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Cr/\(\alpha\)-Cr\(_2\)O\(_3\) monodispersed meso-spherical particles for mid-temperature solar absorber application

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Abstract

Monodispersed meso-spherical particles of Cr/\(\alpha\)-Cr\(_2\)O\(_3\) cermet Aqueous Chemical Growth (ACG) coatings investigated within this contribution could be successfully employed in mid temperature solar absorber applications. Their selectivity depends on their chemical, physical and structural characteristics and related optical properties like reflectance, emittance, solar light absorption, or absorbance and transmittance. Parameters such as deposition temperature, pH of the initial precursor and substrate roughening will greatly influence their relevant optical properties as reported. The coated Cr/\(\alpha\)-Cr\(_2\)O\(_3\) spherical particles on rough Molybdenum and Tantalum substrates by a simple, green and cost-effective method were characterized by scanning electron microscopy, energy dispersive spectrometry, Raman spectroscopy, and diffuse reflectance UV-VIS-NIR spectroscopy. The samples deposited on Tantalum substrate exhibit the targeted high absorbing optical characteristic “Black chrome” while those deposited on molybdenum substrate show a significant high diffuse reflectance.

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1. Introduction

Efficient thermal solar collectors that convert incident solar radiation into useful heat, in applications such as water heating, drying and cooking, use a spectrally selective surface that maximize absorption of solar radiation and minimize thermal radiation losses [1, 2]. There are already high-performing selective surfaces but there are several difficulties with some of them, such as long-term durability, moisture resistance, adhesion, scratch resistance and costly technically advanced production techniques [3]. The most commonly used design is based on a selective solar-absorbing and infrared transparent layer on top of a substrate that has high infrared reflectance. The base material of solar absorbers (i.e. substrate) is often a metal with high thermal conductivity such as copper [4], molybdenum or Tantalum [3]. These metals fulfill the requirement of having high infrared reflectance and can therefore also act as the infrared reflector but are not resistant to the microclimatic conditions in a solar collector [5] if the absorbing coating on top is not also functioning as a protection layer. In order to make thermal solar collectors more accepted and widespread, the price per unit has to be reduced. The most costly component of a thermal solar collector is the spectrally selective surface. The cost has to decrease in order to make thermal solar devices more commercially interesting in developing countries where solar thermal energy still has a very low impact on the energy market. Moreover, the Advantages of the solution-chemical technique are that it is simple and easy to control, the coating can be manufactured under ambient pressure and temperature conditions, the chemicals involved are environmentally friendly and it is low in material consumption. Furthermore, Electroplated black chromium, which employs a Cr-Cr$_2$O$_3$ cermet material, is the most widely used solar absorber [6, 7], 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 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 [8, 9]. More accurately, we report results of an initial study of the influence of the substrate on the optical properties of the uniform fine “in the range nano to micron” spherically shaped core-shell particles of Cr/$\alpha$-Cr$_2$O$_3$.

2. Experimental techniques

The growth of the monodispersed meso-spherical particles of hydrated Cr$_2$O$_3$ was conducted according to Ref. 7. The synthesis was performed with reagent grade chemicals. An aqueous solution (MilliQ, 18.2 M$\Omega$ cm) of 1mM of chromium potassium sulfate dodecahydrate (KCr(SO$_4$)$_2$.12H$_2$O) at pH 6.5 mixed in a glass bottle with autoclavable screw cap (e.g., Duran laboratory) containing a rough Molybdenum and Tantalum substrates were heated in a laboratory oven at a constant temperature of 75°C for 24h. 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$_2$O$_3$ quasi-monodisperse and spherically shaped particles. The structural characterization of Cr/$\alpha$-Cr$_2$O$_3$ cermet nano-coatings are investigated using a X-ray diffractometer “model Bruker AXS D8 Advance” with irradiation from K$\alpha$ line of copper “\(\lambda=1.5406\) Å” and Perkin Elmer Spectrum one FTIR with diamond ATR accessory. The particles and the coating morphologies are investigated using a Leo-StereoS can 440 scanning electron microscope “SEM”. The chemical composition is determined using energy dispersive spectroscopy “EDS”. Diffuse reflectance spectra were recorded in the wavelength range 300–2,500 nm using Varian Associated Cary 500 double beam spectrophotometer. The infrared emissivity ($\varepsilon$) 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 discussions

3.1. Structural characterization

XRD patterns of Cr/$\alpha$-Cr$_2$O$_3$ particles deposited on molybdenum and tantalum substrates are shown in Fig. 1 and Fig. 2, along with the Miller indices of the crystallographic planes corresponding to each diffraction peak. 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 [10]. These peaks are attributed to Rhombohedral structure (space group R3c) with unit cell parameters a = 4.96070 and c = 13.59900 Å of α-Cr₂O₃ phase, while peaks denoted by stars belong to the used molybdenum and tantalum substrates. Moreover, no Cr peak shown in both cases may be due to its low concentration or to its amorphous nature [9].

3.2. Attenuated total reflection (ATR) study

Fig. 3 and Fig. 4 depict the Attenuated Total Reflection (ATR) spectra for Cr/α-Cr₂O₃ monodispersed meso-spherical particles deposited on molybdenum and tantalum substrates, respectively. Furthermore, both samples 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-Cr₂O₃ stoichiometry [11]. Both bands are associated with Cr–O stretching modes (symmetrical stretching and antisymmetrical stretching) in α-Cr₂O₃ and are due to various combinations of O²⁻ and Cr³⁺ displacements in the lattice. The pair of sharp bands at 442 and 411 cm⁻¹ corresponds to two specific O²⁻ displacements in the lattice. From the ATR and XRD results we concluded the existence of pure α-Cr₂O₃. Moreover Chromium metal doesn’t show any peaks in the ATR spectra in the wave-number range studied which suggested the use of electron energy dispersive spectroscopy (EDS) technique to investigate the existence of Cr in Cr/α-Cr₂O₃ monodisperse meso-spherical particles.
3.3. SEM and EDS analysis

SEM micrographs in the inset of Fig. 5 reveal that the Cr/α-Cr₂O₃ coatings consist of meso-spherical particles with an average size of about 498nm. 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 monodispersed meso-spherical particles by EDS shows that the coatings contain black chromium “see Fig. 5”, but since no chromium was found by XRD/ATR measurements, it is confirmed that the film contains chromium.

3.4. Diffuse reflectance and the infrared emissivity (ε)

Fig. 6 represents the total diffuse reflectance “specular and non-specular reflectivities” of Cr/α-Cr₂O₃ monodispersed meso-spherical particles deposited on molybdenum and tantalum substrates over the UV-VIS-NIR spectral range. Furthermore, it is observed that the spectral reflectance in our study depend on the used substrates. In general, very low reflectance spectra obtained with the sample deposited on Ta substrate. A quantitative comparison of the total solar absorptance [calculated by numerical integration using measured total diffuse reflectance spectrum of Fig. 6 in the solar radiation region of 300–2,500 nm 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 deposited on Ta substrate are very high 0.91 and 0.59 respectively, but its emissivity can be reduced by a suitable heat mirror such as SnO₂:F. For samples deposited on Mo substrate, the absorptivity is relatively high 0.87 and the emissivity low 0.45; hence such nano-coatings are potentially competitive for solar absorbers application. However, this difference in the optical properties is strongly dependent on the used substrates and can be attributed to many factors such as the film microstructure, surface composition and morphology [12-13].

Table 1. The solar selectivity of Cr/α-Cr₂O₃ monodispersed meso-spherical particles coated on molybdenum and tantalum substrates.

<table>
<thead>
<tr>
<th></th>
<th>Absorptance (α)</th>
<th>Emittance (ε)</th>
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<tbody>
<tr>
<td>Cr/α-Cr₂O₃/Mo</td>
<td>0.87</td>
<td>0.45</td>
</tr>
<tr>
<td>Cr/α-Cr₂O₃/Ta</td>
<td>0.91</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Fig. 5. SEM/EDS of Cr/α-Cr₂O₃ monodispersed meso-spherical particles deposited on very rough; (a) molybdenum and (b) tantalum substrates.

Fig. 6. The total diffuse reflectance in the UV-VIS-NIR range of Cr/α-Cr₂O₃ monodispersed meso-spherical particles.
4. Conclusion

Chromium-Chromium (III) oxide Cr/α-Cr₂O₃ monodispersed meso-spherically shaped particles were deposited using the Aqueous Chemical Growth “ACG” technique with high adhesion to the metallic substrates. This ACG technique has demonstrated that it is a potential method to produce reproducible high quality-low cost coatings. Samples deposited on tantalum substrate show high absorptivity and emissivity but this can be reduced by a suitable heating mirror. Samples deposited on molybdenum substrate show high absorptivity and low emissivity. As conclusion, these preliminary results indicate that this type of nano-coatings onto molybdenum or tantalum rough substrates, are good candidates for solar absorbers applications at temperature lower than 500°C.

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