Cr/ α-Cr₂O₃ monodispersed spherical core-shell particles based solar absorbers

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Abstract. Monodispersed spherical core-shell particles of Cr/α-Cr₂O₃ cermet ACG coatings investigated within this contribution could be successfully employed in thermal converters. Their selectivity depends on their chemical, physical and structural characteristics and related optical properties like reflectance, emittance, solar light absorption, or absorptance and transmittance. Parameters such as particles size, aging-time and substrate roughening will greatly influence their relevant optical properties as reported. The coated Cr/α-Cr₂O₃ spherical particles on rough copper substrates by a simple self-assembly-like method were characterized by scanning electron microscopy, energy dispersive spectrometry, Raman spectroscopy, and diffuse reflectance UV-VIS-NIR spectroscopy. The samples aged for more than 40h at 75°C exhibit the targeted high absorbing optical characteristic "Black chrome" while those aged for ≤ 40h show a significant high diffuse reflectance.

1. Introduction

The development of new and low-cost selective solar photothermal absorbers is gaining momentum and efforts in a number of research laboratories all over the world. Spectrally selective coatings used in solar collector are known to enhance the efficiency of solar thermal conversion. In photo-thermal systems, the solar energy is generally obtained in the form of heat, usually absorbed by a black body like surface such as surfaces coated with a thin film of black paint. To enable effective solar energy utilization, the absorption of the incident solar radiation should be maximized while the thermal losses from the collector minimized. Hence, the solar absorbing surface is one of the key components of a solar collector, and its optical properties and quality influence both the heat losses and gains. Therefore, it is important to develop a spectral-selective solar energy absorbing surface which is characterized by a maximum absorptance (α) over the solar spectrum (0.3–2.5 μm) and low thermal emittance (ϵ) at the operating temperature. This is translated by a low reflectance of absorbing surface in the solar main irradiation spectrum (nearly zero) and high reflectance (close to one) in the IR region. For practical reasons, a good selective coating features optical properties of $\alpha \sim 0.9$ and $\epsilon \sim 0.2$ [1]. More recently, many efforts have focused on developing new types of ceramic-metal nano-composite materials for improving their performance and thermal stability as solar selective absorbers [2]. Metal-dielectric composites, known as cermets, exhibit a strong absorption peak in the main solar radiation

region while remaining substantially transparent in the thermal infrared region. A large number of different metal-dielectric composites [3,4], of Cu, Au, Ni, Mo, Cr, Co, Pt, or W in SiO, SiO_2, Al_2O_3, or MgO have been studied as selective absorbers with certain detail, and some of them have reached commercial application. Electroplated black chromium, which employs a $Cr-Cr_2O_3$ cermet material, is the most widely used solar absorber of this kind [5,6], but preparation of a black chromium solar coating using an electroplating technique is not suitable due to environmental pollution.

In this paper, we describe the preparation of large surface coatings of black chromium-chromium (III) oxide cermet by an environmentally friendly and 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 [7,8]. 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 $Cr/\alpha-Cr_2O_3$ 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.

2. Experimental techniques

The growth of the monodisperse spherical particles of hydrated Cr_2O_3 was conducted according to Ref. 7. The synthesis was performed with reagent grade chemicals. An aqueous solution (MilliQ, 18.2 MΩ cm) of 1mM of chromium potassium sulfate dodecahydrate ($KCr(SO_4)_2.12H_2O$) at pH 6.5 mixed in a glass bottle with autoclavable screw cap (e.g., Duran laboratory) containing a rough copper substrate was heated in a laboratory oven at a constant temperature of 75 °C with different aging times. Subsequently, the durable and scratch resistant thin films are thoroughly washed with water to remove any residual salts. Afterward, the particulate coatings are heat treated in a flowing H_2 gas at 500 °C, based on thermal analysis data, for 1h to obtain $Cr/\alpha-Cr_2O_3$ quasi-monodisperse and spherically shaped core-shell particles. The structural characterization of $Cr/\alpha-Cr_2O_3$ cermet nano-coatings are investigated using Raman spectroscopy "model Horiba Jobin Yvon, LabRAM HR UV/Vis/NIR" and Perkin Elmer Spectrum one FTIR with diamond ATR accessory. 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". Diffuse reflectance spectra were recorded in the wavelength range 300–2500 nm using Varian Associated Cary 500 double beam spectrophotometer. The infrared emissivity (ε) was measured in the wavelength range of 3 to 30 μm by the D&S Emissometer, Model AE1 within ±0.01 emissivity units, which is close to the required prediction accuracy.

3. Results and descutions

3.1. Raman spectroscopic study

The Raman spectra of $Cr/\alpha-Cr_2O_3$ monodispersed spherical core-shell particles are depicted in Fig. 1. However, all the detected peaks exhibit only three E_g and one A_{1g} modes of chromium (III) oxide, and no Cr peaks due to its metallic behavior. Moreover, chromium (III) oxide has a corundum structure that belongs to the D^6_{3d} space group and consists of a hexagonal close packed array of oxide anions with 2/3 of the octahedral holes occupied by chromium. The site symmetry for the Cr atoms is C_3, whereas the O atoms are on sites having C_2 symmetry. The irreducible representations for the optical modes in the crystal are $2A_{1g}$, $2A_{1u}$, $3A_{2g}$, $2A_{2u}$, $5E_g$ and $4E_u$ vibrations with only two A_{1g} and five E_g vibrations are Raman active [9]. Hart *et al.* [10], in their Raman investigations of Cr_2O_3 single crystals, observed seven Raman bands. In this present work, we found that all peaks belonging to samples aged at 20, 30, 40 and 50h showed only three E_g and one A_{1g} modes of chromium (III) oxide (see Fig. 1). The observation of these only four modes in the samples could be caused by the polycrystallinity of $Cr/\alpha-Cr_2O_3$ (micron to nano)-spherical particles. On other hand, it is evident from figure 1 that Raman intensity increases with increase of ageing time and it become nearly constant after 50h in line with a

high crystallinity. These results reveal that the size and amount of the particles is nearly stable after 50h, this is also confirmed by the scanning electron microscopy results in our previous study on the growth kinetics of α-Cr_2O_3 spherical particles [8].
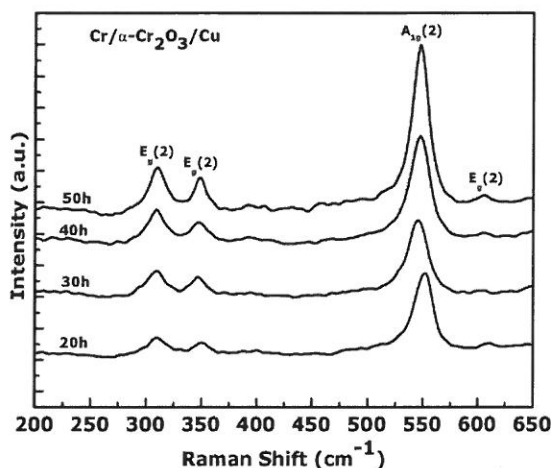

Figure 1. The Raman spectra of Cr/α-Cr_2O_3 monodispersed spherical core-shell particles

3.2. Attenuated Total Reflection (ATR) study

Figure 2 depicts the Attenuated Total Reflection (ATR) spectra for Cr/α-Cr_2O_3 monodisperse spherical core-shell particles deposited on copper at different aging time, and heated at 500 °C in a flowing H_2 gas. As one could notice that a gradual disappearance of Cr-O and O-O bands with increasing aging time is observed. This may be due to the black thin layer of chromium metal coated on the surface of the particles. Furthermore, samples aged for 20 and 30h reveal two strongest bands centered at 539 and 611 cm^{-1}. These values fall well within the range reported in the literature for samples having the exact α-Cr_2O_3 stoichiometry [11]. Both bands are associated with Cr–O stretching modes (symmetrical stretching and antisymmetrical stretching) in α-Cr_2O_3 and are due to various combinations of O^{2-} and Cr^{3+} displacements in the lattice. The pair of sharp bands at 442 and 411 cm^{-1} corresponds to two specific O^{2-} displacements in the lattice. From the ATR and Raman results we concluded the existence of pure α-Cr_2O_3. Moreover chromium metal doesn't show any peaks in the Raman/ATR spectra in the wave-number range studied which suggested the use of electron energy dispersive spectroscopy technique to investigate the existence of Cr as a shell in Cr/α-Cr_2O_3 monodisperse spherical core-shell particles
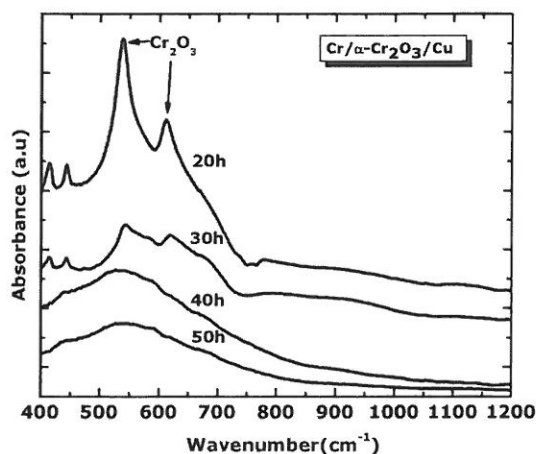

Figure 2. The Attenuated Total Reflection spectra for Cr/α-Cr_2O_3 monodisperse spherical core-shell particles

3.3. Scanning Electron Microscopy (SEM) and EDS analysis

SEM micrographs in the inset of Figure 3 reveal that the Cr/α-Cr_2O_3 coatings consists of spherical particles with an average size of about 498, 990, 1010 and 1185 nm respectively. This result demonstrated that Cr/α-Cr_2O_3 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-Cr_2O_3 monodisperse spherical core-shell particles by EDS shows that the coatings contain black chromium "see Figure 3", but since no chromium was found by Raman/ATR measurements, it is confirmed that the film contains 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-Cr_2O_3, 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. Figure 4 reports a comparison of EDS spectra acquired by positioning the electron probe through only the shell and through the core and shell "see Figures 4a and 4b", respectively. However, the atomic percent composition of the shell is 76.2 at.% chromium and 23.8 at.% oxygen. On the other hand, the atomic percent composition of the core is 29.6 at.% chromium and 70.4 at.% oxygen. It is apparent that the shell is dominated by Cr, while the core is rich in α-Cr_2O_3, suggesting that the shell of the large-size particle is Cr.
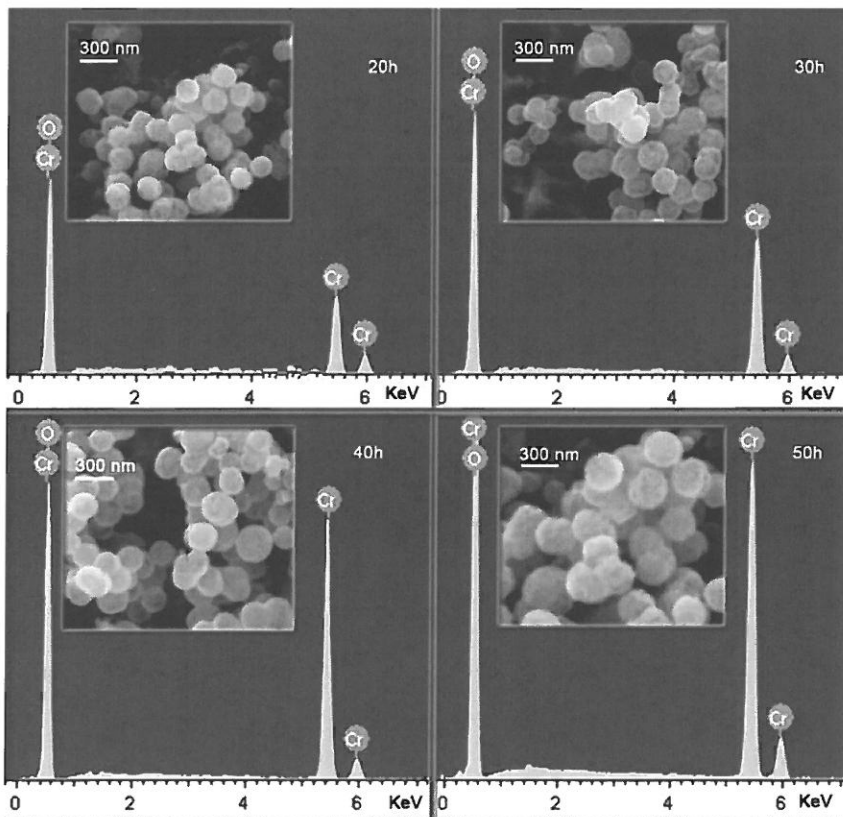

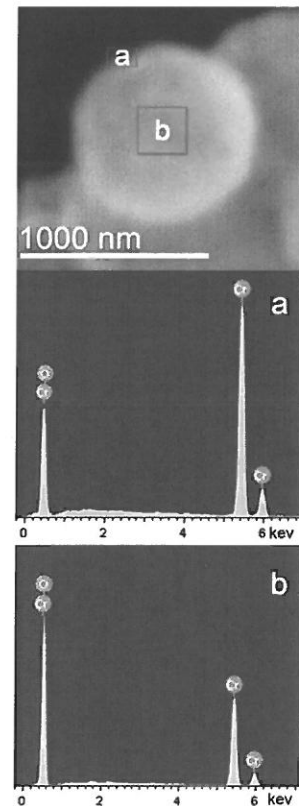**Figure 3.** SEM/EDS of Cr/α-Cr_2O_3 monodispersed spherical core-shell particles

Figure 4. Investigation of shell and core of one Cr/α-Cr_2O_3 monodispersed particle

3.4. Diffuse reflectance and the infrared emissivity (ε): preliminary study

Figure 5 represents the total diffuse reflectance "specular and non-specular reflectivities" of different samples over the UV-VIS-NIR spectral range. In general, very low reflectance spectra are obtained with samples aged for more than 40h at 75°C. Furthermore, it is observed that the spectral reflectance of the materials decreases with increasing aging time. A quantitative comparison of the total solar absorptance [calculated by numerical integration using measured total diffuse reflectance spectrum of figure 5 in the solar radiation region of 300–2500nm and the solar irradiance at Air Mass 1.5 (AM1.5)] and the measured infrared emissivity of all the samples is presented in Table 1. The absorptivity and emissivity of sample aged for high aging time t ~50h is very high, but its emissivity can be reduced by a suitable heat mirror such as SnO_2:F. For samples aged at lower aging time t~20h the absorptivity is relatively high and the emissivity low, hence such nano-coatings are potentially competitive for solar absorbers application. However, this difference in the optical properties is strongly dependent on the aging time of the samples and can be attributed to many factors such as the film microstructure, surface composition and morphology.
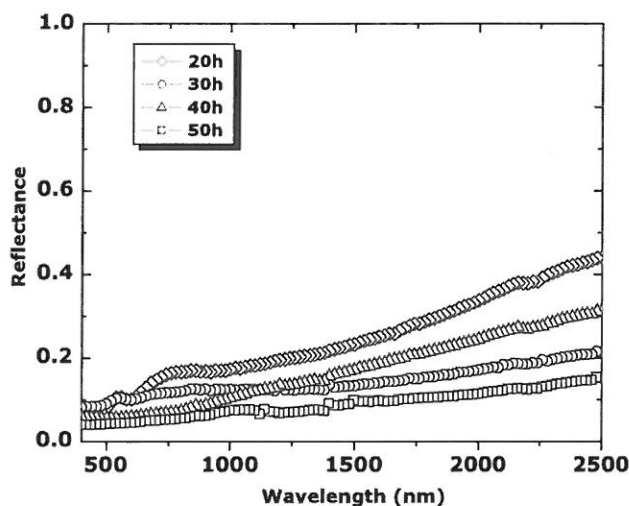

Figure 5. The total diffuse reflectance of different samples over the UV-VIS-NIR range.

	Aging time (h)	Absorptance (α)	Emittance (ε)
Sample 1	20	0.84	0.49
Sample 2	30	0.88	0.77
Sample 3	40	0.90	0.60
Sample 4	50	0.94	0.80

Table 1. The solar selectivity of Cr/α-Cr_2O_3 monodispersed spherical core-shell particles coated on Copper substrates

4. Conclusion

Chromium-Chromium (III) oxide $Cr/\alpha-Cr_2O_3$ monodispersed spherically shaped core-shell particles were deposited by simple self-assembly method with high adhesion to the substrate: the Aqueous Chemical Growth "ACG". This ACG technique has demonstrated that it is a potential method to produce reproducible high quality-low cost coatings. Samples deposited for longer aging time show high chromium percentage on the surface of the particles, high absorptivity and emissivity but this can be reduced by a suitable heating mirror. Samples deposited for lower aging time show high absorptivity and low emissivity. 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.

Acknowledgements

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