants ($C_{ij}$) matrix and its inverse matrix $S_{ij}$. The Young’s modulus ($E$), Shear modulus ($G$), Zener anisotropy factor ($A$) and bulk modulus ($B$) of a polycrystalline cubic system were estimated by Voigt, Reuss and Hill formulas [28]. Voigt approximations exhibit the higher limits:

$$B_v = \frac{1}{9}(C_{11} + C_{22} + C_{33}) + \frac{2}{9}(C_{12} + C_{13} + C_{23})$$

$$G_v = \frac{1}{15}(C_{11} + C_{22} + C_{33} - C_{12} - C_{13} - C_{23}) + \frac{1}{5}(C_{44} + C_{55} + C_{66})$$

On the other hand, Reuss approximations assume equations for lower limits:

$$B_R = \frac{1}{(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})}$$

$$G_R = \frac{15}{4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})}$$

Hill formulas express the arithmetic mean values as:

$$B_H = \frac{B_R + B_v}{2}$$

$$G_H = \frac{G_R + G_v}{2}$$

Finally, the polycrystalline Young’s modulus and Poisson ratio can be obtained using:
The Zener anisotropy factor \(A\) is estimated according to \([29]\):

\[
A = \frac{2C_{44}}{C_{11} - C_{12}}
\]  

For a cubic structure, the following mechanical stability conditions should be satisfied \([29]\):

\[
C_{11} - C_{12} > 0, C_{11} > 0, C_{44} > 0, C_{11} + 2C_{12} > 0, C_{12} < B < C_{11}
\]  

The optimised lattice parameter \(a\), elastic constants \((C_{ij})\), bulk modulus \((B)\), shear modulus \((G)\), Young's modulus \((E)\), Zener anisotropy factor \((A)\) and Poisson ratio \((\nu)\) for cubic TiN are listed in Table 1 at the ground state; 0 K. As shown in Table 1, the calculated elastic constants satisfy all of the above mentioned conditions of Equation 10. As Table 1 portrays, our estimated values agree well with experimental and other theoretical values. The large \(C_{11}\) value indicates a low compressibility along the \(c\)-axis. The shear modulus reflects the resistance of the material to changes in shape at a constant volume. Knowing the bulk modulus and shear modulus of a material, enables one to predict its hardness using developed formulas by Chen et al. \([30]\) and Jiang et al. \([31]\]. It was shown, by Jiang et al., that there is a clear linear correlation between shear modulus and hardness based on experimental data for several covalent crystals \([31]\). Poisson’s ratio displays the level of directionality of covalent bonding. Strong directional covalent bonds lead to a Poisson’s ratio close to 0.2, while the value for metals is about 0.4 \([20]\). Our calculated bulk modulus in Table 1 of 295 GPa is in a good agreement with analogous experimental values of 318 and 292 GPa obtained by Wolf et al. \([12]\).

### Table 1.

Calculated lattice constant \((a)\), elastic constants \((C_{ij})\), bulk modulus \((B)\), shear modulus \((G)\), elastic modulus \((E)\), Zener anisotropy factor \((A)\) and Poisson ratio \((\nu)\).

<table>
<thead>
<tr>
<th></th>
<th>Present work</th>
<th>Ref ([13]) experimental</th>
<th>Ref ([12]) experimental</th>
<th>Ref ([20]) calculated</th>
<th>Ref ([17]) calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) (Å)</td>
<td>4.255</td>
<td>4.202</td>
<td>4.18–4.25</td>
<td>4.18–4.25</td>
<td></td>
</tr>
<tr>
<td>(C_{11}) (GPa)</td>
<td>611</td>
<td>625</td>
<td>778</td>
<td>590</td>
<td>535–649</td>
</tr>
<tr>
<td>(C_{12}) (GPa)</td>
<td>138</td>
<td>165</td>
<td>139</td>
<td>145</td>
<td>118–129</td>
</tr>
<tr>
<td>(C_{44}) (GPa)</td>
<td>159</td>
<td>163</td>
<td>169</td>
<td>169</td>
<td>175–194</td>
</tr>
<tr>
<td>(B) (GPa)</td>
<td>296</td>
<td>352</td>
<td>294</td>
<td>257–302</td>
<td></td>
</tr>
<tr>
<td>(G) (GPa)</td>
<td>190</td>
<td>216</td>
<td>189</td>
<td>187–188</td>
<td></td>
</tr>
<tr>
<td>(E) (GPa)</td>
<td>469</td>
<td>418–556</td>
<td>499–530</td>
<td>466</td>
<td>492–429</td>
</tr>
<tr>
<td>(A) (GPa)</td>
<td>0.671</td>
<td></td>
<td></td>
<td>0.527</td>
<td></td>
</tr>
<tr>
<td>(\nu)</td>
<td>0.23</td>
<td></td>
<td></td>
<td>0.235</td>
<td></td>
</tr>
</tbody>
</table>

\[
E = \frac{(9B_{H}G_{H})}{(B_{H} + G_{H})}
\]  

\[
\nu = \frac{(3B_{H} - 2G_{H})}{2(3B_{H} + G_{H})}
\]  

**3.3. Electronic properties**

In this section, the changes in total electron density of state due to pressures (0, 33 and 60 GPa) is discussed. It can be seen that, the TiN structure is metallic in the entire pressure range which is in good agreement with the analogous literature values depicted in \([14,18–20]\). The total and partial density of state (PDOS) in range of \(-20\) to \(10\) eV for \(c\)-TiN are presented in Figure 2. These plots were used to evaluate the pressure dependency of electron structure of TiN.
The strong hybridisation of N-2p and Ti-3d shows the formation of covalent bond between Ti and N atoms, similar to the theoretical results of Gupta et al. [18]. One can see that P3 around Fermi level is dominated by Ti-3d states hybridised by N-2p anti-bonding states. These peaks are observed to shift towards the higher negative energy as the pressure increases from 0 to 60 GPa, i.e. the P1 shifts from −14.85 to −15.6 eV. Overall, no significant broadening is observed in the DOS curve under the influence of pressure.

3.4. Phonon spectra

The normalised phonon density of states \( g(\omega) \) for \( N \) number of unit cells is defined as

\[
g(\omega) = \frac{1}{N} \sum_j \delta(\omega - \omega_j)
\]

where \( q \) and \( j \) are wave vector and band index, respectively. The phonon density of states (PDOS) of the TiN crystal shown in Figure 3 is in good agreement with experimentally obtained neutron scattering values [33]. The present acoustic and optical phonon calculations are in reasonable agreement with theoretical values for the acoustic phonons by Kress et al. [11] and both acoustic and optical phonons by Gupta et al. [18]. Our calculations clearly show that there is a gap of almost 6 THz between the phonon branches of optical and acoustical. This is due to considerable mass ratio of Ti and N atoms. All positive PDOS dispersion curves indicate the dynamical stability of TiN in the NaCl-type structure (the rock salt form).

3.5. Thermodynamic properties

Thermal behaviour of any given material can be obtained by exploring the combined temperature–pressure effects on its thermodynamic properties. Since TiN is a promising material in the coating technology, it is crucial to understand its thermal properties under high pressure and temperature conditions. At a constant volume, a number of thermodynamic properties can be derived from non-equilibrium vibrational Helmholtz free energy.
Phonon properties are sensitive to the changes in volume of unit cell because the crystal potential signifies an anharmonic function of volume. Our results demonstrate that phonon frequency tends to decrease when the volume increases. Typically, changes in volume lead to variation of the phonon properties because the potential of the crystal is an anharmonic function of crystal volume. Togo et al. [26] examined phonon frequencies for a unit cell with several different volumes. Their calculations showed that changes in volume slightly affect the slope of phonon modes. However, phonon frequencies tend to shrink constantly as the volume of unit cell gets larger. As mentioned above, phonon energy is measured based on frequency of phonons and displays a profound sensitivity as volume varies. Therefore, one can transform the thermodynamic properties at constant volume to constant pressure based on the following governing relationships:

\[ \alpha = \frac{\gamma_{th} C_v}{V B_T} \]  

where \( \gamma \) signifies the thermodynamic Grüneisen ratio [22]. The Debye temperature (\( \Theta_D \)) also can be obtained from the implemented Debye–Slater model in Gibbs2:
of atoms per formula and universal gas constant, respectively) [35]. Figure 4(d) presents the changes in \( C_p \) with respect to temperature between 0 and 3100 K, at fixed pressure values. Figure 5(a) shows the \( V/V_0 \) ratio as a function of temperature up to 3100 K at fixed equidistance pressures (in range 0–60 GPa). Here, \( V_0 \) is volume of the primitive cell of TiN at 300 K (i.e. 19.27 Å³). Experimental results by Aigner et al. [34] from XRD at 1 atm are also included for comparison. Results suggest that TiN cell volume is a non-linear function of pressure. The cell compression due to pressure is more distinct at higher temperatures. This in turn indicates that, pressure reduces the thermal expansion of TiN at high temperatures. Figure 5(b) also shows changes in \( V/V_0 \) ratio as a function of pressure at fixed temperatures (in range of 0–3100 K). It is observed that volume expands as the temperature increases. Following the aforementioned points regarding the effect of pressure on thermal expansion, it can be observed in Figure 6(a) and (b) that pressure reduces the volumetric thermal expansion of TiN progressively (based on Equation (16)). Reduction in thermal expansion of TiN does not obey a linear relation while the pressure increases from 0 to 60 GPa. The thermal expansion tends to drop more sharply at pressures below 40 GPa revealing that the TiN is rather uncompressible under very high pressures. The calculated entropy (\( S \)) based on Equation (12) for TiN are

\[
\Theta_D = \frac{\omega_D}{k_B} = \frac{1}{k_B} \left( \frac{6\pi^2 n}{V} \right)^{1/3} V_0 \tag{19}
\]

where \( n \) and \( V_0 \) are the number of vibrational states and static equilibrium frequency of the phonon, respectively. Figure 4(a) depicts the changes in total heat capacity (\( C_p \)) of TiN, at a constant pressure (1 atm) and constant volume between 0 and 3100 K. The experimental results of Chase et al. [27] and Lengauer et al. [34] are also included in the plot. It can be seen that calculated heat capacity, using the Debye–Slater model, agrees very well with the experimental data. For example, the calculated \( C_p \) at room temperature amounts to 34.4 J/mol/K; very close to the experimental value 33.74 J/mol/K [3]. The changes in heat capacity at constant volume (\( C_v \)) of TiN are shown in Figures 4(b) and (c) as functions of pressure (at fixed temperature values) and temperature (at fixed pressure values), respectively. The plots reveal that, when the pressure increases from 0 to 60 GPa at 300 K, the \( C_v \) is reduced by 28.6% from 32 to 24 J/mol.K. However, this tendency in reduction of \( C_v \) is less profound at elevated temperatures. The \( C_v \) approaches constant values at higher temperatures due to the suppression of anharmonic effects as it gets closer to the Dulong–Pettit limit of \( 3nR = 50 \text{ kJ/mol/K} \) (where \( n \) and \( R \) are the number of atoms per formula and universal gas constant, respectively) [35]. Figure 4(d) presents the changes in \( C_v \) with respect to temperature between 0 and 3100 K, at fixed pressure values.

Figure 5(a) shows the \( V/V_0 \) ratio as a function of temperature up to 3100 K at fixed equidistance pressures (in range 0–60 GPa). Here, \( V_0 \) is volume of the primitive cell of TiN at 300 K (i.e. 19.27 Å³). Experimental results by Aigner et al. [34] from XRD at 1 atm are also included for comparison. Results suggest that TiN cell volume is a non-linear function of pressure. The cell compression due to pressure is more distinct at higher temperatures. This in turn indicates that, pressure reduces the thermal expansion of TiN at high temperatures. Figure 5(b) also shows changes in \( V/V_0 \) ratio as a function of pressure at fixed temperatures (in range of 0–3100 K). It is observed that volume expands as the temperature increases. Following the aforementioned points regarding the effect of pressure on thermal expansion, it can be observed in Figure 6(a) and (b) that pressure reduces the volumetric thermal expansion of TiN progressively (based on Equation (16)). Reduction in thermal expansion of TiN does not obey a linear relation while the pressure increases from 0 to 60 GPa. The thermal expansion tends to drop more sharply at pressures below 40 GPa revealing that the TiN is rather uncompressible under very high pressures. The calculated entropy (\( S \)) based on Equation (12) for TiN are
using QHA and quasi-harmonic Debye methods, respectively. In both cases, the bulk modulus starts to decline at about 200 K at constant pressures. Debye temperature is a sign of thermal stability and hardness of solids [18]. It is also closely related to the thermal vibration of atoms, specific heat and thermal coefficient. Figure 9(a) and (b) show the computed Debye temperature for TiN crystal in a wide pressure and temperature ranges obtained based on Equation (19). The experimental data for pure TiN obtained from X-ray diffraction is shown with empty circles in Figure 9(a) [37]. The calculations reveal that the Debye temperature is 870 K at 300 K; a value that is very comparable to 754 and 809 K calculated by Gupta et al. [18] and Jacob et al. [38]. Nonetheless, all these theoretically obtained values somehow deviate from the average reported experimental values for TiN; 671 K [37] and 580 ± 20 K [39]. A plausible explanation for this deviation may stem from the choice in the deployed methodology. For example, metals with d-orbitals are better to be described by the DFT + U methodology rather than via plain DFT. The effect of the U values in the DFT + U treatment on thermo-elastic properties of transitional metal nitrides will be investigated in due course.

plotted in Figure 7(a) and (b) as functions of temperature (isobar) and pressure (isotherms), respectively. The experimental data from Chase et al. [27] at 1 atm in Figure 7(a), display good agreement with our calculations. Changes in entropy proved to be more sensitive to temperature than pressure.

According to Equation (16), the isothermal bulk modulus (B) was calculated as the second derivative of the isothermal Helmholtz free energy against volume. Bulk modulus values are illustrated as a continues function of temperature and pressure in Figure 8(a) and (b), respectively. The calculated bulk modulus at 0 K and 0 pressure gives a value of 286.8 GPa; correspond very well with analogous values by Chen et al. [15] at 280.1 GPa (represented by empty circles). It is inferred herein that pressure increases the bulk modulus systematically. Variation of bulk modulus when T < 100 K is relatively small which is in connection with the relatively constant volume of the unit cell at this temperature range. As the temperature increases, the volume of the cell expands and at the same time, bulk modulus declines. However, bulk modulus reduces as the temperature increased at any given pressure. The combined effect of temperature and pressure on bulk modulus of TiN is comparable to the calculation of Erba et al. [23] for γ-Al₂O₃ crystal and Ma et al. [36] for Cr₂N using QHA and quasi-harmonic Debye methods, respectively. In both cases, the bulk modulus starts to decline at about 200 K at constant pressures.

Debye temperature is a sign of thermal stability and hardness of solids [18]. It is also closely related to the thermal vibration of atoms, specific heat and thermal coefficient. Figure 9(a) and (b) show the computed Debye temperature for TiN crystal in a wide pressure and temperature ranges obtained based on Equation (19). The experimental data for pure TiN obtained from X-ray diffraction is shown with empty circles in Figure 9(a) [37]. The calculations reveal that the Debye temperature is 870 K at 300 K; a value that is very comparable to 754 and 809 K calculated by Gupta et al. [18] and Jacob et al. [38]. Nonetheless, all these theoretically obtained values somehow deviate from the average reported experimental values for TiN; 671 K [37] and 580 ± 20 K [39]. A plausible explanation for this deviation may stem from the choice in the deployed methodology. For example, metals with d-orbitals are better to be described by the DFT + U methodology rather than via plain DFT. The effect of the U values in the DFT + U treatment on thermo-elastic properties of transitional metal nitrides will be investigated in due course.
4. Conclusions

In summary, using first principle calculations, the electronic structure, phonon spectra and thermodynamic properties of TiN in rocksalt form were thoroughly investigated based on a DFT–QHA approach. The lattice constant, elastic constants and bulk modulus values are in good agreement with previous literature values. The electronic density and band structure curves show that TiN exhibits a metallic character. One can see that Ti-3d hybridised with N-2p anti-bonding orbitals dominate the states around the Fermi level. The PDOS spectra showed that, the TiN is dynamically stable. The temperature and pressure dependency of several mechanical and thermal properties of TiN were thoroughly investigated and discussed in the context of their physical significance.

Acknowledgement

A.S acknowledges Murdoch University for the award of a postgraduate research scholarship.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the Australian Research Council; computational time grants from the National Computational Infrastructure (NCI) in Canberra; the Pawsey Computing Centre in Perth.

References

Predicting high temperature mechanical properties of CrN and CrAlN coatings from in-situ synchrotron radiation X-ray diffraction

Ehsan Mohammadpour a, Zhong-Tao Jiang a,⁎, Mohmmednoor Altarawneh a,⁎, Zonghan Xie b,c, Zhi-feng Zhou d, Nicholas Mondinos a, Justin Kimpston e, Bogdan Z. Dlugogorski a

a School of Engineering & Information Technology, Murdoch University, Murdoch, WA 6150, Australia
b Department of Mechanical and Biomedical Engineering, City University of Hong Kong, Kowloon, Hong Kong, China
c School of Mechanical & Electrical Engineering, Wuhan Institute of Technology, Wuhan 430073, PR China
d Australian Synchrotron, 800 Blackburn Rd., Clayton, VIC 3168, Australia

⁎ Corresponding authors.
E-mail addresses: Z.Jiang@murdoch.edu.au (Z.-T. Jiang), M.Alтарawneh@murdoch.edu.au (M. Altarawneh).

A R T I C L E   I N F O
Article history:
Received 15 June 2015
Received in revised form 10 December 2015
Accepted 23 December 2015
Available online 29 December 2015

Keywords:
Hard coatings
Strain
Williamson–Hall
Synchrotron radiation
High temperature X-ray diffraction
Rietveld refinement
GSAS

A B S T R A C T
This contribution investigates the phase composition of CrN and CrAlN coatings by in-situ high temperature synchrotron radiation (SR-XRD), with the coatings deposited on steel substrate by closed field unbalance magnetron sputtering. Rietveld refinement on the SR-XRD spectra indicated CrN as the major phase, over the temperature range of 25 °C–700 °C, for both coatings. At the high temperature of 700 °C, a Cr2N phase was observed in the CrN coating while the CrAlN coating also had a Cr phase. Williamson–Hall plots, from the refined data, afforded estimating variations of the strain and crystallite size of the major phase, up to 700 °C. The crystallite size (10 nm) for the CrAIN coating, at 25 °C, agrees very well with previous GI-XRD and TEM results obtained at room temperature Li et al. (2012).

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Magnetron-sputtered hard-surface coatings composed of transition metal nitride have been utilised to improve the productivity of cutting machinery in a wide range of applications such as drills, mills and cutting tools [2–4]. The main merit of magnetron sputtering is the attainment of robust control of the composition and microstructure of hard films and other nanostructured composite materials [5].

Due to their exceptionally high hardness characteristics and outstanding wear resistance, TiN coatings are major component in cutting machinery. However, TiN coatings exhibit only moderate resistance to oxidation and corrosion lessening their duration of use. In contrast, CrN coatings display enhanced performance under oxidative and corrosive conditions that is primarily derived from the formation of an isolating adhesive chromium oxide layer on the coated surface [6]. In some applications, the thickness of film coating is an important parameter in deciding the type of coating to use. The maximum thickness of TiN coatings is typically limited to 10 μm, while CrN coatings can be made with thicknesses of more than 40 μm [7]. However, CrN coatings are associated with significantly lower hardness (i.e. 12.0–18.0 GPa), compared with TiN coatings (>-20 GPa). The demand for improved properties has resulted in development of ternary and multinary coatings such as CrAlN, CrAlYN, CrSiN, CrAlSiN and CrAlTiN [8].

Incorporating (alloying) Al in the cubic lattice of c-CrN coatings forms a metastable phase that considerably improves the hardness of the coating. Since c-CrN exhibits high solubility for c-AlN, ternary CrAlN nanocomposite coatings are promising pseudo binary nitrides in which Al and Cr sesquioxides provide effective resistance against oxygen diffusion through the coating [9]. Outward diffusion of Cr and Al ions, to the surface in CrAlN coatings, results in the formation of complex surface oxides which enhance the thermal properties of CrAlN by acting as barriers against further oxidation [5]. Additionally the hardness and thermal stability of CrAlN are enhanced by Al substitution of Cr atoms in the face-centred cubic structure of c-CrN [8]. The solute atoms are believed to hinder slip by diffusing to and segregating around dislocations [10]. These two hardness-enhancing mechanisms in coatings are determined by the Al content and are characterised by formation of a metastable solid solution that produces internal lattice strains. Properties of such coating are highly sensitive to Al content where excessive addition of Al beyond 64 at.% alters the structure from rock-salt (NaCl) crystal structure (Fm3m) to wurtzite structure (P-31 m) resulting in deterioration of hardness and anti-oxidation.
properties with alteration of preferred growth orientation [11]. Formation of hexagonal h-AlN structures significantly decreases hardness and thermal stability of CrN coatings reducing the benefit of Al alloying [12].

High temperature properties of hard coatings primarily depend on their crystalline-phase structures. Alloying elements, present in the phase formed during the deposition stage, exert a noticeable influence on the durability and the expected service life of hard coatings [13-19]. Any significant variations in grain size of coatings may affect their thermal stability [20]. Therefore, any unforeseen changes in microstructure and phase composition of coating material can potentially reduce the thermal resistance and hardness [21] of the coatings. Since coatings deposited by the sputtering techniques are in a non-equilibrium condition [22], it is of vital importance to study the microstructure of the coatings at elevated temperatures.

Literature articles and reviews discuss overall mechanical and thermal properties including various preparation techniques of CrAlN coatings, in terms of their microstructure [23], effects of atomic ratio (i.e. Al/ Cr ratios) on their phase composition [2,24], deposition control parameters [25,26], and high temperature oxidation properties [18,19].

Tribological properties of CrN coatings with Al and Si dopants deposited by cathodic arc, studied by Polcar et al. [27], showed high hardness, excellent oxidation resistance and thermal stability up to 800 °C. X-ray analysis showed that, the dominant structure in Al and Si-doped coating material was cubic solid solution of Al in CrN. However, hexagonal AlN was also detected in the AlCrSiN coating. Sánchez-López et al. [12] studied the tribological behaviour of CrAl(Y,Zr)N coatings at 300, 500 and 650 °C, and concluded that the CrAlN coating had lower film wear due to high hardness and presence of Al2O3 on the coating surface. Forsen et al. [28] reported improved hardness of CrAlN coating by addition of Ti which improves the formation of h-AlN at annealing temperatures above 1100 °C. The enhanced hardness was due to spinodal decomposition into coherent TiCr and Al-rich structures of the coating material, causing age hardening that stabilised the significantly improved hardening. Wang et al. [18] deposited CrN and CrAlN using single electron beam plasma assisted physical vapour deposition (PAPVD) system, annealed them at 500 °C–1000 °C and then cooled down to 25 °C for characterisation. Their analysis showed orthorhombic CrN structure in the CrN coating, CrN was converted to Cr2N at about 500 °C and Cr2O3 was detected above 700 °C. A solid solution of CrAlN was detected in the CrAlN coating and was stable up to 900 °C. The hardness of CrN coating dropped from 24.8 GPa to 16 GPa at 600 °C. On the other hand, the original hardness of CrAlN amounted to 30 GPa which decreased to 21.6 GPa after annealing at 600 °C. CrAlN solid solutions can be deposited with up to 66.0 at.% of Al input [29,15], which precipitates into a more stable h-AlN phase with low mechanical properties, above 800 °C, as a result of a spinodal reaction [30].

Kirchlechner et al. [31] studied the deposition of CrN coating by reactive magnetron sputtering at temperatures of 25 °C – 850 °C. They employed high intensity synchrotron radiation beamline to obtain diffraction spectra from both coating and steel substrate simultaneously which enabled determination of strains and internal stresses of the coating and the substrate. Rivadulla et al. [32] used synchrotron radiation (λ = 0.44397 Å) in combination with ab initio calculations to identify the cubic to orthorhombic transformation of CrN at pressures of about 1 GPa. This transformation reduces the bulk modulus of the coatings.

The promising properties of CrAlN coatings highly depend on their complex phase behaviour and more detailed studies on their nanostructure could lead to fabrication of improved hard coatings. In our previous studies [2] [11], we employed multiple surface and subsurface analysis characterisation techniques to investigate CrAlN coatings on various substrates. Results revealed the formation of CrAlN solid solution, with amorphous AlN present at columnar CrN grain boundaries. The next step necessitates an accurate investigation of the role of Al on the change of crystal structure phases of CrN coatings at temperatures up to 700 °C. We explore the phase composition and crystal structure of the aforementioned coating in the temperature range of 25 °C to 700 °C using in-situ SR-XRD measurements. Finally, we analysed the SR-XRD measurements to derive the crystallite size and strain of the main phases up to 700 °C.

1.1. Experimental procedure

CrN and CrAlN coatings were deposited on M2 high speed steel substrates using closed field unbalanced magnetron sputtering system (Teer Coatings Ltd., UK) with four-target configuration. The coating process has been described in detail elsewhere [1,33]. To observe a phase formation in the CrAlN coatings, in-situ SR-XRD measurements were carried out as a function of temperature. Synchrotron radiation has a number of advantages including the ability to tune the wavelength to avoid the formation of sample fluorescence, superior energy bandpass and significantly higher signal/noise (S/N) compared to a laboratory instrument. The experiment was performed on the Powder Diffraction beamline at the Australian Synchrotron with monochromated X-rays of wavelength 0.82647 Å. The X-ray diffraction data were collected on a Mythen microstrip detector and the wavelength was determined by Rietveld refinement of a Standard Reference Material, LaB6 660b, as supplied by the National Institute of Standards and Technology (USA). The coated substrates were mounted on a Pt heating strip in an Anton Paar HTK-2000 high temperature furnace and aligned to the centre of rotation on the diffractometer. The samples were heated from ambient temperature up to 700 °C with a heating rate of 10 °C/min and X-ray diffraction data were collected over the angular range 10° ≤ 2θ ≤ 89°. The sample surface temperature was calibrated before experiment.

Samples made with CrN coating on M2 steel will be denoted as CrN-M2ST and samples made with CrAlN – xN coating on M2 steel will be denoted as CrAlN-M2ST.

1.2. Theoretical procedure

In the present study, assuming Bragg–Brentano geometry, phase analysis of SR-XRD data was performed by the Rietveld method using the GSASII software package [34]. Initially refinement was applied to the unit cell parameter while all other structural parameters were fixed to the original standard values of the JCPDF data files listed in the results and discussion section. The crystal strain, atomic position, atomic isotropic temperature, zero shift, background as Chebyshev polynomial of fifth degree, peak profile, sample displacement and texture were then successively refined. The fittings were performed using analytic Hessian refinement derivatives. These corrections help to obtain physically realistic intensities, displacement and peak width models when analysing diffraction patterns in non-standard geometries.

2. Results and discussions

The coating composition was analysed at room temperature by X-ray Photoelectron Spectroscopy (XPS) [1] and the results are listed in Table 1.

The phases in the coatings, from SR-XRD, are: CrN (JCPDF 011-0065), AlN (JCPDS 046-1200), Al (JCPDS 004-0787), Cr2N (JCPDS 00-035-0803), Cr (JCPDS 00-900-8467) and Al2O3 (JCPDS 00-901-1413) on a substrate of Fe (JCPDS 006-0698) dominated M2 steel. For clarity, only the Miller indices of appropriate phases are indicated in the SR-
XRD plots of Figs. 1–3. Peaks without Miller indices are due to the M2 steel substrate.

Fig. 1 (a) and (b) shows the SR-XRD patterns for CrN coating (18° – 30° 2θ range) and CrAlN coatings (18° – 27° 2θ range) respectively, at 25, 200, 500, 600 and 700 °C. The emphasis is on the CrN, AlN, Al, Cr2N and Cr phases.

For the CrN-M2ST samples, CrN is the main phase over the entire temperature range with a Cr2N phase produced above 600 °C. For the CrAIN-M2ST samples, CrN is a major phase over the entire temperature range. A cubic AlN phase is observed up to 500 °C. From 600 °C the c-AlN phase disappears. Due to the similar crystal structure of CrN and c-AlN phases, it is possible that they form a solid solution, as there is a shift of peaks in the diffraction pattern of CrN with increasing temperature. It is also possible that, the grain size of AlN has become very small and undetectable by XRD. Above 600 °C, a significant Cr phase and a very small amount of AlO2 phase appear. Lu et al. [39] have investigated aluminium peroxide (AlO2) formation in the interfacial region of Pt-Al2O3 (sapphire) couple (≈ 1 mm plates). It’s interesting that the authors state that formation of AlO2 occurs in the range of 1200 °C to 1400 °C but not below 1100 °C.

The room temperature XPS results indicate the appearance of oxygen for both samples. The Cr2p3/2 and Cr2p1/2 bonding states of CrAIN-M2ST sample indicate a combination of CrN and Cr2O3 on the surface. The Al2p peak indicated a combination of AlN and Al2O3 on the surface. The N1s spectra consisted of a CrN component (strong peak) and a Cr–O–N component (weak peak). The binding energy characteristic of Al2O3 and Cr2O3 oxides in the very top atomic layers of the surface can explain most of the detected oxygen [35]. Oxidation of CrN at high temperatures is understood to occur through outward diffusion of chromium, aluminium and nitrogen while oxygen diffuses inwardly and forms oxides inside coating layers [36,37]. The formation of Cr–O–N was discussed by Minami et al. [38] which crystallized in similar
cubic structure of CrN with strong diffraction in (111) and (200) directions. CrN coating material exhibits remarkable oxidation resistance due to its fine and dense equiaxial crystal structure which reduces the oxygen diffusion rate significantly. Formation of adhesive aluminium and chromium oxides on the surface also hinders oxygen diffusion. Combination of these effects can restrict the formation of oxides only on very top surface layers which can be detected by XPS. There were no signs of Al2O3 and Cr2O3 phases in the SR-XRD results of CrAlN-M2ST samples below 600 °C presumably due to only a very small amount of oxides presented on the surface. However, the presence of AlO2 (≈2.8%) was detected between 600 °C and 700 °C, due to the increase of temperature. CrN phase, with a rock-salt (NaCl) like unit cell, dominated the structure of the coating film. The crystallographic characteristic of coating was determined from refined synchrotron data. Results showed a significant change of the CrN lattice parameter in the CrAlN coating. The lattice parameter value of reference for the CrN phase was 4.145 Å (JCPDF 011-0065). Refinement of the lattice parameter resulted in a value of 4.209 Å at room temperature (25 °C) continuously decreasing to 4.167 Å at 600 °C and then abruptly increasing to 4.176 Å at 700 °C. The initial decrease of the lattice parameter, from room temperature value, can be attributed to the formation of a solid solution of Al/CrN from the diffusion of Al (from the cubic AlN and amorphous Al that is in the grain boundaries) into the CrN structure substituting the Cr atoms. The smaller size of Al atoms effectively reduces the lattice constant of the dominant phase in CrAlN. The TEM images of similar coating, discussed by Munroe et al. [1] and Rahman et al. [2], generated from cross section of the columnar CrN grains confirmed the presence of amorphous AlN phase between CrN grains, at room temperature. The continuous decline of unit cell value may indicate two simultaneous phenomena: (1) the higher amount of Al dissolution in the structure and (2) strain release due to temperature increment. CrN showed high solubility of Al which improves mechanical properties of coating material through the formation of a solid solution [9].

A major change in microstructure of CrAIN-M2ST samples occurred at the temperature range above 600 °C with the appearance of CrN-CrAlN-Cr multi-phase grain composition by crystallisation of Cr from the boundary into the grain due to thermal activation and Al from the amorphous boundary forming AlO2. It should be noted that, there is much less Al/AIN within the grains than in the amorphous boundaries.

Fig. 2 depicts the refined SR-XRD pattern of the CrAIN-M2ST sample at 700 °C with emphasis on the main Cr, AlO2 diffraction peaks. Main differences between experimental and fitted plots were due to the substrate peaks are identified as a combination of Fe and Fe3W3C phases. Formation of metallic Cr and AlO2 in the nanocomposites coating at 700 °C may underline the initiation of changes in mechanical properties of the film coating. Protective nanocomposite coatings can only preserve their hardness and mechanical properties provided the nanostucture remains stable and unchanged.

Careful analysis of diffraction patterns in Figs. 1 and 2 reveals changes in peak positions and widths as the temperature increased to 700 °C. Such shifts in peak positions and widths usually indicate change in lattice parameter and/or strain in the crystal structure. The high resolution refined SR-XRD data of the CrN and (Cr,Al)N phases are analysed to give some indication of the domain/crystallite sizes and strains in both the CrN-M2ST and CrAIN-M2ST samples, respectively, over the 25 °C – 700 °C temperature range. The same analysis is performed for the Cr phase at 700 °C.

The crystallite domain size and lattice strain are deduced from the Williamson–Hall equation [36]:

\[ \beta \cos \theta = 4\varepsilon \sin \theta + \frac{K\lambda}{D} \]  

(1)

Fig. 3. Williamson–Hall plots for CrN phase in (a) CrN-M2ST and (b) CrAIN-M2ST samples at different temperatures.
where $\beta$, $\varepsilon$, $D$ are the full width at half maximum, microstrain and domain/crystallite size, respectively. $K$ is a constant which equals to 0.89 and $\lambda$ is the X-ray wavelength [32]. GSAS refinement produced data of $(hkl)$, $d$, $2\theta$ and FWH values for all of the identified phases in the samples. This data is used to make plot of $\beta$–$\cos \theta$ and $\sin \theta$ (see Fig. 3).

According to Eq. 1, the strain component ($\varepsilon$) is calculated from the slope and the crystallite domain size ($D$) from the intercept ($K\lambda/D$) at each temperature. The strain and domain/crystallite size of the CrN phase in CrN-M2ST and CrAlN-M2ST samples were estimated up to 700 °C and results are shown in Table 2 and Fig. 4.

Similar estimates of the strain and crystallite size for the Cr phase at 700 °C indicate crystallite size $\approx$ 11 nm and strain $\approx$ 0.0024.

The plots of Fig. 4(b) indicate that, the crystallite sizes of the CrN phase are smaller in the CrAlN-M2ST samples than in the CrN-M2ST samples at all temperature. Furthermore, sizes increase as temperatures approach 700 °C, for both coatings. Previous room temperature GI-XRD and TEM studies of the same CrAlN-M2ST samples showed the size of crystallite domains of approximately 10 nm, in good agreement with current SR-XRD result at 25 °C [4]. Interestingly, the size of crystallites corresponds to about 11 nm at the high temperature of 700 °C, which is about the same size of the CrN crystallites in CrAIN-M2ST sample up to 200 °C.

The plots of Fig. 4(a) indicate that the strain for the CrN phase follows a similar pattern with the crystallite size variation. The strains are less in the CrAIN-M2ST samples than in the CrN-M2ST samples. Similarly, the strain decreases as the temperature increases up to 700 °C for both sample coatings. Since the Cr phase occurs above 600 °C, its strain value is unimportant.

The solid solution of AlN into CrN generally increases the strains of the lattice in bulk sized material. However thin films synthesised using plasma technology may not follow the general trend due to the complicated plasma effects. These may include very fast reaction and grain growth of the thin films at very short time periods. The direction of plasma and resulting non-equilibrium interactions add to the complication of the thin film growth mechanism. The higher strain results of CrN phase in the CrN-M2ST samples than in the CrAIN-M2ST samples are most probably due to the differing plasma interactions occurring at film synthesis. Interestingly at 600 °C and above the values for strain and crystallite size for the CrN phase in both samples are the same (within experimental errors). This could be due to the AlO$_2$ and Cr formation within that temperature range.

The calculated strain and size values imply that, the mechanical properties (such as hardness, elastic modulus) of the coatings deteriorate as the temperature increases from 25 °C – 700 °C. However measuring strains, hardness and grain sizes at very high temperatures is very challenging and in some cases probably impossible.

### 3. Conclusions

Rietveld analysis of in-situ high temperature synchrotron radiation X-ray diffraction (SR-XRD) of CrN and CrAlN coatings, deposited on M2 steel substrate by closed field unbalance magnetron sputtering, revealed CrN, Cr$_2$N, AlN, Al and Cr phases in the coatings. Analysis indicated that CrN is the major phase in both coatings at all temperatures. At the high temperature of 700 °C, formation of CrN, Cr and AlO$_2$ (~2.8%) phases in the CrAlN coatings was detected. Similarly Cr$_2$N phase was detected in the CrN coating.

Williamson–Hall plots were used to estimate the crystallite size and strains of the CrN phase for temperatures up to 700 °C. Analysis indicates a decrease in crystallite size and strains of the major phase, in both coatings, over the temperature range. The strains and crystallite size of the CrN phase in the CrAlN coating are less than those in the CrN coating for temperatures below 600 °C while they are equal above 600 °C. An estimate for the Cr phase indicated very small crystallites of ~11 nm at 700 °C. The estimate crystallite size of ~10 nm at 25 °C of CrN phase, for the CrAIN coating agrees well with previous TEM results.

### Acknowledgment

This study has been supported by School of Engineering and Information Technology at Murdoch University. The authors gratefully acknowledge support provided by the Australian Synchrotron beam time award AS141/P0/7582. E. M greatly appreciates Murdoch University for the award of a postgraduate scholarship.

---

**Table 2**

Calculated strain and crystallite size of CrN phase in the CrN-M2ST and CrAlN-M2ST samples at different temperatures ($T$).

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>Strain CrN-M2ST</th>
<th>Strain CrAlN-M2ST</th>
<th>Crystallite size (nm) CrN-M2ST</th>
<th>Crystallite size (nm) CrAlN-M2ST</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.853</td>
<td>0.779</td>
<td>40.1</td>
<td>9.8</td>
</tr>
<tr>
<td>200</td>
<td>0.807</td>
<td>0.556</td>
<td>42.0</td>
<td>10.5</td>
</tr>
<tr>
<td>500</td>
<td>0.469</td>
<td>0.423</td>
<td>54.7</td>
<td>45.1</td>
</tr>
<tr>
<td>600</td>
<td>0.263</td>
<td>0.323</td>
<td>56.5</td>
<td>55.4</td>
</tr>
<tr>
<td>700</td>
<td>0.180</td>
<td>0.180</td>
<td>61.8</td>
<td>56.8</td>
</tr>
</tbody>
</table>

---

![Fig. 4.](image-url) Calculated (a) strains vs. $T$ and (b) crystallite size vs. $T$ for CrN phase in the CrN-M2ST and CrAlN-M2ST samples.
Experimental and predicted mechanical properties of Cr$_{1-x}$Al$_x$N thin films, at high temperatures, incorporating in situ synchrotron radiation X-ray diffraction and computational modelling†

Ehsan Mohammadpour, Zhong-Tao Jiang, Mohmmednoor Altarawneh, Nicholas Mondinos, M. Mahbubur Rahman, H. N. Lim, N. M. Huang, Zonghan Xie, Zhi-feng Zhou and Bogdan Z. Dlugogorski

Cr$_{1-x}$Al$_x$N coatings, synthesised by an unbalanced magnetic sputtering system, showed improved microstructure and mechanical properties for $\sim$14–21% Al content. In situ SR-XRD analysis indicated various crystalline phases in the coatings that included: CrN, AlN, $\alpha$-Cr with small amounts of Al$_2$O$_3$ and Cr$_3$O$_4$ over the 25–700 °C range. Al doping improves resistance to crystal growth, stress release and oxidation resistance of the coatings. Al doping also enhances the coating hardness (H) from 29 to 42 GPa, elastic modulus (E) from 378 to 438 GPa and increased the resistance to deformation. First-principles and quasi-harmonic approximation (QHA) studies on bulk CrN and AlN were incorporated to predict the thermo-elastic properties of Cr$_{1-x}$Al$_x$N thin film coatings in the temperature range of 0–1500 °C. The simulated results at $T = 1500 \, ^\circ\text{C}$ give a predicted hardness of $H = \sim$41.5 GPa for a $\sim$21% Al doped Cr$_{1-x}$Al$_x$N coating.

Vacuum sputtering technique is an outstanding method for synthesising high quality CrN ceramic thin film coatings with superior structural, mechanical and tribological properties. These studies have been extended to ternary combinations of CrN with doping of other elements, e.g., Al, Si, Ti, V, Nb or Cu. The doping elements mainly distribute in the amorphous layers which surrounds the columnar structured nano-crystalline (nc-) CrN grains. These amorphous layers can effectively enhance many mechanical properties of such thin film coatings. In particular, Al has shown great potential in improving the hardness as well as corrosion and oxidation resistances. This Cr–Al–N framework is of particular interest as they can form aluminium oxides on the top surface layers which suppress the diffusion of oxygen into the coating film.

1. Introduction

3-d transition metal nitrides, such as CrN and TiN, combine attractive physico-chemical, electronic, optical, magnetic, mechanical and thermal properties. These composite materials have shown a wide range of technical applications in various key industrial areas. For example, due to their extreme hardness, high melting point and superior chemical stability, nitride-based ceramic coatings have been used for high-speed machining, cold forming, moulding dies, sliding parts and rocket nozzles. It is noted that CrN has significant superiority over TiN in wear, corrosion resistance, and anti-oxidative properties at temperatures up to 700 °C.

---

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ra00342k
producing a combination of superior hardness and excellent damage resistance in nc-CrN frameworks.\textsuperscript{18}

In the present work, \textit{in situ} synchrotron radiation powder diffraction (SR-XRD) beamline was employed to quantitatively investigate the changes in phase composition and microstructure of Cr\textsubscript{1-x}Al\textsubscript{x}N thin film coatings as a function of Al content at different measurement temperatures in an environmental atmosphere. Rietveld analysis of high resolution SR-XRD data and nanoindentation measurements will provide quantitative results, hence making a connection between microstate phases and mechanical properties of the coating. Density Functional Theory (DFT) calculations and Quasi-Harmonic Approximation (QHA) are employed to estimate the cell-volume, thermal expansion and hardness of Cr\textsubscript{1-x}Al\textsubscript{x}N system at temperatures up to 1500 °C.

2. Experimental

2.1 Thin film coatings preparation

Cr\textsubscript{1-x}Al\textsubscript{x}N coatings with a total film thickness of 2 µm were deposited on M2 high speed steel substrates at 550 °C using a closed field unbalanced magnetron sputtering system (Teer Coatings Ltd, UK) with a four-target configuration. The coating process were described in detail by Li \textit{et al.}\textsuperscript{18} and Wo \textit{et al.}\textsuperscript{19}

2.2 \textit{In situ} SR-XRD characterizations

\textit{In situ} SR-XRD experiments were performed on the Powder Diffraction beamline at the Australian Synchrotron with monochromatic X-rays, λ = 0.827 Å, verified by standard reference material (LaB6 660b) as supplied by the USA National Institute of Standards and Technology (NIST). The incidence angles of the X-ray beam (ω₀) were in range of 4.1 to 5.9°. The diffraction data were collected by a Mythen microstrip detector over the range of 10° ≤ 2θ ≤ 89° in flat-plate asymmetric reflection geometry. The coated substrates were mounted on a Pt heating stage in an Anton Paar HTK-2000 high temperature furnace and aligned to the centre of rotation of the diffractometer. The heating rate was 10 °C min\textsuperscript{-1} from ambient temperature up to 700 °C in air atmosphere.\textsuperscript{20} The temperature difference between the sample surface and Anton Parr furnace was calibrated manually before the \textit{in situ} experiments carried out. Diffraction patterns were obtained at three temperatures (25, 200 and 500 °C) below and two temperatures (600 and 700 °C) above the deposition temperature of 550 °C due to time constraints at the synchrotron facilities. Each data acquisition at designated temperature was 120 s.

The diffraction patterns were analysed with the TOPAS v5 academic software\textsuperscript{21} using the Rietveld method.\textsuperscript{22} The atomic positions for the structural models, based on the main identified phases of the coating, were extracted from Crystallography Open Database.\textsuperscript{23} Modelled peak shapes were used to determine the volume-weighted mean crystallite sizes (L\textsubscript{cocr}) and microstrain (ε\textsubscript{m}). An accurate description of the peak shapes, in all of the diffraction patterns, was obtained by applying correctional functions for a flat plate in fixed incident beam geometry.\textsuperscript{24–26} The initial parameters for the refinement, as well as phase determination, were obtained from the JCPDS cards.

2.3 Nanoindentation measurements

Young’s modulus and hardness of the coatings were measured, at room temperature (≈25 °C), by a calibrated Ultra-Micro Indentation System, UMIS-2000 equipped with a Berkovich indenter. A maximum load of 20 mN was applied in 10 increments. The loading rate used was 2.5 mN s\textsuperscript{-1} and represented the static response of the materials. The area function of the indenter tip was calibrated using a standard fused silica specimen. Load control method with a maximum loading of 5 mN was employed for calibration. The peak loading is based on the considerations that the maximum displacement during indentation should be no more than 10% of the coating thickness. For better resolutions, the number of test points were 20 for loading and 20 for unloading.

2.4 DFT computational simulations

All structural optimizations and calculations were performed with the generalized gradient approximations (GGA) using the PW91 functional\textsuperscript{27} as implemented in the VASP package.\textsuperscript{28} Energy cut-off for plane waves included in the expansion of wave functions was 500 eV. Pseudo-atomic calculations were performed for Cr: 3d\textsuperscript{5}4s\textsuperscript{1}, Al 3s\textsuperscript{2}3p\textsuperscript{1} and N 2s\textsuperscript{2}2p\textsuperscript{3}. k-Point sampling for reciprocal space integration was optimised and adopted a 21 × 21 × 21 Gamma scheme for cubic structures. CrN in contrast to other early transition metal (Ti, Sc, V, ...) nitrides, needed additional effort due to the local magnetic moments of the Cr atoms in CrN structure. The calculations for bulk CrN was carried out for both paramagnetic (CrN-m) and non-magnetic (CrN-nm) structures.

The thermodynamic properties of cubic phases were explored using the quasi-harmonic Debye–Slater model as implemented in Gibbs2 code.\textsuperscript{29} In all temperature dependent property calculations, the Vinet’s equation of state was adopted to fit the energy–volume curves.\textsuperscript{30} To calculate the elastic constants and determine the second derivatives, we used a finite differences method as implemented in VASP package (IBRION = 6).

3. Results and discussion

3.1 Structural analysis \textit{via in situ} synchrotron radiation XRD technique

The surface elemental composition and chemical bonding state, obtained from previous XPS analysis and full discussion of the coatings by Li \textit{et al.}\textsuperscript{18} indicated the existence of CrN, Cr\textsubscript{2}O\textsubscript{3}, AlN and Al\textsubscript{2}O\textsubscript{3} phases in the coating surface region, are summarised in Table 1.

The JCPDS cards used for phase identification in the SR-XRD spectra: 00-076-2494 (CrN), 00-025-1495 (AlN), 00-901-4565 (Al\textsubscript{2}O\textsubscript{3}), 00-900-9676 (Al\textsubscript{2}O\textsubscript{3}), 00-035-0803 (Cr\textsubscript{2}N), 00-901-3484 (α-Fe) and 00-041-1351 (Fe\textsubscript{3}W\textsubscript{3}C). The atomic positions for Fe\textsubscript{3}W\textsubscript{3}C were taken from.\textsuperscript{31} The \textit{in situ} full patterns of all samples, for all temperatures, are included in the ESI section (Fig. S1–S4). For clarity the spectra for each temperature are combined in one plot for each sample.
Table 1  Elemental composition of the Cr$_{1-x}$Al$_x$N coatings determined by XPS

<table>
<thead>
<tr>
<th>Coating notation</th>
<th>Element (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>C1</td>
<td>33.4</td>
</tr>
<tr>
<td>C2-14% Al</td>
<td>27.5</td>
</tr>
<tr>
<td>C3-17% Al</td>
<td>16.6</td>
</tr>
<tr>
<td>C4-21% Al</td>
<td>19.1</td>
</tr>
</tbody>
</table>

The Rietveld refinement of the diffraction spectra resulted in $R$-weighted pattern ($R_{wp}$) values in the range of 15–20. The largest errors in the refinement models are mainly due to the incomplete crystallographic data for the substrate. An example of a typical fitted spectrum is indicated by Fig. 1, which shows the Rietveld refinement for the C1 sample at 700 °C with $R_{wp} = 15$. The allowed $hkl$ values for each phase are indicated by the small vertical bars. The difference between experimental and modelled results is indicated by the difference plot above the $hkl$ bars.

Basically all 20 spectra shown in Fig. S1–S4 of the ESI† section were analysed by Rietveld analysis with similar plots as Fig. 1 producing data used for further analysis as indicated in Fig. 2–6. The phases of the C1 sample at different temperatures was similar to the sample (denoted as CrN-M2ST) recorded in Mohammadpour et al. 20

SR-XRD diffraction patterns at ~25 °C of as-deposited Cr$_{1-x}$Al$_x$N coatings are depicted in Fig. 2. For clarity the 2θ range in Fig. 2 is from 18° to 35° 2θ consisting of the main peaks for each individual phase.

The compositions of the main phase in as-deposited CrAlN thin film coatings were determined to be CrN and AlN phases. Thin film coating C1 showed strong intensity in (200), (220) directions at ~22.8° and ~32.4° 2θ, respectively for the CrN phase. In the Al doped samples the dominant orientations of the CrN phase are in the (200) and (111) planes. These diffraction peaks became broader and of lower intensity as the Al content increased (C3-17% Al and C4-21% Al) indicating a combination of small grain size and high concentration of possible amorphous nature. The peaks at 20.2°, 23.4° and 33.3° 2θ in the C4-21% Al sample are identified as diffractions from c-AlN (111), (200) and (220) planes, with some overlap with substrate (α-Fe) diffraction peaks. The confirmation of the AlN phase in SR-XRD pattern agrees with the NEXAFS results by Mahbubur et al. 32 and XPS analysis by Li et al. 33 from similar coatings. All samples in as-deposited condition (~25°) had Al$_2$O$_3$ and Cr$_2$O$_3$ phases detected by XPS but SR-XRD did not show any noticeable peaks related to those oxides. This could be due to (i) most of oxygen accumulate in the top surface layers of thin films, and (ii) possible amorphous state of the oxide phases. However, at temperatures >500 °C minor amounts of Al$_2$O$_3$ and metastable AlO$_2$ were observed from the diffraction patterns (Fig. 3).

Fig. 3 indicates the main phases of these coatings at 700 °C. Diffraction spectra of CrAlN coatings at 700 °C show α-Cr, Al$_2$O$_3$ and Al$_2$O$_5$ phases. Peaks at 22.6°, 26.16° and 37.33° 2θ can be determined as α-Cr (111), (200) and (220), respectively. Agouram et al. 34 concluded that the phase content of CrN$_2$-based coatings is strongly influenced by deposition processes. The presence of α-Cr in CrN coatings can reduce the hardness; however, it may improve the coating toughness or as a metallic source which diffuse outward and contribute in the formation of surface oxidation layers. Although hexagonal-structured Cr$_2$N (h-Cr$_2$N) exhibits higher hardness than cubic CrN, it is more susceptible to oxidation which can deteriorate the thermal stability of the...
C1 thin film with considerable h-Cr$_2$N content especially at high temperatures.$^{20}$ It seems Al doping successfully prevents the formation of h-Cr$_2$N in the CrAlN coatings even at lowest Al percentage (C2-14% Al) in the temperature range of study. Our observations did not confirm any possible existence of Cr$_2$O$_3$ crystalline phases in the column structure of coatings; that may indicate (i) small amorphous structures distributing in grain boundary regions, and (ii) either amorphous or crystalline phase structure in the very top surface layers of thin films where normal XRD cannot fully determine the phases (Grazing incidence SR-XRD would be able to provide more precise surface crystalline information). The shifts of diffraction peaks from substrate, especially for Fe (111) at 23.8° is probably due to the thermal expansion of the unit cells at elevated temperatures. Peaks related to CrN and AlN phases exhibited some sharpening with increasing temperature.

Fig. 2  SR-XRD diffraction patterns at ~25 °C of as-deposited Cr$_{1-x}$Al$_x$N coatings with various Al contents. The dashed vertical lines indicate substrate peaks.

Fig. 3  SR-XRD diffraction patterns at 700 °C of Cr$_{1-x}$Al$_x$N coatings with various Al contents. The dashed vertical lines indicate substrate peaks.
From the Rietveld refined SR-XRD data, the lattice constants of the CrN and c-AlN phases in the Cr$_{1-x}$Al$_x$N coatings were calculated and plotted as a function of temperature in Fig. 4. The lattice constant of CrN decreases continuously from 4.21 Å to 4.17 Å for C1 and to 4.19 Å for the Al doped samples. The overall changes of the lattice constant for the CrN phase are slightly smaller in the samples with Al doping than without doping. Overall, the lattice parameter values agree with the experimental values from other sources, such as Barshilia et al. 4 (4.09 to 4.16 Å) and Elangovan et al. 44 (4.15 to 4.17 Å). Lattice constants of c-AlN (in sample C4-21% Al) increased steadily from approximately 4.09 Å at room temperature to 4.1 Å at 700 °C indicating unit cell expansion by 0.5%. The lattice constant of α-Cr phase, in all samples at 700 °C, were 3.65 Å ± 10%.

The crystallite size and microstrain as a function of temperature, from Rietveld analysis, for the CrN phase are shown in Fig. 5. The effect of adding Al onto the microstructure of the as-deposited coatings is more pronounced in C3-17% Al and C4-21% Al coatings exhibiting about 30% smaller crystallite sizes compared to Al free and C2-14% Al samples. The crystallite sizes in all samples gradually increased in the temperature range 25 to 600 °C and then abruptly increased from 600 to 700 °C. C1 and C2-14% Al show the highest crystallite size growth by ~100% and ~67%, respectively. The higher Al content in C3-17% Al and C4-21% Al effectively prevented the crystallite growth of CrN during heating below 700 °C. Above, 600 °C the CrN crystallite size in C4-21% Al increases by ~34%. The most stable crystallite size for CrN is exhibited by C3-17% Al with an 8% crystallite growth. The crystallite sizes of the α-Cr phase are 1832 (C2-14% Al), 1780 (C3-17% Al) and 828 (C4-21% Al) nm in the 700 °C Cr$_{1-x}$Al$_x$N samples.

Our observations showed that microstrain in C1 sample decreased by ~67% during heating which is almost ~1.7× of the microstrain release in samples with Al contents. The residual stress in these types of coatings could be due to two mechanisms (1) thermal stress and/or (2) accumulation of defects (dislocations, vacancies, etc.) in the coating layer. Thermal stress is a resultant of the difference in the coefficient of thermal expansion (CTE) value for coating and substrate. The decline of internal stress in the coatings could be a result of absorption and annihilation of defects during annealing. It allows the defects to diffuse through the lattice and to be absorbed at grain boundaries and dislocation cores. This seems to be more pronounced in the binary CrN coating case. The presence of amorphous content in Cr$_{1-x}$Al$_x$N coatings at grain boundaries hinders stress release in the coatings which resist against coating softening.

The stress in the coating structure, from the changes in $d$ space for CrN (220), is shown in Fig. 6. Similar plots for the (111), (200) and (311) planes of CrN phase are included in Fig. S5–S7 of the ESI section.† The stress ($\sigma$) in the coating were calculated based on eqn (1) using the elastic properties of CrN (elastic modulus, $E = 300$ GPa and Poisson ratio, $\nu = 0.28$).46

$$\sigma = \frac{E}{(1 - \nu)} \times \frac{d - d_0}{d_0}$$  

(1)

where $d$ and $d_0$ are from the experimental diffraction patterns and JCPDS card of CrN, respectively. Refinement data show that there is considerable amount of residual stress in the as-deposited coating structure. Stress values in Al free coating decreases progressively as temperature increases from 25 to
resistance to deformation is indicated by errors, between the as-deposited and heated sample. The coatings are set out in Table 2 and Fig. S8 and S9 of the ESI.

3.2 Experimental mechanical properties of CrAlN coatings

Nanoindentation tests, for Cr$_{1-x}$Al$_x$N coatings at as-deposited conditions and after the completion of the in situ SR-XRD experiment (heated samples), were undertaken at room temperature. The hardness ($H$) and elastic modulus ($E$) for these coatings are set out in Table 2 and Fig. S8 and S9 of the ESI section. Analysis of Table 2 and the plots clearly indicate that there is no difference in $H$ and $E$, within the experimental errors, between the as-deposited and heated sample. The resistance to deformation is indicated by $H^3/E^2$ and plotted in Fig. S10 of the ESI section. The coatings with smaller crystallite size/higher microstrain present greater hardness (C3-17% Al and C4-21% Al samples) in as deposited condition. Improvement in coating hardness confirms the microstructure refining effect of Al dopants.

These findings are consistent with the quantitative SR-XRD measurements of crystallite size and micro strains in the Al doped coatings that exhibited very little hardness drop after heating. The calculated ratio of $H^3/E^2$ improved significantly in samples containing Al compared to the reference sample (C1).

However, there is no change in resistance to deformation between as deposited and heated conditions of the samples. The combination of microstructure and nanoindentation studies indicate that the hardness of the as-deposited nano-crystalline coatings can be controlled by several parameters such as phase composition, crystallographic directions, crystallite size and residual stress/microstrain.

3.3 Density functional theory modelling

3.3.1 Structural optimization. The energy and lattice constant of bulk CrN-nm, CrN-m and c-AlN were optimized to find the most stable ground state. Fig. 7 shows changes in energy of the unit cell ($\Delta E = E - E_0$) versus primitive unit cell volumes for each structure used for predictions of thermodynamic properties.

Table 3 lists experimental lattice parameter values from SR-XRD data and DFT calculations from present work and available literature. The calculated lattice parameter for CrN-m (spin-polarised) is closer to SR-XRD results. The magnetic moment for each Cr atoms in CrN-m structure converged to 2.044 $\mu_B$ which is within range of 1.9 to 2.28 $\mu_B$ from calculations of Filippetti et al. The QHA method (Debye model) was used to predict the thermal expansion of the studied bulk structures as a function of temperatures. Fig. 8(a) and (b) are plots of the experimental and theoretical lattice parameters, with respect to temperature, for bulk CrN and c-AlN phases in the temperature range 0–1500 °C, respectively. Fig. 8(a) also includes lattice constant calculated from the experimental thermal expansion coefficient, $\alpha(T)$, of Zhou et al. with $a_0 = 4.14$ Å (standard CrN phase) at room temperature. Fig. 8(a) clearly shows the CrN-m model is highly compatible to the experimentally obtained data. The CrN lattice constant at room temperature for all samples differ from the simulation values within ~1.6%. Interestingly these converge to the simulated results with increasing temperature resulting in a ~0.4% difference at 700 °C. The most significant drop in lattice constant values of CrN occurs to C1 sample which is very close to QHA model at 700 °C.
CrN structure which can expand the lattice constant as observed for CrSiN coating.\cite{39,41}

The c-AlN lattice parameter in C4-21% Al are in good agreement with experimental data from Tkadletz et al.\cite{55} as indicated in Fig. 8(b). The experimental results are within $\sim \pm 0.3\%$ of the simulated QHA results up to 700 °C.

Overall the differences between the simulated and experimental results is due to the use of pure homogeneous bulk material in the Debye (QHA) model calculations, and the solid solution of different nitride phases of the thin film coatings.

3.3.2 Prediction of elastic constants. Three independent elastic constants are needed to describe the behaviour of cubic-structured materials to stress and can be used to describe the nature of the bonds between atoms in the crystals. These constants ($C_{11}$, $C_{12}$ and $C_{44}$) were calculated for CrN-nm, CrN-m, and c-AlN at zero K and zero pressure and listed in Table 4. The mechanical stability of these phases can be ascertained by using the following criterion for cubic systems: \cite{57}

$$C_{11} + 2C_{12} > 0, \quad C_{11} - C_{12} > 0, \quad C_{44} > 0, \quad C_{11} > 0, \quad C_{11} > B > C_{12}$$

(2)

All of these conditions were satisfied by the CrN and c-AlN phases indicating the mechanical stability of these structures. The overview of available literature as shown in Table 4 indicates that the reported calculated values for elastic constants and modulus are widely scattered and depend on the choice of $k$-points, cut-off energies, functional ($\omega$) and simulation packages. As an example, Yan et al.\cite{52} and Brik et al.\cite{53} used the CASTEP module of Materials Studio package with different settings of $k$ points grids and cut off energies for CrN-nm analysis. With $8 \times 8 \times 8$ (400 eV) and $10 \times 10 \times 10$ (320 eV) $k$ points grids the authors calculated $C_{11}$ values of 526 and 346 GPa, respectively.

ESI section Tables S2 and S3\cite{57} show the influence of $k$-points grids selection on the elastic constants of CrN-nm and CrN-nm for the present project. To calculate the elastic constants for CrN-m and CrN-nm, $k$-point grids of $21 \times 21 \times 21$ and $31 \times 31 \times 31$ were chosen for the simulations. The results of these analyses are tabulated in Table 4. The calculated elastic constants for CrN-nm in present study are comparable ($\sim 2\%$) with calculations of Zhou\cite{54} who used similar approach via VASP package and projector-augmented wave (PAW) method. The values of $C_{11}$ and $C_{12}$ for c-AlN underestimate by $\sim 9\%$ the calculations of Wang et al.\cite{55} carried out by VASP package and PAW method.

The positive difference between $C_{11}$ and $C_{44}$ ($C_{11} - C_{44} = 582$ for CrN-nm), known as Cauchy pressure, indicates the metallic bonding nature of Cr-N structure\cite{55} which is comparable to much smaller difference for AlN ($C_{11} - C_{44} = 83$). Cauchy pressure is also a sign of the ductility of materials, since it indicates the angular character of atomic bonding in metals. A positive Cauchy pressure reveals ductility of crystal, while a brittle material exhibits a negative value.\cite{56} Bulk modulus (B), shear modulus (G) and Young’s modulus (E) for each phase were estimated by applying Voigt–Reuss equations\cite{57} and compared with available literature.
The calculated results, at 0 K, from Table 4 are spread out but have similar magnitudes including the 2 experimental values at \(-25^\circ\mathrm{C}\). The \(k\)-point grids that optimised the calculation of the elastic constants and unit cell volumes will be used in the DFT and QHA simulations.

QHA method for CrN and c-AlN are used to predict the hardness of two binary compounds (CrN and c-AlN) in a wide temperature range (25–1500 \(^\circ\mathrm{C}\)). The method for calculating the hardness of materials is based on atomic potentials and bond strength developed by Šimůnek and Vackář for single crystals and then extended to binary compounds. The hardness of a crystal can be calculated by introducing its bond strength \(S_{ij}\):

\[
S_{ij} = \frac{\sqrt{\epsilon_i \epsilon_j}}{d_{ij} n_{ij}}
\]

where \(\epsilon_i\) and \(\epsilon_j\) are atomic potentials of \(i\) and \(j\) atoms, respectively, and are defined as the valence electron number divided by the radius of the atom; \(d_{ij}\) is the distance of the nearest atom \(j\) to atom \(i\) and \(n_{ij}\) is the number of bonds between atom \(i\) and its neighbouring atoms \(j\).

For binary compounds, the difference between atomic potentials is:

\[
f_r = \left[ \frac{\epsilon_i - \epsilon_j}{\epsilon_i + \epsilon_j} \right]^2
\]

The hardness of such a system with volume \(V\) is defined as:

\[
H = \frac{C}{V} \frac{\sqrt{\epsilon_i \epsilon_j}}{d_{ij} n_{ij}} e^{-\sigma f_r}
\]

where \(C\) and \(\sigma\) are constants \((C = 1450\) and \(\sigma = 2.8)\). The DFT results (at \(T = 25^\circ\mathrm{C}\)) for c-CrN and c-AlN are listed in Table 5. The difference between the calculated value and the experimental value for the CrN phase in C1 sample is \(-15\%\). This difference can be explained by considering the columnar orientation of the coating which is completely different from an ideal single crystal.

Temperature dependent variations in unit cell volume for each structure were obtained from QHA modelling up to 1500 \(^\circ\mathrm{C}\) (Fig. 8). Subsequently the bond length, \(d_{ij}\), as a function of temperature was deduced from the cell volumes and by use of eqn (5) the hardness values for CrN (CrN-nm and CrN-m) and c-AlN phases. The results of hardness over a wide range of temperatures are shown in Fig. 9. Also plotted in Fig. 9 are the high temperature (25–500 \(^\circ\mathrm{C}\)) in situ nanoindentation data for commercially available Al\(_{0.7}\)Cr\(_{0.3}\)N coatings studied by Fox-Rabinovich et al. and Beake et al. Room temperature nanoindentation results for the current projects’ Cr\(_1\)\_Al\(_x\)N coatings are also incorporated in Fig. 9.

Based on predicted material behaviours, hardness values for both phases reduced constantly at elevated temperatures. However, there are considerable differences in the reduction slopes depending on the phase type. Hardness values for CrN-nm structure showed the highest resistance to temperature while AlN was more susceptible to temperature. Experimental hardness in Table 2 of Cr\(_1\)\_Al\(_x\)N samples showed that nano-composites of CrN in amorphous AlN matrix can effectively improve the resistance to grain boundary sliding which makes these samples harder than C1 sample. In addition, the deposition process and doping significantly distorts the lattice of CrN/AlN mixture, as is evident in microstrain and residual stress plots, which can also contribute to improve the deformation resistance of doped samples. According to Šimůnek and Vackář the hardness of multicomponent compound systems is expected to be a geometrical sum of the values of hardness of all binary systems in the solid (given by their eqn (6)). Interestingly for the current multicomponent system (at 25 \(^\circ\mathrm{C}\)), consisting of CrN and AlN phases, \(H = H_1 + H_2 = 22.5 + 21 = 43.5\) GPa \((H_1\) for

### Table 4

Calculated elastic constants \(C_{ij}\), bulk modulus \(B\), Young’s modulus \(E\), Poisson ratio \(\nu\) of CrN (non-magnetic and spin-polarized) and c-AlN phases. Calculated and experimental data from literature are denoted by c and e, respectively.

<table>
<thead>
<tr>
<th>Phase</th>
<th>(C_{11})</th>
<th>(C_{12})</th>
<th>(C_{44})</th>
<th>(B) (GPa)</th>
<th>(G) (GPa)</th>
<th>(E) (GPa)</th>
<th>(\nu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrN-nm</td>
<td>588.0</td>
<td>215.1</td>
<td>5.9</td>
<td>340</td>
<td>44</td>
<td>126</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>526(^e)</td>
<td>226(^e)</td>
<td>5(^e)</td>
<td>326(^e)</td>
<td>35(^e)</td>
<td>101(^e)</td>
<td>0.43(^e)</td>
</tr>
<tr>
<td></td>
<td>502(^e)</td>
<td>214(^e)</td>
<td>4.1(^e)</td>
<td>310(^e)</td>
<td>58(^e)</td>
<td>163(^e)</td>
<td>0.41(^e)</td>
</tr>
<tr>
<td></td>
<td>580(^e)</td>
<td>210(^e)</td>
<td>5(^e)</td>
<td>327(^e)</td>
<td>100–250(^e)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>546(^e)</td>
<td>184(^e)</td>
<td>20(^e)</td>
<td>340(^e)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrN-m</td>
<td>352</td>
<td>88.7</td>
<td>61.0</td>
<td>176.4</td>
<td>93.9</td>
<td>239.0</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>369(^e)</td>
<td>125(^e)</td>
<td>114(^e)</td>
<td>192(^e)</td>
<td>111(^e)_25</td>
<td>279(^e)</td>
<td>0.25(^e)</td>
</tr>
<tr>
<td>c-AlN</td>
<td>387</td>
<td>149</td>
<td>305</td>
<td>254.3</td>
<td>209</td>
<td>303</td>
<td>0.2788</td>
</tr>
<tr>
<td></td>
<td>423(^e)</td>
<td>167(^e)</td>
<td>306(^e)</td>
<td>251(^e)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>221(^e)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## Table 5

DFT calculated hardness, at \(T = 25^\circ\mathrm{C}\), of bulk CrN, AlN based on \(d_{ij}\). Current project and literature experimental data included for comparison.

<table>
<thead>
<tr>
<th>Phase</th>
<th>(d_{ij})</th>
<th>(\epsilon_i)</th>
<th>(\epsilon_j)</th>
<th>(f_r)</th>
<th>(H_{DFT})</th>
<th>(H_{EXPT})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrN-nm</td>
<td>2.028</td>
<td>3.125</td>
<td>4.904</td>
<td>0.0490</td>
<td>24.1</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>19–28.6</td>
<td>(ref. 36)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>24–25</td>
<td>(ref. 62)</td>
</tr>
<tr>
<td>CrN-m</td>
<td>2.071</td>
<td></td>
<td></td>
<td>22.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c-AlN</td>
<td>2.034</td>
<td>2.793</td>
<td>4.545</td>
<td>0.056</td>
<td>21.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(ref. 62)</td>
</tr>
</tbody>
</table>
CrN-m and $H_2$ for AlN) compares remarkably well with the experimental value of 42 GPa for the C4 sample. Here the values correspond to a numerical sum of eqn (5) as opposed to a geometric sum. To show this point more clearly, the simulated data for CrN-m and AlN are added and the plot included in Fig. 9.

The experimental results of Fox-Rabinovich et al., are in some agreement with the simulated CrN-m, CrN-nm and AlN results for temperatures up to ~150 °C while they deviate significantly for higher temperatures up to ~500 °C, whilst Beake et al.** results are in agreement over the same temperature range. It should be noted that the materials in Beake’s investigation has a high percentage Al content (~70%) whilst our materials have a maximum of ~21% Al content (C4). The hardness of experimental result from C4 and computational modelling from the summation of the CrN-m and AlN components are very similar at room temperature, see Fig. 9. If this is a real relationship, then the magnetic properties of the Cr are important for the formation of stable and hard Cr$_{1-x}$Al$_x$N coatings.

Based on the results from both experiments and computational calculation, the temperature dependent hardness of the synthesized CrN/AlN thin film nanocomposites can be predicted in the temperature range from 25 °C to 1500 °C, refer to Fig. 9. Furthermore a numeric sum for the hardness of the 2 components, at $T = 1500$ °C give a predicted hardness $H \sim 41.5$ GPa. Only real experimental measurements at the 200–1500 °C range show if the hardness of the CrN/AlN multicomponent thin film has the predicted direct sum values.

4. Conclusions

Synthesised Cr$_{1-x}$Al$_x$N coatings, with a maximum Al content of ~21%, by unbalanced magnetic sputtering system showed improved microstructure and mechanical properties compared to undoped CrN coating. Analysis of in situ synchrotron X-ray diffraction at temperatures range of 200–700 °C established: (i) remarkable resistance to crystal growth and stress release up to 700 °C for coatings with Al doping greater than ~14%. (ii) Al-dopants improve oxidation resistance of the coatings by preventing the formation of Cr$_2$N at high temperatures.

Nano indentation results at ~25 °C show: (i) Al doping improved the coating hardness ($H$) and elastic modulus ($E$) from 29 to 42 GPa and 378 to 438 GPa respectively, and (ii) resistance to deformation increased as the Al content increased.

First-principles and quasi-harmonic approximations (QHA) studies for bulk magnetic and non-magnetic CrN (CrN-m and CrN-nm) and AlN over the temperature range of 0–1500 °C were undertaken to calculate elastic constants ($C_{ij}$) and hardness ($H$). Comparison of DFT-QHA models and the nanoindentation results indicate that hardness of Cr$_{1-x}$Al$_x$N coating with ~21% Al content may be the sum of values from CrN-m and AlN phase. Our computational modelling predicts that the hardness ($H$) of Cr$_{1-x}$Al$_x$N coating with the Al content of ~21% can reach to about 41.5 GPa at $T = 1500$ °C.

Acknowledgements

Ehsan Mohammadpour is highly grateful to the Murdoch University for the awarded scholarship (MIPS). The authors wish to acknowledge the support provided by the Australian Synchrotron with the beamline proposal AS141/PD/7582. The study has also been supported by grants of computing time from the National Computational Infrastructure (NCI), Canberra, Australia and the Pawsey Supercomputing Centre, Perth, Australia. We acknowledge the support from Dr M. Rowles (Curtin University) for invaluable discussions.

References

Paper

31 Pierre Villars, PAULING FILE, in Inorganic Solid Phases, SpringerMaterials [online database], Springer, Heidelberg
