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journal homepage: www.elsevier.com/locate/physbBlack Cr/ α -Cr₂O₃ nanoparticles based solar absorbersS. Khamlich^{a,b,c,*}, O. Nemraoui^a, N. Mongwaketsi^a, R. McCrindle^b, N. Cingo^{a,c}, M. Maaza^{a,b,c}^a NANOAFNET, MRD – iThemba LABS, National Research Foundation, 1 Old Faure road, Somerset West, South Africa^b Faculty of Sciences, Pretoria – Tshwane University of Technology, Private Bag X 680, Pretoria, South Africa^c Council for Scientific and Industrial Research (CSIR), National Laser Centre (NLC), African Laser Centre (ALC), CSIR campus, P.O. Box 395, Pretoria, South Africa

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ABSTRACT

Monodisperse spherical core-shell particles of Cr/ α -Cr₂O₃ with high adhesion were successfully coated on rough copper substrates by a simple self-assembly-like method for the use in solar thermal absorbers. The structure and morphology of the core-shell particles of Cr/ α -Cr₂O₃ were effectively controlled by deposition temperature and the pH of the initial precursor solution. Their characterizations were carried out with X-ray diffraction, scanning electron microscopy, energy dispersive spectrometry and attenuated total reflection, as well as UV–vis diffuse reflectance spectroscopy. The samples aged for more than 40 h at 75 °C exhibit the targeted high absorbing optical characteristic “Black chrome” while those aged for \leq 40 h show a significant high UV–vis diffuse reflectance “green color”.

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1. Introduction

Black chromium is a chromium–chromium (III) oxide cermet (Cr–Cr₂O₃) nano-composite-type. It exhibits attractive solar absorption characteristics with a high solar absorption α and low emissivity ε over a large temperature range [1]. It is used widely as selective solar heat thermal collector nano-coatings for temperature \leq 400 °C in Concentrated Solar Photothermal “CSP” devices. The black chromium selective solar absorbers have been and are produced by various high vacuum technologies such as reactive sputtering [2,3], pulsed sputtering [4], e-beam and evaporation techniques [5] or by using the electroplating approach of black chrome. This latter employs Cr–Cr₂O₃ cermet material and is the most widely used solar absorber [6,7]. Based on the survey of Kennedy [8], electrodeposited black chromium cermet on Ni, Fe, Cu, stainless-steel substrates, has an α/ε (100 °C)=0.97/0.09 for temperatures $<$ 300 °C [9–16]. Black chrome is commercially produced by MTI on Ni-plated Cu in the United States, by Chrome-Coat of Denmark on copper, and on stainless-steel by Energie Solaire in Switzerland [17]. Researchers have found that a layer of Ni between the substrate and black chrome coating enhances the thermal stability up to 400 °C [18]. Among the sources of the degradation and hence limitation of lifespan of the black chromium, one could single out the oxidation and the interfacial diffusion phenomena. More accurately, oxidation of the metallic Cr crystallite and densification of the crystallites primarily cause

the degradation of the selective coating [19]. At high temperatures, Ni diffusion from the substrate contributes to the optical degradation [20]. When the Cr⁺³ concentrations in the standard black-chrome baths were reduced, laboratory samples were produced that are stable in air for 3908 h and 670 h at 350 °C and 400 °C [21], respectively. The reflectance after exposure at 350 °C in air is approximately equivalent to that after exposure at 400 °C in vacuum [22]. Heat treatments established that black chrome failed optically between 500°–600 °C after 1 h in both air and vacuum in addition to the mechanical peeling after 600 °C in air [23]. It was demonstrated that improvements in performance are possible with the addition of an AR top coating and if a metallic layer is used at the interface to act as the IR reflector instead of the Cu or Al substrates. The reason is that the diffusion of Cu and Al from the substrate at higher CSP operating temperatures becomes significant. At last, one should mention that black chrome solar selective films can be improved by admixing molybdenum, up to a limit of about 20% of the chromium content [24].

The objective of the research work presented within this contribution, is the demonstration of the possibility of preparation of large surface coatings of black chromium–chromium (III) oxide cermet by a novel cost effective physical–chemical method: the Aqueous Chemical Growth “ACG”. This method presents several advantages such as being simple, easy to scale up, cost effective and versatile in operation [25,26]. More accurately, we report on the influence of aging time on the formation of Cr on the surface of the uniform fine “in the range nano to micron” spherically shaped core-shell particles of Cr/ α -Cr₂O₃ with high adhesion onto metallic substrates using the ACG low temperature-soft physical-chemistry preparative technique and as well as on the effect of aging on the optical properties.

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2. Experimental techniques

The quasi-monodisperse spherical core-shell particles of Cr/ α -Cr₂O₃ were prepared in an aqueous solution of chromium potassium sulfate dodecahydrate “KCr(SO₄)₂·12H₂O” following the procedure of Vayssieres and Manthiram [25]. Typically, copper or stainless steel metallic sheets properly cut and sand blasted

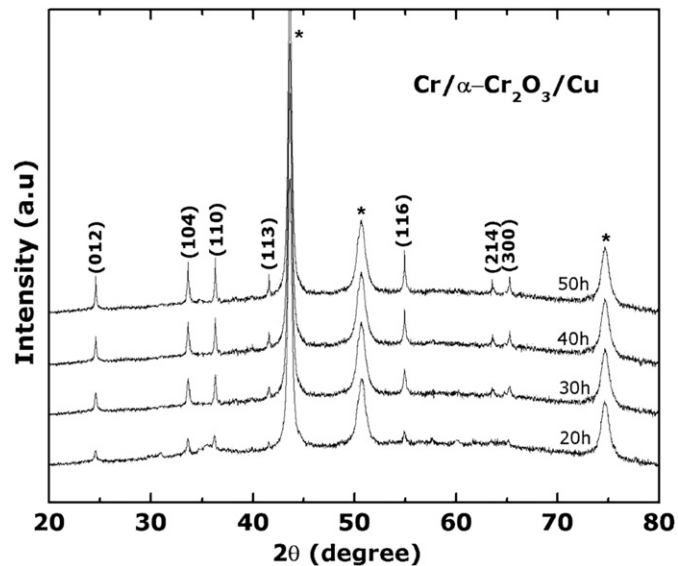


Fig. 1. X-ray diffraction patterns of the Cr/ α -Cr₂O₃ spherical core-shell particles deposited on Cu substrate and annealed at 500 °C for 1 h.

with silica beads of $\sim 50 \mu\text{m}$ particle size are used substrates. Once, their surface roughness is enhanced, the substrates were cleaned by ultrasonic washing and degreased with trichloroethylene, acetone and methanol in appropriate proportions. The clean substrates are then immersed into 1 mM aqueous solution “MilliQ, 18.2 M Ω cm” of KCr(SO₄)₂·12H₂O and placed in a regular laboratory oven at a constant temperature 75 °C with different aging times. Subsequently, the resultant meso-particulate thin films are thoroughly washed with de-ionized water to remove any residual salts and then dried at 90 °C for ~ 1 h. Afterward, the particulate coatings are heat treated in a flowing H₂ gas at 500 °C, based on thermal analysis data, for 1 h to obtain Cr/ α -Cr₂O₃ quasi-monodisperse and spherically shaped core-shell particles. The crystalline structure of Cr/ α -Cr₂O₃ cermet nano-coatings are investigated using an X-ray diffractometer “model Bruker AXS D8 Advance” with irradiation from K α line of copper “ $\lambda = 1.5406 \text{ \AA}$ ”. The particles and the coating morphologies are investigated using a Leo-StereoScan 440 scanning electron microscope “SEM”. The chemical composition is determined using electron energy dispersive spectroscopy “EDS”. The optical properties of α -Cr₂O₃ particles are investigated using Perkin Elmer Spectrum one FTIR with diamond ATR accessory and UV-vis diffuse reflectance spectroscopy.

3. Results

3.1. X-ray diffraction

The results of the XRD experiments on Cr/ α -Cr₂O₃ core-shell particles synthesized at various aging time are shown in Fig. 1,

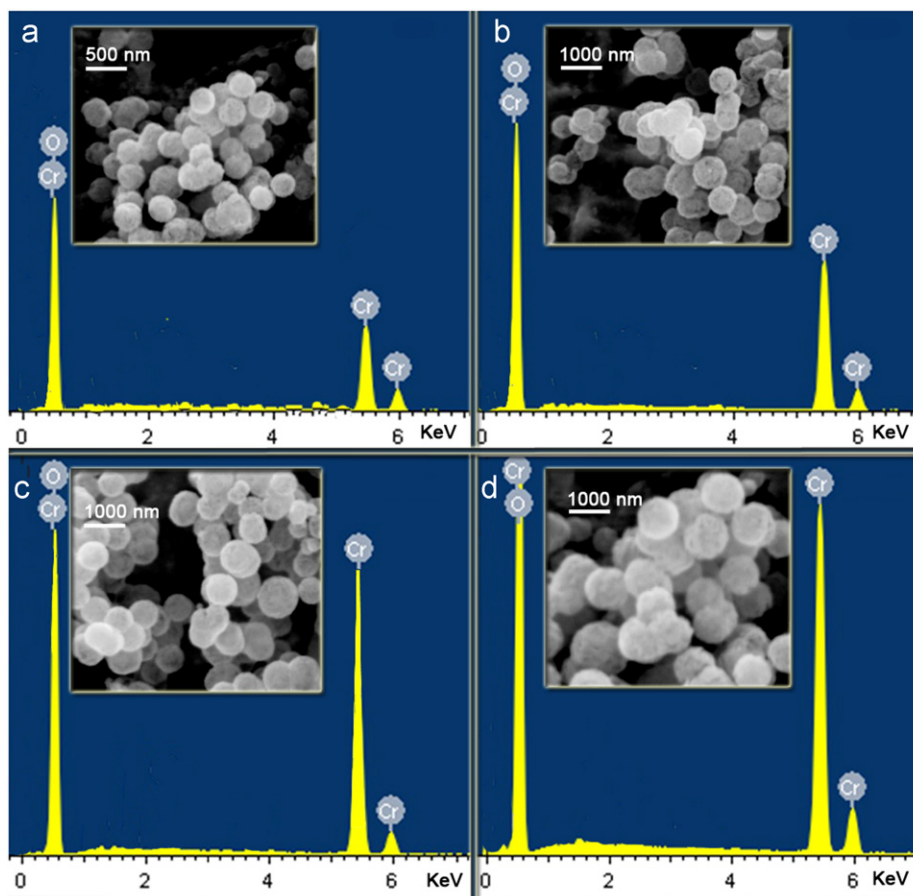


Fig. 2. SEM/EDS of Cr/ α -Cr₂O₃ monodisperse spherical core-shell particles deposited on very rough Cu substrate.

together with the diffraction peaks of the copper substrate material. The XRD profiles of the majority of the Cr/ α -Cr₂O₃ coatings onto Cu roughened substrates indicate that the chromium layer on the surface of the particles as a shell is amorphous. However, all the peaks that occurred coinciding with those given in the Joint Committee on Powder Diffraction Standards “JCPDS” card 74-0326 of the Cr₂O₃ structure. These peaks are attributed to rhombohedral structure (space group R $\bar{3}$ with unit cell parameters of; $a \sim 4.96070$ and $c \sim 13.59900$ (Å) of pure α -Cr₂O₃ phase, while peaks denoted by stars belong to the used copper substrates. As one could expect in relation to the crystallization process, the intensity of the peaks increased while their width at half maximum decreased as a result of increasing aging time. Such a trend indicates that there is a net increase in the α -Cr₂O₃ crystallite size.

3.2. SEM and EDS analysis

SEM micrographs in the inset of Fig. 2 reveal that the Cr/ α -Cr₂O₃ coatings consists of spherical particles with an average size of about 498, 990, 1010 and 1185 nm, respectively”, similar to our

previous SEM study on α -Cr₂O₃ mono-disperse spherical particles [26]. This result demonstrated that Cr/ α -Cr₂O₃ can be produced with well-defined surface morphology, narrow size distribution and excellent shape control not only onto standard amorphous substrates but also on metallic ones. The chemical composition analysis of the Cr/ α -Cr₂O₃ monodisperse spherical core-shell particles by EDS shows that the coatings contain black chromium “see Fig. 2”, but since no crystalline chromium was found by XRD measurements, it is surmised that the film contains amorphous chromium. A closer EDS analysis confirmed that the percentage of chromium increases with increasing aging time. In view of discriminating the shell of Cr from the core of α -Cr₂O₃, a fine electron probe beam of 3 nm in the EDS system was used. Thereafter, EDS spectra were acquired by positioning at different parts of the large-size particles. Fig. 3 reports a comparison of EDS spectra acquired by positioning the electron probe through only the shell and through the core and shell “see Figs. 3a and b”, respectively. It is apparent that the shell is dominated by Cr, while the core is rich in α -Cr₂O₃, suggesting that the shell of the large-size particle is Cr.

3.3. Attenuated total reflectance (ATR)

Fig. 4 shows the absorbance ATR spectra for Cr/ α -Cr₂O₃ monodisperse spherical core-shell particles deposited on the roughest Cu substrate at 75 °C for different aging times, and annealed in low vacuum atmosphere (10⁻³ Pa) in a flowing H₂ gas at 500 °C for 1 h. The spectrum reveals one strongest band centered at 539 cm⁻¹. This value falls well within the range reported in the literature for samples having the stoichiometric α -Cr₂O₃. This band is associated with Cr–O stretching modes, more accurately, anti-symmetrical stretching in Cr₂O₃. This vibrational mode is due to various combinations of O²⁻ and Cr³⁺ displacements in the lattice. The attenuated total reflection measurement reveals that the absorbance decreased with increasing aging time in the IR spectral range. These results indicate that the samples synthesized for longer aging time have good infrared reflectance behavior, a suitable trend for the targeted solar absorbers application.

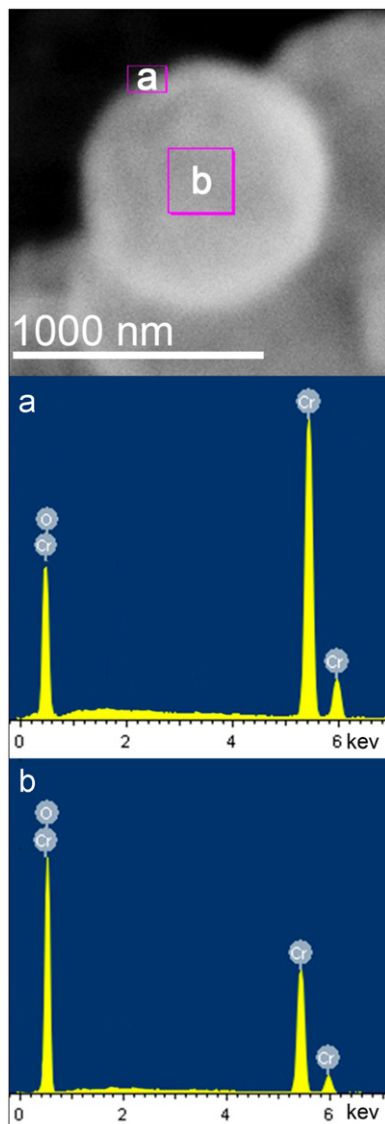


Fig. 3. Investigation of shell and core-shell of one Cr/ α -Cr₂O₃ monodisperse particle aged for 50 h and annealed at 500 °C for 1 h in a flowing H₂ gas.

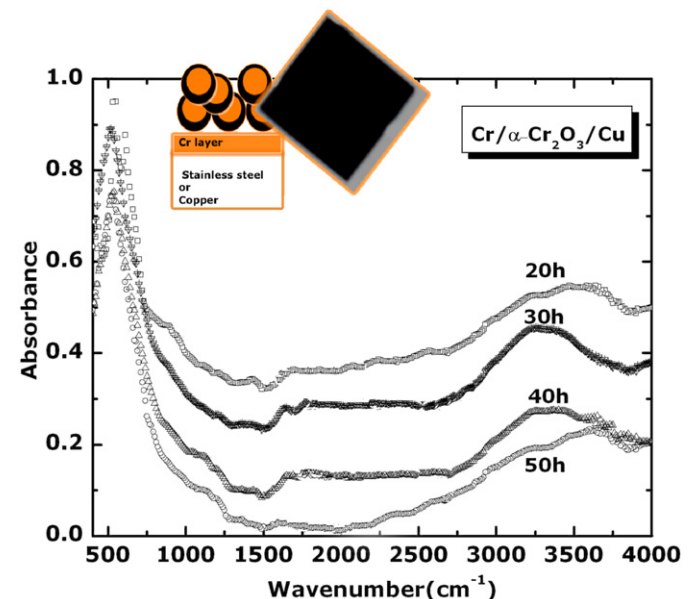


Fig. 4. (ATR) of different samples over the infrared range.

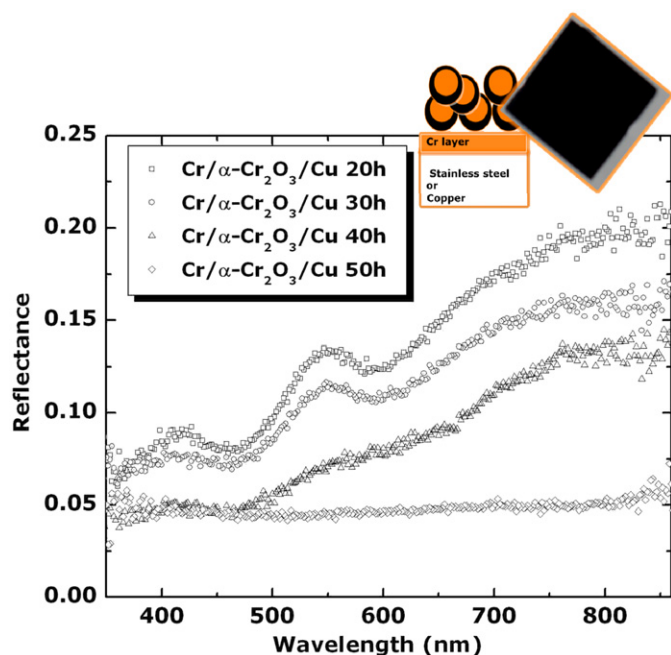


Fig. 5. Diffuse reflectance of different samples over the UV–visible range.

3.4. UV–vis diffuse reflectance

Fig. 5 represents the total diffuse reflectance “specular and non-specular reflectivity” of different samples over the UV–vis range. In general, very low reflectance spectra are obtained with samples aged for more than 40 h at 75 °C, hence such nano-coatings are potentially competitive for solar absorbers application. However, this strongly depends on the aging time of the samples. For example the solar reflectivity of samples aged at high aging time $t \sim 50$ h are relatively low without showing any Cr_2O_3 maxima at 420 and 540 nm due to the black thin layer of chromium metal coated on the surface of the particles. In contrast, samples aged at low aging time $t \sim 20$ h (Fig. 5) exhibit two maxima, one smaller maximum at ~ 420 nm and a broader one at ~ 540 nm similar to those of bulk Cr_2O_3 [27] with a width of about 100 nm. The latter maximum determines the color resulting from this reflectance spectrum. A third broad maximum appears in the NIR region at ~ 860 nm. This maximum, however, does not affect the apparent color and vanishes with increasing the thickness of the particles layer of chromium shell. The difference in optical properties of films deposited at various aging time can be attributed to many factors such as the film microstructure, surface composition and surface morphology, etc.

4. Conclusion

Black $\text{Cr}/\alpha\text{-Cr}_2\text{O}_3$ based on uniform fine “in the range of micron–nano” spherically shaped core-shell particles of $\text{Cr}/\alpha\text{-Cr}_2\text{O}_3$ were

deposited by simple self-assembly method with high adhesion to the substrate: the Aqueous Chemical Growth “ACG”. Samples deposited for longer aging time show high chromium percentage on the surface of the particles, low infrared reflectance and high UV–visible absorbance. As conclusion, these preliminary results indicate that this type of nano-coatings onto Cu or stainless steel rough substrates, are good candidates for solar absorbers applications at temperature lower than 500 °C.

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