Electrochemically grown cobalt-alumina composite layer for solar thermal selective absorbers

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A B S T R A C T

Due to its potential use as selective surface in solar thermal absorbers, cobalt has been electrodeposited into porous alumina obtained by anodization of aluminum sheet. A 3^2 factorial design has been applied to find out the effects of the electrochemical variables, electrodeposition time and applied cell potential, on optical properties and to optimize the solar energy selectivity of the obtained surfaces. Effective-medium optical models have been used to reproduce their reflectance spectra and to estimate the thickness of the different layers that form the selective surface.

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1. Introduction

Solar energy is an extensive low-intensity energy source whose economic feasibility relies on efficient collection, retention, and utilization [1]. The performance of a solar absorber in solar thermal harvesting is influenced by the optical properties of the surface employed to intercept the incident solar radiation [2]. For an effective solar energy collection, a selective surface as an absorber must be used. In the field of solar energy a selective absorber efficiently captures solar energy in the visible and the near infrared spectral regions while exhibiting poor infrared radiating properties. Solar selective surfaces are based on different physical principles, i.e., optical trapping, particulate coatings, composite films, absorbing semiconductor – reflecting metal tandem and multilayer thin films, or a combination of them [3].

Most of the commercial selective absorbing surfaces are based on metal–ceramic or metal–semiconductor composites, the so called cermets. Cermets can be formed by several techniques, i.e., electron beam coevaporation [4], sputtering [5] and spin coating [6]. Also an electrochemical approach [7,8] is commonly used to make these composites. It is a low-cost technique that works at room temperature and provides great control over all parameters that govern the formation of cermet nanostructures.

One common design of a selective solar absorber cermet type is based on the inclusion of metal particles into a dielectric porous substrate, such as porous alumina layer [2,9]. The porous alumina provides an ideal dielectric matrix for the nano-sized metal particles to produce a major absorption in the solar spectrum region. Porous alumina layers with inclusion of transition metals like Fe, Co, Ni, Cu, Au, Ag, Mo, Cr, and W have been widely studied [10–12] and in solar absorber applications it has led to a solar absorptance (α_s) of 0.93 and thermal emittances (ε_T) ranging 0.04–0.10 [7,13]. Metallized porous alumina has also others applications mainly for electronic nanostructured devices [14–17].

In order to obtain ordered pore arrays and pores with straight sidewalls, a double anodization process has been proposed by Masuda and Fukada [18]. Ordered pore arrays are useful when the porous alumina is used as template, for example, in the electrodeposition of metallic or semiconducting nanowires and nanorods with the aim of achieving electronic devices [19–22]. When alumina is used as a porous matrix to form cermets in solar thermal selective surfaces, pores do not need to be so straight nor to exhibit regular diameter, so in the present work a single anodization process has been carried out [7,9,11,23].

Comparatively to nickel, cobalt in porous alumina has been less studied as solar absorber [4,24]. These studies led to a solar absorptance (α_s) of 0.92 and thermal emittance (ε_T) of 0.28 [25]. In order to obtain effective solar absorbers, these values of thermal emittances need to be lowered. In the present work, we have optimized the electrodeposition process of cobalt metal inclusions

into a porous alumina layer obtained by a one step anodization process to generate a low-cost, structurally stable solar absorber with a high solar selectivity.

2. Experimental

Starting material for porous alumina is 1050A aluminum sheets, $(40 \times 80 \times 0.5 \text{ mm}^3)$. All substrates are first degreased by ultrasonic cleaning process in soapy distilled water for 10 minutes. Substrates are then electropolished at 20 V and 25 °C for 4 min in a standard electrolyte containing the relation 1:4 of ethanol: $HClO_4$ [11,26]. Afterwards, these are rinsed with distilled water.

Anodization process was exactly the same for all substrates and has been reported elsewhere [12,27]. It is conducted under constant cell potential, 15 V DC, using 2 M phosphoric acid at 25 °C as electrolyte for 15 minutes. The aluminum sheet serves as anode and a graphite plate $(6 \times 9 \times 2 \text{ mm}^3)$ as counter-electrode (cathode). This procedure led to a porous aluminum oxide layer with pore fraction about 60% by volume. The alumina thickness was about 700 nm with pore diameter of approximately 40 nm [23]. The formation of the cobalt nanorods inside of the alumina pores (see Fig. 1) is achieved by means of AC electrodeposition using a 0.2 M H_3BO_3+0.1 M $CoSO_4$+0.16 M $MgSO_4$, pH=4 electrolytic bath with a power frequency of 50 Hz and a voltage varying from 13 V to 15 V AC at 25 °C. [14,19,28,29]. The deposition time varied from 30 s to 50 s. A graphite plate $(6 \times 9 \times 2 \text{ mm}^3)$ served as counter-electrode (cathode).

Experimental characterization has been carried out with scanning electron microscopy (SEM), X-ray diffraction (XRD) and UV–vis–IR spectroscopy. Microphotography was carried out with a Helios 650 scanning electron microscope from FEI. Image analysis was used to estimate the pore size distribution using the Feret's diameter defined as distance between two parallel tangents on opposite sides of the image of a randomly oriented particle [30]. X-ray diffraction (XRD) spectra were obtained using Cu Ka radiation ($\lambda=1.5406$ Å) in a Philips X´Pert PRO MPD diffractometer (Bragg–Brentano). Spectral hemispherical reflectance and normal transmittance measurements were done in the UV–vis-NIR range (200–2500 nm) with a Cary 5000 spectrometer from Varian, provided with an integrating sphere of Spectralon, and in the IR range (2–17 μm) with a IFS66 FT-spectrometer from Bruker with an integrating gold sphere of 20 cm in diameter. The chemical composition in depth was studied by X-ray photoelectron spectroscopy (XPS) combined with sputter depth profiling (4 keV Ar$^+$) in a PHI 5700 equipment with a standard X-ray source, 15 kV, 300 W, Mg Ka (1253.6 eV). Spectra were handled with PHI-Access V.6 and Multipak software, both from Physical Electronics (Eden Prairie, MN). Atomic concentrations have been determined from C 1s, O 1s, Al 2p and Co 2p XPS peak areas by using Shirley background subtraction [31] and sensitivity factors provided by the spectrometer

manufacturer (Physical Electronics). The 4 keV Ar$^+$ sputter rate is supposed to be 1.85 nm/min as determined from a 100 nm SiO_2 layer.

3. Results and discussion

Different anodization conditions lead to different pore diameters, wire lengths and spaces between pores. However, under specific conditions, highly ordered hexagonal pore arrays can be produced. With a 10 wt% phosphoric acid solution and an anodization voltage of 160 V at 3 °C, periodic arrangements of almost perfect hexagonal ordered domains over a wide range of distances can be obtained [32]. With the intention of reducing costs and thinking in future industrial upscaling, the anodization was carried out at room temperature of about 25 °C. When changing the temperature, the applied potential should also be changed to obtain an adequate pore size and distribution.

In order to find the electrodeposition conditions that would lead to the best combination of optical parameters, i.e. solar absorptance α_S and thermal emittance ε_T, that define the characteristics of the anodized surface as a solar absorber, the experimentation was planned as a full factorial design of 3^2. The selected design factors were electrodeposition time (t_d) and applied cell potential (E_d); the responses are α_S and ε_T. Table 1 shows the real and symbolic values of electrodeposition time and cell potential used for cobalt electrodeposition.

3.1. Morphological and structural characterization

Fig. 2 shows FE-SEM micrographs of the aluminum substrate (before and after the electropolishing treatment) and of the synthesized porous alumina layer. It can be seen that before the electropolishing procedure (Fig. 2a), the aluminum substrate exhibits several grooves due to the mechanical procedure used in the fabrication of the commercial aluminum sheets. However, after the electropolishing process these grooves disappear and the surface becomes less rough. A homogeneous reticular pattern can be seen after electropolishing (Fig. 2b), which can be due, as

Table 1
Symbolic and real values of time and cell potential.

Factor	Level	Value
Cell potential	−1	13 V
	0	14 V
	+1	15 V
Time	−1	30 s
	0	40 s
	+1	50 s
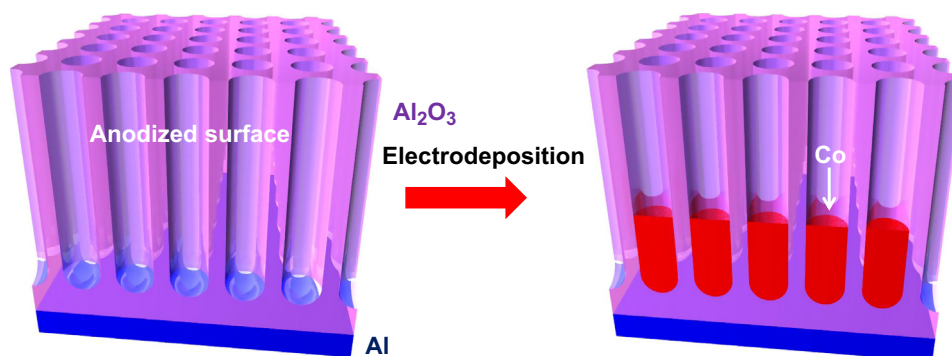
Fig. 1. Artist view of the anodized surface before and after cobalt electrodeposition.