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Near-edge X-ray absorption fine structure studies of Cr$_{1-x}$M$_x$N coatings

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Abstract

Cr$_{1-x}$M$_x$N coatings, with doping concentrations (Si or Al) varying from 14.3 to 28.5 at.%, were prepared on AISI M2 tool steel substrates using a TEER UDP 650/4 closed field unbalanced magnetron sputtering system. Near-edge X-ray absorption fine structure (NEXAFS) characterization was carried out to measure the aluminum and silicon K-edges, as well as chromium L-edge, in the coatings. Two soft X-ray techniques, Auger electron yield (AEY) and total fluorescence yield (TFY), were employed to investigate the surface and inner structural properties of the materials in order to understand the structural evolution of CrN matrix with addition of Al (or Si) elements. Investigations on the local bonding states and grain boundaries of the coatings, using NEXAFS technique, provide significant information which facilitates understanding of the local electronic
structure of the atoms and shed light on the origins of the high mechanical strength and oxidation resistance of these technologically important coatings.

Keywords: Coating materials; oxidation; grain boundaries; NEXAFS; synchrotron radiation.

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1. Introduction

Over the past decade, scientists and engineers around the world have shown significant interest in the investigations of metallic nitrides (e.g., GaN, AlN, InN, CrN, TiN [1-7]) with dopants such as Si [1], Al [8], Mn, C [8] and Cr [4-7] owing to their unique properties, e.g. large band-gap [2-3, 9-11], high surface acoustic velocity [2], corrosion resistance [2], oxidation resistance [12], excellent chemical and thermal stability as well as mechanical robustness [13]. Recently, superhardness (hardness, or $H >$ 40 GPa) has been obtained in TiN, and CrN by Si doping [14-16]. It is believed that the addition of Si changes the microstructures of the binary compounds from closely-packed columnar grains into nanocrystalline structures integrated in a $\text{Si}_3\text{N}_4$ amorphous matrix [14-15]. Superhardness [17] has also been reported in CrN with a suitable amount of Al-doping. Al atoms are found to be segregated around the grain boundaries to form an amorphous AlN structure. The measured superhardness of CrSiN and CrAlN is due to the combination of the fine grain size together with a strong interfacial bonding between the nanocrystalline and amorphous structures. It is well-established that the hardness of CrN coatings is mainly governed by grain size and boundary structure [18]. Generally, the hardness of a material increases with a decrease in its grain size [19]. With infusion of Si, Al or Ti into CrN, the grain size within the material has been found to reduce to a nanoscale that results in an increase in hardness of the coating [20]. At nanoscale grains, the formation of dislocations becomes tough and the hardness of the coatings can be controlled by changing the grains size [21]. Recently, a high resolution transmission electron microscopy (HRTEM) study showed that $\text{Cr}_{1-x}\text{M}_x\text{N}$ coatings consist of nanocrystalline grains surrounded by amorphous boundaries [22]. The impact of these
amorphous boundaries on the material hardness has yet to be studied. Thus, it is important to tailor the structure of the amorphous boundary for enhancement of coating properties.

Introduction of a suitable amount of dopant has been found to enhance the physical properties by inducing various defects such as vacancy, atom substitution, cluster formation and deformation [8]. X-ray absorption near-edge structure (XANES) has been previously used to study the structural properties of Al-incorporated titanium nitride [23]. In this study, the bonding structural evolution of the TiN thin films with an increase in Al-addition was discussed and the spectral changes were correlated and ultimately afforded a complete understanding about the local atomic structure. Meanwhile, attempts at producing new doping materials and research on improving their novel properties are still ongoing [24]. Lately, carbon doping on CrAlN has been performed by Zeng et al. [8] to study the effect of the dopant on a material’s electromagnetic properties. At the end of their investigations, authors concluded that carbon-doped dispersed clusters enhanced resistivity at the low frequency while high rate of carbon doping induced disorder, thereby resulting in weakened magnetic coupling [8]. Nirai et al. [25-28] reported that, above 75 at.% of Cr-doping, AlN thin films demonstrate a structural phase transition from rock salt crystalline phase to a wurtzite structure.

During the period of volcanic eruption in Chile in 2011, planes were grounded all over Australia, which prompted scientists and technologists to design and test novel coatings that can prevent mechanical damage to jet engines due to intrusion of volcanic ash [29]. Chromium nitride (CrN) is a prominent material which can be engineered onto the surface of metals as a protective layer to enhance mechanical performances and
durability of coated metals [30]. CrN has been found to show good wear and corrosion resistance, nonetheless the extension of such coatings is hindered by its relatively low hardness and poor oxidation resistance nature [31]. Moreover, the oxidation resistance of materials at high temperatures is typically controlled by surface chemistry and the construction of grain boundaries [32]. In Cr\textsubscript{1-x}M\textsubscript{x}N coatings, native oxide layers are generally formed on the surface of the coatings [33], leading to a substantial increase in their heat-resistance. Addition of Si, Al or Ti generally hinders the penetration of oxygen along the grain boundaries which may diminish the hardness of the coatings. Thus, a detailed study of the structural and compositional characteristics of the oxide layer will provide us with more information pertaining to the impact on Cr\textsubscript{1-x}M\textsubscript{x}N coatings.

Over the past decades, scientists have used the synchrotron radiation facilities to characterize the electronic structure of homogeneous alloys in virgin and doped states. Owing to the unique advantages of synchrotron radiation facilities such as polarization control, coherence, high brightness and photon-energy tenability [34], they are widely used in the identification of the atoms, molecules and compounds. Up to the 1990s, the extended X-ray absorption fine structure (EXAFS) spectroscopy has received more attention than NEXAFS [35] due to the correlation between EXAFS oscillations and the local crystallographic structure about the central excited atom. It has been well-established that in the range of 30-50 eV above the absorption edge of NEXAFS and EXAFS, regions match nicely [36]. Since then, the development and utilization of EXAFS have made great strides in the understanding of near-edge structure of molecules, ordered and disordered solids, inorganic complexes and biological systems [36]. Generally, XANES technique is used for the structural investigations of solids and
inorganic complexes while NEXAFS is employed more for surface studies. NEXAFS technology is widely used in understanding complex systems and identifying the coexistence of various phases either in ordered (crystalline) or in disordered (amorphous) form. In previous investigations [12], it was observed that the addition of silicon could remarkably improve physical hardness of the material such as toughness, as well as oxidation resistance. As the silicon content increased, the sample was found to ‘lose’ its crystallinity by exhibiting peak broadening. Furthermore, it was noticed that silicon appeared in the form of silicon nitride with the addition of 9 to 14 at.% of silicon, (Ni$_2$N$_4$) [1]. Nirai et al. [25-28] reported that above 75 at.% of Cr-doping on the AlN thin films resulted in a structural phase transition from rock salt crystalline phase to a wurtzite structure.

Electronic structures of nitride based materials can be successfully studied through various techniques e.g., X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES). XAS and XES techniques probe the unoccupied and occupied densities of states of a material on an element and orbital angular momentum based dipole selection rules [37]. NEXAFS spectroscopy essentially provides a unique opportunity to probe differences in the electronic structure as the composition of transition metal nitride (CrN) changes as seen in shifts in the Al K-, Cr L-, and Si K-edge absorption energies. Here, we will focus on establishing the bonding structural evolution in Cr$_{1-x}$Mn$_x$N upon progressive incorporation of Al and Si. The effects of aluminum and silicon doping to CrN from 14.3 to 28.5 at.% have been investigated by measuring the Al K-, Cr L-, and Si K-edge NEXAFS spectra using the Synchrotron radiation. This study aims to gain novel insights into the roles of dopants (Si, Al) in tailoring the structure of
the grain boundary within Cr$_{1-x}$M$_x$N coatings through NEXAFS experiments, as well as the surface chemistry of the oxide layer. The results will lead to the development of extremely hard, oxidation-resistant coatings by means of surface and grain boundary engineering.

2. Experimental Details

2.1. Specimen Preparation Technology

Aluminum and silicon-doped chromium nitrides with the composition Cr$_{1-x}$M$_x$N, where M is Al and Si, and x was varied from 10 to 50 at.% had been coated on AISI M2 tool steel substrates at the City University of Hong Kong using a TEER UDP 650/4 closed field unbalanced magnetron sputtering system. A four-target configuration manufactured by Teer Coatings Ltd., Droitwich, Worcestershire, UK, had been used for this purpose. Low, medium and high amounts of doping had been added to all the samples. In addition, the reference samples of CrN, AlN, Si$_3$N$_4$ were prepared as well. Surfaces of samples were mechanically cleaned in ultra-high vacuum by means of a diamond needle file and tungsten-wire brush. Special care has been taken in ultrasonic cleaning of the samples for NEXAFS study. Table 1 indicates the at.% of Al/Si content as of low, medium and high doping elements in CrN coatings.

2.2. Structural Characterization of CrSiN and CrALN Thin Film Coatings

Structural characterizations of CrSiN and CrALN films has been previously performed by means of cross-sectional bright field TEM (XTEM), high resolution X-ray photoelectron spectroscopy (HRXPS), XRD and nanoindentation techniques [38]. The
XTEM method was used to observe the factors influencing the mechanical properties of CrSiN coatings with the progressive addition of Si-content while XPS and nanoindentation methods elucidated the surface chemical composition and physical hardness, elastic modulus and residual stress, respectively. Grazing incidence X-ray diffraction (GIXRD) patterns of CrN coatings had been reported to be unaffected with the Al-doping [38]. Undoped samples and samples doped with low, medium and high amounts of Al were identified to be cubic structure; however, other studies reported the existence of wurtzite structure of CrN with Al-doping. XPS study [38] found the existence of an amorphous phase of AlN at the grain boundaries. Preferred orientations have been found to be altered by the Al-substitutions. According to the GIXRD data, it had been observed that (200) preferred orientation was reduced monotonically with the increase in Al-content while a linear increase in the intensity was observed on (111) and (220) reflection planes [38].

2.3. Hardness Test of CrSiN and CrAlN

In the past few years, CrNs have been widely studied owing to their good combination of mechanical and thermal properties [39-40] in comparison with other transition metal nitrides [41]. Transition metal nitrides (i.e., CrN, TiN etc) have been found to show superhardness (hardness > 40 GPa) with suitable doping (i.e., Si, Al etc.) [14-16, 38]. The Si or Al dopant significantly modifies the microstructures of the binary compounds from closely-packed columnar grains into nanocrystalline structures embedded in an amorphous matrix [14-15]. In addition to the exceptionally high hardness, improved oxidation resistance [42] and higher thermal stability [43] of binary
CrN coatings were also reported. Compressive stress of CrN coatings is increased about 52% with the increase of Al-dopant up to ~28.5 at.%. In a similar fashion, the mechanical hardness and Young’s modulus of the CrN thin film coatings have been noticed to increase ~48% and ~16%, respectively, with the addition of ~28.5 at.% of Al-content [38]. Furthermore, the elastic strain to failure ($H/E$) [44] and plastic deformation resistance factor ($H^2/E^2$) [45] increase ~29% and ~140%, respectively, with the highest amount Al-doping to the binary CrN coatings reflecting a potential increase in the wear resistance. Al atoms are found to be segregated around the grain boundaries to form an amorphous AlN structure. The superhardness in CrN with Si and Al substitutions reflects the combination of the fine-grain size together with the strong interfacial bonding between the nanocrystalline and amorphous phases.

2.4. Near-edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

NEXAFS measurements of the coatings were performed using the soft X-ray spectroscopy at the Australian Synchrotron facility based in Melbourne. The storage ring was operated at 3 GeV. In the top-up mode operation, the beam current was 200 ± 1 mA. A collimated light plane grating monochromator (SX700), with a grating of 1200 lines/mm was used to monochromatize the X-ray beam coming out of the storage ring. A minimum pressure of $1 \times 10^{-10}$ mbar was maintained in the analysis chamber throughout the NEXAFS measurements. The hemispherical analyzer is mounted in the horizontal plane at a glancing incidence of 55° (the magic angle [46]) with the X-ray beam (the magic angle is to do with the photoemission and the asymmetry parameter which becomes zero for all electron energy orbital quantum numbers e.g., $2p_{3/2}$, $4f_{7/2}$ etc.).
NEXAFS spectra were collected at Si K-edge (1820-1920 eV), Al K-edge (1520-1620 eV) as well as Cr L-edge (670-730 eV) by using the Auger electron yield (AEY) and total fluorescence yield (TFY) modes. Electrons strongly interact with matter, as the incidence X-rays pass into the sample, electrons will be generated throughout the depth of the material, however only those electrons generated close to the sample surface can escape and be detected. Hence electron yield methods are always strongly surface sensitive. The fluorescence yield, likewise to the electron emission will be generated throughout the depth of the material, but as these fluorescent X-rays pass relatively easily through matter the sampling depth is always much deeper than that of electron yield methods. The fluorescent yield signal is therefore indicative of the bulk of the samples are always free of artifacts produced by self absorption however this is not always the case for fluorescent yield. AEY investigated the surface oxide layer and probed the interaction of oxides with underlying materials while the TFY revealed the bulk structure of materials e.g., chemical bonding at the grain boundary. The spectra obtained in AEY and TFY were normalized with respect to the incidental photon flux. This has been accomplished by dividing the samples signal $I_{\text{sample}}$ by the incident photon flux $I_0$. Since the grain boundaries are amorphous in nature, it was believed that TFY and AEY of metal K-edges in the grain boundaries might be shifted or broadened with the enhancement of dopant concentrations. The shifts have been compared with the reference materials spectra. In this study, NEXAFS measurements were performed by AEY mode and TFY mode with a channeltron facing sample positioned $30^\circ$ above the incoming beam. Both the AEY and TFY modes of measurements were performed at room temperature using a plane grating monochromator with 1200 lines/mm. All the samples were well grounded and mounted.
on adhesive carbon tapes to avoid the surface charging. Prior to analysis the NEXAFS spectra were normalized to the primary beam current.

3. Results

3.1. NEXAFS Spectra at Cr L-edge of CrAlN and CrSiN Coatings

Figs. 1 to 4 show the NEXAFS spectra of Cr L-edge for CrAlN and CrSiN samples doped with low, medium and high at.% of Al and Si as well as a reference CrN sample for comparison in the AEY and TFY modes. All the AEY and TFY spectra for both samples are of similar trend. The local environments of Cr are of similar type with the subsequent doping of either Al or Si to the CrN reference sample. For the TFY spectra of CrSiN sample, first peak observed around 572±1 eV can be assigned to a transition from Cr 1s core state to the Cr 3d states. This peak is observed in all the compositions that reveal the fact that the local structures surround Cr atoms are C3v symmetry [47]. In an earlier XANES study [47], a peak in AlCrN sample has been found to split into two parts: one corresponding to the non-bonding level while the other to the anti-bonding level with a splitting range of 1.5 eV consistent with the first-principle calculations [48]. However, this splitting has not been observed in our experiment.

For TFY spectra of both samples, a tiny peak assigned at ~575 eV arises due to the transitions from the Cr 1s state to the anti-bonding state resulting from hybridizing between the Cr4s and the N2s states. This hybridization can also be considered as the partial mixing of the N2p state because less intensity relative to the peak is observed at ~573.9 eV. The shift of the peak at lower intensity might be related to the increase in lattice constants of the samples [46]. From a comparison of AEY and TFY spectra, it has
been seen that the first spectrum in TFY mode is marginally shifted towards a lower energy position. In TFY mode, a small peak is observed to be followed by the first spectrum. However, in both modes, all the second peaks correspond at ~584.5 eV. Intensities of the peaks observed at either ~577.2 eV or ~584.5 eV do not show substantial changes with the addition of Al or Si content to the CrN coatings. This feature again confirms the uniqueness of the local environments of Al and Si in the CrN sample. It is well-established that the L-edges spectra for transition metal compounds with unfilled $d$-shells can be described on the basis of multiplet and crystal field transitions from $2p^6d^n$ to $2p^5d^{n+1}$ state for an appropriate site symmetry determined by ligands [49]. Multiplet calculations for Cr ligand formed with oxygen and other transition metals in typical bonding environments are available in the literature [50-52]. These reports show the sensitivity of L-edge spectra to the oxidation state and local symmetry of the metal. Localized excitations at Cr L-edges arise from ligand field splitting of Cr3d levels. As shown in Figs. 1 to 4, Cr L-edge absorption in AEY mode is much stronger than that in TFY mode. This feature can be attributed to the fact that the fluorescence yield in Cr L shell decay is much lower than the corresponding Auger yield due to larger efficiency of the Auger decay process [53]. For CrAlN and CrSiN samples, in AEY mode, features observed at 577.2 eV and 584.5 eV of Cr L-edge spectrum are very similar to that of Cr$_2$O$_3$ according to the earlier investigations [53]. Both in AEY and TFY modes, it is also noticed that two principal peaks are separated by a few electron volts (from ~7.5 to ~10 eV) with additional structures. These additional fine structures might result from the multiplet effects arising from an addition of an extra electron to the 3d$^3$ configuration. The separation energy between the two main peaks is comparable to the width of the
valence band [53]. Even though the experimental pin-point of Cr3d states is difficult, however, comparison to band structure calculations suggest that Cr3d states straddle most of the valence band and hybridize strongly with the O2p states at the bottom of the valence band [53]. It is also assumed that the scattering at the Cr L-edge results in excitation of 3d → 3d transitions arising from the ligand field splitting of the Cr3d states.

3.2 NEXAFS Spectra at Al K-edge of CrAlN Coatings

The Al K-edge NEXAFS spectra of CrAlN with low, medium and high at.% of Al-content and Al reference sample in AEY and TFY modes are displayed in Figs. 5 and 6, respectively. For the NEXAFS spectra of all the CrAlN samples, it is clear that all the curves have the same trend confirming that the local environments of Al remain unchanged in this sample. This means that the local environments of Al are independent of the composition. The intensities of the peaks have been found to increase markedly with the increase in Al percentage in the coatings. By comparing the NEXAFS data of CrAlN with that of the reference AlN in both modes, it is noticed that the edges (~1556.7 eV), tiny peak (at ~1560.1 eV) and central peak with maximum intensity (at ~1565.5 eV) and peaks at ~1568.6 eV and ~1584.6 eV are overlapped. This reflects the existence of AlN in CrAlN samples with the progressive addition of Al-content. The peak observed at ~1560.1 eV is weak, possibly due to the result of dipole forbidden 1s→ a₁ (3s like) transition. The major peaks seen at ~1565.5 eV could be assigned to the allowed transition of Al 1s electrons to the antibonding t₂ (3p like) transition while the peaks at ~1576.6 eV and ~1613 eV are related to the transitions of Al 1s electrons to the e and t₂ (3d like) states, respectively. These peaks are known as the symmetry forbidden shape
resonances [54-55]. On the other hand, peaks at ~1568.6 eV and ~1584.6 eV might correspond to multiple scattering from more distant shell atoms [56]. The increase of intensity of Al K-edge with the progressive addition of Al-doping can be explained on the basis of the increase in coordination of Al, increase in effective charge on Al atoms and weaker Al-O bonding [57]. Li et al. [57] also reported that addition of Al would increase intensity of the Al K-edge with an increase in Al-content, which is related to the increase in Al-content to the respective octahedral and tetrahedral sites. The increase of intensity also supports the fact that the absorption coefficient is proportional to the number of absorbing atoms as well as the absorption cross-section.

3.3 NEXAFS Spectra at Si K-edge of CrSiN coatings

Figs. 7 and 8 show the NEXAFS spectra around Si K-edge of CrSiN samples with different Si-content as well as an amorphous reference sample of Si$_3$N$_4$ for comparison in AEY and TFY modes. It is obvious that no significant changes in the spectral lineshape as a function of aluminum content from low to high at.% indicating that the local environment of Si remains invariant in this sample. The intensities of peaks increase significantly with the increase in Si-content in the coatings. In both modes of measurements, all peaks are found to exist around the same energy. The increase of peak intensity with the increase in Si-content is associated with a valence increase from +3 to +4 as well as +5 or +6 [58-60]. It is also believed that the increased intensity might be related to a reduction of crystalline domains down to the nano-scale [61]. The presence of high valence Cr might have been involved in the large intensity with the increased Si at.% in the coatings. Furthermore, the increase of intensity peaks with higher Si-content
may be due to the existence of chemical interactions between Cr and Si. These new chemical interactions give rise to Cr3d Si2p hybridization [1]. Comparing the NEXAFS data of CrSiN with that of the reference Si3N4 coatings, it is evident that in all cases the spectral lineshape is of the same trend with Si3N4. A tiny peak at ~1861 eV has been observed for all samples in both modes as well. Edge positions around ~1840 eV and features observed at ~1847 and ~1862 eV typical of Si3N4 are clearly seen in all CrSiN samples without marked changes with the progressive addition of Si-doping. Thus, the indication of the formation of amorphous type Si3N4 compound in the CrSiN coatings with the progressive addition of Si-content is clear. Our results have been found to be in good agreement with an earlier report of XANES spectrum of Si-doped TiN sample [1]. In that report, the researchers presented the XANES spectrum of Si-doped AlCrN sample and reported that peak observed at 1847 eV is aligned with the spectrum for SiO2 single spectrum. This would imply oxygen contamination of Si in SiO2 form. The edge positions along with the other features of our coatings are found to be consistent with Si3N4 and SiO2 reference samples [67]. Our study has also been found to be in good agreement with an earlier investigation [1]. Further observation confirms that there is no evidence of the presence of any kind of complex spectral lineshape as compared to the reference Si3N4 sample. Thus, the formation of any kind of ternary compounds is not identified. For electron diffraction and TEM investigations, the presence of an amorphous region in the CrAlN with the addition of Si has been reported in terms of the possible formation of SiOx, however, no experimental evidence for the presence of SiNx has been reported [58]. Only a trace amount of SiNx compound at nanometer scales were observed in fast Fourier transform (FFT) [58]. On the other hand, an XPS study of Wo et al. and a
few other reports [40-41] found the experimental evidence of the existence of SiNₓ along with the presence of SiOₓ. According to their report [16] Cr, N and O were identified on the coating surfaces of all CrSiN samples. Presence of Cr₂O₃ peak at 576.7 eV indicates the bonding of oxygen in the surface of all samples. A weaker peak of Cr-O-N at 398.9 eV was observed due to the surface oxidation as well [63]. Moreover, another component central peak at 397.4 eV due to Si₃N₄ [64-65] was identified in the N1s spectra for all four CrSiN films.

4. Discussion

With the introduction of Al to the CrN, some Cr atoms were found to be replaced by Al atoms, because of a smaller atomic radius of Al (0.121 nm) that that of Cr (0.139 nm) [54]. This leads to the formation of CrAlN solid solution, a decrease in the lattice parameter (from 0.416 to 0.411 nm), and the lattice distortion which increases the strain energy of the coatings [38]. Grain sizes of the CrAlN coatings were also decreased slightly with an increase of Al-substitution [38]. CrN coatings present a columnar structure which consists of vertically-aligned grains [38] that remain unaltered with an increased Al content. The average grain size of CrN coatings with fine-grain structures is 10.9 nm that reveals a formation of a large number of nucleation sites during the coating growth mechanism. A very subtle variation of the grain size of the coatings with the Al alloying indicates insignificant effect of Al on the nucleation and grains growth of CrAlN coatings. As the Al-substitution varies from a low to high amount, the amorphous structure of the coatings has been noticeably enhanced. Owing to this enhanced amorphous grain, boundary sliding becomes extremely difficult which causes further
hardening to the thin film coatings [38]. XPS study of CrAlN coatings by Li et al. [38] showed the existence of Cr$_2$O$_3$ and Al$_2$O$_3$ phases in the CrAlN coatings that created an oxidation layer at the surfaces of the samples which in turn improved the oxidation resistance behaviors of the coatings. This also confirmed the existence of an amorphous phase of AlN at the grain boundaries. Al-enriched oxide layer and Al-N bonding have been observed to play a significant role in the oxidation resistance behavior and thermal stability of the coatings, respectively [42-43]. It has also been reported that an increase hardness of coatings may be due to the presence of AlN phase at the grain boundaries in conjunction with the high residual stress [17, 66-69]. The hardness of the CrN coatings increases with an increase of Al doping reaching to a maximum of 42.5 GPa at 28.5 at.%. Al-content reveals the hardening effect associated with the amorphous AlN formed along the grain boundaries. Extraordinary hardening (hardness > 40 GPa) of the thin film coatings can be attained by synthesizing nanocomposite structures which consist of nanograins surrounded by extremely thin amorphous matrix with typical thickness of 3-5 nm [70] that can successfully protect the movements of grain boundaries during deformation and thereby increased the hardness [71]. Moreover, the hardness of materials is affected by compressive residual stress [72]. As the Al-content is increased from a low to high amount, the compressive residual stress of the CrN coatings is increased up to ~52 % [38] that helps to resist the shear sliding of the grains and increases the hardness of the coatings. Thus, the synthesized coatings can adapt to deformation. Therefore, columnar-structured CrAlN coatings can effectively accommodate deformations [73] while a substantial amount of energy is dissipated and stress concentration is reduced. As a result, a remarkable increase in damage resistance and load-carrying occurs [38].
The hardness of CrSiN coatings has been found to vary between 24 and 32 GPa [40, 74–77]. Hardness, \( H \) and elastic modulus, \( E \) of CrN coatings with the progressive addition of Si have been measured as a function of the indentation contact depth of the coatings. CrN coatings doped with medium Si-content shows the highest hardness and elastic modulus as 35.8 ± 3.2 GPa and 397 ± 21 GPa respectively, while the sample having the highest Si content exhibited the lowest modulus (\( E = 347 ± 31 \) GPa) [16]. At low Si contents, the increase in hardness is due to the formation of a solid solution of Si in crystalline CrN [74–75, 78] while at higher Si doping up to ~13 at.%, the increase in hardness is ascribed to the reduced grain size [40, 74–75, 79–80]. In CrSiN coatings, CrN grains show a \( \{200\} \) preferred orientation [40, 74–75, 79–80] that is more resistant to deformation while the coatings where the grains exhibit a \( \{111\} \) preferred orientation [78] are found to be less resistant. As the Si-content is increased up to ~ 28.5 at.%, the hardness of the coatings has been found to be lowered that reveals the formation of localized defects tends to be aligned parallel to the film growth direction. For this reason, coatings offer less resistance to the deformation under a stress normal to the coating surface. In the coating with highest Si-content, compressive residual stress, hardness and elastic modulus have been found to be reduced to a level very much closer to that measured in the CrN coating because of the disappearance of columnar grains, despite the apparently smaller grain size in this sample. Furthermore, a significant reduction of grain sizes results in the reduction of the lattice distortion that leads to lowering the compressive residual stress [16]. Moreover, the presence of a very high volume fraction of amorphous Si$_3$N$_4$ disorders the crystal structure along with lowering the density and hence reduces the residual stress. Additionally, in this coating the CrN crystals are too
small (i.e., ~50 nm, as seen in [16]) to tolerate the higher internal stress by the creation of structural defects such as dislocations and, consequently, fine cracks emerge in the amorphous Si$_3$N$_4$ structure.

5. Conclusions

The effects of 14.3 to 28.5 at.% Al and Si doping on local electronic structure of CrAlN and CrSiN coatings deposited by a TEER UDP 650/4 closed field unbalanced magnetron sputtering system have been investigated. In CrN samples, features corresponding to AlN have been observed in all cases without any significant changes in the spectral lineshape with the gradual increase in Al-content. For CrSiN coatings, features corresponding to Si$_3$N$_4$ and SiO$_2$ have been observed in all cases. No remarkable changes in the spectral lineshape have been noticed with the progressive doping of Si-content as well. Thus, it is conclusive that the local environments of both Al and Si have been found to remain unchanged in these samples with an increase in either Al or Si at.%.

The hardness of the CrN coatings was increased significantly due to the existence of an amorphous AlN phase at the grain boundaries and high residual stress. The amorphous nature of CrN is enhanced with the progressive addition of Al-content that toughens the coatings. The presence of chromium and aluminium oxides at the coatings surface enhances the oxidation resistance of the coatings. The highest hardness and elastic modulus of the CrN coatings have been observed with the medium Si-doping. The hardness and elastic modulus of CrN increases with an increase in Si-doping in crystalline CrN. With high Si-content, hardness, residual stress and elastic modulus decrease due to the creation of localized defects, and lattice distortion.
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Figure Captions

Fig. 1. NEXAFS spectra of Cr L-edge of Cr$_x$Al$_{1-x}$N coatings and AlN reference sample in AEY mode with progressive addition of Al-content.

Fig. 2. NEXAFS spectra of Cr L-edge of Cr$_x$Al$_{1-x}$N coatings and AlN reference sample in TFY mode with progressive addition of Al-content.

Fig. 3. NEXAFS spectra of Cr L-edge of Cr$_x$Al$_{1-x}$N coatings and CrN reference sample in AEY mode with progressive addition of Si-content.

Fig. 4. NEXAFS spectra of Cr L-edge of Cr$_x$Al$_{1-x}$N coatings and CrN reference sample in TFY mode with progressive addition of Si-content.

Fig. 5. NEXAFS spectra of Al K-edge of Cr$_x$Al$_{1-x}$N coatings and AlN reference sample in AEY mode with progressive addition of Al-content.

Fig. 6. NEXAFS spectra of Al K-edge of Cr$_x$Al$_{1-x}$N coatings and AlN reference sample in TFY mode with progressive addition of Al-content.

Fig. 7. NEXAFS spectra of Si K-edge of Cr$_x$Al$_{1-x}$N coatings and reference Si3N4 sample in AEY mode with progressive addition of Si-content.

Fig. 8. NEXAFS spectra of Si K-edge of Cr$_x$Al$_{1-x}$N coatings and reference Si3N4 sample in TFY mode with progressive addition of Si-content.
Table 1. Chemical compositions of $\text{Cr}_1-x\text{M}_x\text{N}$ with different Al/Si contents.

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Amount of Al/Si</th>
<th>Al/Si content (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cr}_1-x\text{M}_x\text{N}$</td>
<td>Low</td>
<td>14.3</td>
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<tr>
<td></td>
<td>Medium</td>
<td>21.2</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>28.5</td>
</tr>
</tbody>
</table>
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7
Fig. 8
Highlights

Al or Si is doped on CrN and AlN coatings using magnetron sputtering system

NEXAFS analysis is conducted to measure the Al and Si K-edges, and chromium L-edge

Structural evolution of CrN matrix with addition of Al or Si element is investigated