3d Transition Metal Oxide based Sol-gel Derived Coatings for Photothermal Applications

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***Abstract*: Photothermal devices require high performance solar selective materials for the surface of solar energy converters. A good solar selective surface exhibits high spectral absorptance in the visible range and low thermal emittance in the infrared to far-infrared range of the solar spectrum. 3d transition metal oxide based thin film coatings are explored as high solar selective material to be used in solar energy harvesting devices. Solar selectivity of such coatings depends on the deposition conditions, crystal structure, chemical composition, microstructural morphology, composition uniformity and stoichiometry. This report highlights and summarizes the optical properties and mechanical characteristics of some recently developed sol-gel dip-coating derived from $Cu_xCo_yO_z$ transition metal oxides based solar selective surfaces thinfilms. X-ray photoelectron spectroscopy (XPS), UV-Vis spectrometer, FTIR spectrophotometer, nanoindentation and Synchrotron radiation X-ray diffraction (SR-XRD) techniques are utilized to realize various features involved in such coatings.**

Keywords: Photothermal, solar selective surface, solar absorptance, thermal emittance, optical thin films, sol-gel, solar selectivity.

I. Introduction

Owing to their impressive structural diversity and good combinations of a number of physical, mechanical, chemical and electrical properties of transition metal oxides based thin film coatings found a wide variety of technological applications including photothermal conversions. Wide-spread applications and steadily increasing scientific interests on metal oxides based films have been dedicated to the development of new species of solar selective coatings with superior properties. Since the solar selective surfaces are the easiest and most direct way of harvesting the solar energy, in recent years, transition metal oxides based thin film coatings have received significant perception for mid and high temperature applications [1-6]. A spectrally selective surface is, generally, used to improve the photothermal conversion solar energy in the visible range while 100% of the IR energy is reflected back from the absorbing surface indicating that no heat is lost through thermal radiation. A good solar selective surface can be designed by an absorber-reflector assembly that possesses two characteristics: high absorptance, α in the solar spectrum region (0.3 to 2.5 μm) and low emittance, ε i.e., high reflection in the infra-red (IR) region ($\geq$ 2.5 μm) at the operating temperatures. An ideal selective surface absorbs all the incoming radiation while the reflection is kept as minimum (i.e., ideally reflection should be zero) in the visible range of solar spectrum. In such an approach, the reflector is coated with a highly absorbing layer over the visible solar spectrum while the infrared region is made transparent. Various types of metal oxides thin film based selective solar surfaces such as $Ni_xCo_yO_z$, $Mn_xCo_yO_z$, $Cu_xCo_yO_z$, $PtAl_2O_3$, $MoAl_2O_3$, $CuAl_2O_3$, $NiAl_2O_3$ etc are thoroughly investigated by many groups [3-8]. Transition metal oxides based thin films with general composition AB_2O_4, where A is a divalent metal ion occupying the tetrahedral A-sites while B is a trivalent ion occupying at octahedral B-sites e.g., $CuFe_2O_4$, $CuCo_2O_4$, and $CuMn_2O_4$ are studied by different groups [9]. Spinel $Cu_xCo_{2-x}O_4$ oxides have low thermal stability which has been found to be decreased with the increase in $\frac{Cu}{Co}$ ratio [10]. Mixed metal oxide based thin films have been extensively studied by different groups around the world [11, 12] owing to their wide-spread applications in various areas e.g., selective solar absorbers, dye sensitized solar cells, batteries and memory devices, absorption optimization and industrial applications as well. Cobalt based metal oxides are reported for a wide variety of high-tech applications [13, 14]. Pure copper oxide [15], cobalt-copper oxide, manganese-cobalt oxide, nickel-cobalt oxide [3, 16], copper-aluminium oxide [17] have been reported in the literature for the use of spectrally selective solar absorbers, high absorption optical coatings and industrial applications. The manganese-cobalt oxides have been studied with the attention of the influence of the synthesis conditions on the oxidation states and cationic distribution in the tetragonal and cubic phases [18]. The physicochemical and electrochemical properties of $Cu_xCo_{3-x}O_4$ powder has been investigated for their practical applications as the catalysis in oxygen evolutions reaction (EOR) [19]. Optical and other properties of such materials can be modified by selecting the elements and controlling the process parameters that alters the density of free electrons in their d-bands. In light of the importance of solar selective materials for the photothermal applications, detailed knowledge on the synthesis process and its recent developments would be very useful for material scientists aspiring to optimize its favorable physicochemical properties. As such, this paper briefly highlights the recent developments 3d transition metal oxides based thin film coatings for solar selective surface applications in both the fabrication techniques and materials, and present a brief summary of the current studies carried out by our research group at Murdoch University.

II. Synthesis Techniques and Recent Development

Solar energy collectors transform solar radiation to thermal energy through a transport medium while the photovoltaic (PV) cell is a way of converting the solar energy directly into electricity. The efficiency of a photothermal device can be enhanced by the development of highly effective solar selective materials [20]. The important factors to consider for the production of photothermal absorbers are superior

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selectivity, thermal durability, simplicity, cost-effectiveness in fabrication and low environmental impact. Since the 1950s, when Tabor [21] proposed and demonstrated the effectiveness of selective surfaces for enhancing the photothermal efficiency of solar collectors, numerous types of solar absorbers have been reported and produced [22]. In the development of solar selective surfaces emphasizes are put forward for the fabrication technique and creation of a material which has high selectivity and durability and a cost-effective and environmentally-friendly root. Several techniques have been used to synthesize the absorber selective coatings such as electroplating/electrochemical deposition (including chemical conversion/chemical bath deposition (CBD)), vacuum deposition (physical vapor deposition (PVD)/sputtering), chemical vapor deposition (CVD), and sol-gel methods. Sol-gel dip-coating technique meets these criteria, potentially promising and results in a chemically uniform thin film network [3-6, 16]. However the application of these techniques to synthesize solar selective surfaces is much less common than electrochemical or vacuum-based techniques. Over the past few years 3-d transition metal oxide based coatings have been developed as novel high temperature solar selective coatings for solar thermal applications [23]. Despite the fact that the metal oxides thin film coatings based solar selective surfaces are prepared by various techniques, however the development of low cost, easier and environmentally friendly route together with the high power conversion efficiency is always the key spot for the solar selective surfaces.

To satisfy the multi-fold demand for the approaching energy crisis of the planet, research is needed to develop new, sustainable and improved solar selective surfaces for photothermal applications. In view of the above facts, we are focusing our attention to synthesize copper-cobalt oxides based thin film coatings for selective surface applications with the controlled addition of graphene oxides. Some preliminary results are presented in section 3.3 of this paper.

III. Results and Discussion

The present study reports from the recently published results and some ongoing projects of our group at Murdoch University that aimed on the synthesis of cobalt-based metal oxide thin films on glass and aluminum substrates with and without the addition of graphene oxides via sol-gel dip-coating method and titanium nitride based sputtered coatings deposited on steel substrates, respectively. Identification of the physico-chemical properties of dip-coated metal oxides thin films can essentially be determined via various surface analytical techniques.

III.A. SR-XRD analysis

Synchrotron radiation X-ray diffraction (SR-XRD) measurements of sol-gel derived $Cu_xCo_yO_z$ coatings without graphene oxides and with the addition of 1.5wt% of graphene oxides were carried out in the powder diffraction (PD) beamline at the Australian synchrotron in Melbourne. The SR-XRD data of metal oxides based coatings were recorded at room temperature, 100°, 200° and 300 °C in a 2θ geometry ranging from 16° to 66° in steps of 0.2°. Multiple phases were recorded at all the measuring temperatures. All the films demonstrate highly compact and smooth morphology with homogenously dispersed particles together with excellent adhesion to the substrates. It was further noticed that the influence of temperature is not only related to phase formation and oxygen contamination but also to the morphology and grain growth mode of the coatings that also affects the solar selectivity of these coatings. The phase transitions at high temperatures result in corresponding changes of other properties as well.

III.B. XPS analysis

Synchrotron radiation X-ray photoelectron spectroscopy (SR-XPS) was implemented to determine the surface electronic structure of the thin film coatings. Multiple oxidation states for metal copper e.g., octahedral and tetrahedral Cu^+, octahedral and paramagnetic Cu^{2+} were noticed while metal cobalt composed of mixed $Co^{2+,3+}$ oxidation states. The oxygen was from lattice, surface and subsurface oxygen [3]. It was observed that the increase of copper concentration promoted the formation of octahedral Cu^{2+} and reduced the octahedral Cu^+ ions [4]. Further investigation shows the octahedral Cu^{2+} ions replaced the Co^{2+} site in the cobalt structure host. However, the local coordination of Co, Cu and O are not changed, within experimental errors, by the different concentration ratios of [Cu] and [Co], except for the coating with [Cu]/[Co] = 2 where the local coordination has a small change due to the loss of octahedral Cu^+ [4]. The decoupling of O 1s spectra indicate that metal-O bonding states dominate in the thin films, plus small amount of metal-hydroxyl bonding. The double pair of metal 2p XPS ((*i.e*., Cu 2p ($2p_{3/2}$ and $2p_{1/2}$), and Co 2p ($2p_{3/2}$ and $2p_{1/2}$)) peaks indicate metal-O (oxidized metal) and elemental metal coexist in the thin film coatings. The oxidization state of metal from metal 2p XPS also agrees with the decoupling analysis of O 1s spectra. The C 1s peaks in all the XPS spectra are due to some carbides, C-H from pump oil and/or surface contamination due to air exposure of sample before introduction into vacuum chamber for analysis.

III.C. Optical properties

Systematic studies of the optical properties of $Cu_xCo_yO_z$ thin film coatings with respect to varying [Cu]/[Co] concentration ratio, speed of dip coating, dip heating cycles and sintering temperature are elucidated in the following subsequent sections. Generally the optical performance of a thin film coatings is described by two parameters: optical absorptance (α), and thermal emittance (ε). In order to increasing the effectiveness of a solar thermal energy system, absorption of incident solar radiation should be maximized and thermal losses from the collector minimized. The solar selective absorber surface is the key component of a solar collector determining strongly the efficiency in solar–thermal energy conversion.

The solar absorptance of thin film coatings is strongly dependent on the surface morphology and surface roughness of the deposited layers. A rough surface minimizes the reflection of incoming solar radiation from the film surface whereas pores contribute to reduce the refractive index. The relaxation mechanisms of the coatings together with the multiple reflections and resonant scattering in the pores around the film surfaces also contribute to enhance the absorptance behaviour.

The calculated solar absorptance values of $Ni_xCo_yO_z$, $Mn_xCo_yO_z$, and $Cu_xCo_yO_z$ coatings are based on the AM1.5 solar spectrum standard. The reflectance spectra of these coatings were recorded from 250 to 2500 nm using a UV–Vis-NIR Jasco V-670 double beam spectrophotometer with 60 mm integrating sphere. The solar absorptance values of these thin film coatings were calculated based on reflectance (R%) following the Duffie and Beckman method as described in Ref. [24]. The absorptance values at a dip speed of 60 mm/min and various dip heating cycles are presented in Table 1 [16].

Table 1: Solar absorptance values of sol-gel derived NiCoO, MnCoO, and CuCoO coatings deposited on aluminium substrates.

Samples	Dip-heating cycles	Dip speed (mm/min)	Sintering temperature (°C)	Absorptance (%)
$Ni_xCo_yO_z$	2	60	500	24.80
	6			32.20
$Mn_xCo_yO_z$	2			32.10
	6			32.60
$Cu_xCo_yO_z$	2			41.80
	6			71.30

From Table 1, it is clear that the nickel-cobalt coatings exhibit the lowest absorptance. It is also clear that increasing the dip-heating cycles improved the absorptive capability of all the coatings. This improvement in absorptance is due to the increase of the films thickness resulting from the increased dip heating cycle. A more pronounced effect is detected in the Cu-Co as compared to the Ni-Co and Mn-Co coatings. As such we will concentrate on the Cu-Co coating outcomes.

The reflectance spectra of Cu–Co oxide thin film coatings with various [Cu] and [Co] ratio showed that the absorption edge shifted from shorter wavelengths to longer wavelength range (or high frequency to low frequency) as the dip-speed and concentrations were increased. As the Cu-Co coatings showed the highest absorptance we investigated the effect of deposition conditions on the absorptance of the 500 °C annealed Cu-Co copper–cobalt oxide thin films. The deposition conditions were varied by: (i) changing the dip coating speed over the range 60-180 mm/min for various [Cu] and [Co] concentration ratios such that [Cu]/[Co]=1; (ii) Varying the concentration ratio [Cu]/[Co] from 0.5-2.0 for the optimum dip coating speed. The results are displayed in Table 2 and Table 3 [3].

Table 2: The Solar absorptance of $Cu_xCo_yO_z$ coatings, sintered at 500 °C in air for 1 hour using 4 dip-heating cycle, with varying speed of dip coating parameters.

Sample	[Cu]/[Co] ratio	Dip speed (mm/min)	Absorptance (%)
$Cu_xCo_yO_z$	$\frac{[Cu]}{[Co]} = \frac{0.15}{0.15} = 1$	60	66.10
		120	77.30
		180	77.90
	$\frac{[Cu]}{[Co]} = \frac{0.20}{0.20} = 1$	60	77.00
		120	79.50
		180	79.80
	$\frac{[Cu]}{[Co]} = \frac{0.25}{0.25} = 1$	60	80.40
		120	83.40
		180	84.50
	$\frac{[Cu]}{[Co]} = \frac{0.30}{0.30} = 1$	60	79.40
		120	83.90
		180	84.74

Table 3: The Solar absorptance of $Cu_xCo_yO_z$ coatings, sintered at 500 °C in air for 1 hour using 4 dip-heating cycle, with varying concentration ratio [Cu]/[Co].

Sample	[Cu]/[Co] ratio	Absorptance (%)
$Cu_xCo_yO_z$	$\frac{[Cu]}{[Co]} = \frac{0.125}{0.25} = 0.5$	86.77
	$\frac{[Cu]}{[Co]} = \frac{0.25}{0.25} = 1$	83.40
	$\frac{[Cu]}{[Co]} = \frac{0.25}{0.125} = 2$	74.13

The results from Table 3 suggest the sample with the high absorptance value of 86.77% will be suitable for application as a coating for solar selective surface in photothermal collectors. Infrared reflectance spectra of the $Cu_xCo_yO_z$ coatings were acquired in the wavelength range 2.5 to 15.4 µm using a reflected-off type Perkin Elmer Spectrum 100 FTIR spectrophotometer with integrating sphere in the wavelength range of 2.5 to 15.4 µm. The FTIR reflectance spectra were used to compute the thermal emittance, ε value of this coating [24]. Thermal emittance is defined as a weighted fraction between emitted radiation and the Planck black body distribution and is used to appraise the performance of solar selective surfaces in the mid to far-infrared range of the spectrum [5]. Analysis of FTIR reflectance spectra data of sol-gel derived $Cu_xCo_yO_z$ coatings reported in Ref. [5]. Using the emittance value of $Cu_xCo_yO_z$ coatings as reported in Ref. [5], we presented the solar selectivity results of $Cu_xCo_yO_z$ coatings in the following Table 4 [6].

Table 4: Solar selectivity of sol-gel derived $Cu_xCo_yO_z$ coatings.

Sample	Solar absorptance α (%)	Emittance ε (%)	Solar selectivity ($s = \frac{\alpha}{\varepsilon}$)
$Cu_xCo_yO_z$	86.77	5.54	15.66

A thermal emittance value below 10% is, generally, considered to be good for a thin film material that is to be used as a solar selective surface.

To further explore the solar selective properties of Cu-Co thin film coatings, graphene oxides (GO) was deposited on the Cu-Co oxide coatings via the sol-gel dip-coating technique. Addition of 1.5wt% of graphene oxides to the $Cu_xCo_yO_z$ system resulted in a selectivity of 44.23, which is almost 3x the value shown in Table 4. Full analysis and interpretation of the combined $Cu_xCo_yO_z$ /graphene oxide investigations will be published in a forthcoming journal article.

III.D. Mechanical properties

A nanoindentator (Ultra-Micro Indentation System 2000, Australia) equipped with a Berkovich indenter was used to measure the mechanical properties of the coated Cu-Co-oxide films. From the load vs penetration depth plot, Young's modulus (E), hardness (H), and wear resistance (H/E) were computed. The mechanical properties of the synthesized coatings at various annealing temperatures are presented in Table 5 [6].

Table 5: Mechanical properties of annealed $Cu_xCo_yO_z$ coatings.

Mechanical properties	Sintering temperatures, °C			
	500	550	600	650
Hardness H (GPa)	3.18	3.20	3.22	3.17
Elastic modulus E (GPa)	91.40	101.40	101.50	105.10
Wear resistance H/E	0.035	0.032	0.032	0.030
Poisson's ratio (σ)	0.30	0.30	0.30	0.30

Results from Table 5, reveal that the degree of resistance to deformation increases with increasing annealing temperature reaching up to maximum resistance at 650 °C in this temperature range. Thus, the heat treatment has a positive impact on the mechanical properties of the coating layer.

IV. Conclusions

The structural, surface bonding states, optical and mechanical properties of 3d transition metal oxides ($MeCo_yO_z$; Me = Cu, Ni and Mn) based thin film coatings deposited via sol-gel method demonstrated good performance as solar selective surfaces. Further investigations show that the addition of graphene oxide to the copper-cobalt oxides coatings exceptionally improves the solar selectivity of these films. The advantages of such surfaces are simplicity in production, good selective performance and their cost-effectiveness. Such features are interesting aspects which may be prevalent in future research concerning optimal designs of solar selective surfaces for photothermal applications. There are, nonetheless, many technical obstacles that need to be addressed before such techniques can become fully viable in the context of commercial applications.

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