Optical, structural and thermal characteristics of Cu–CuAl₂O₄ hybrids deposited in anodic aluminum oxide as selective solar absorber

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A new selective solar absorber coating of Cu–CuAl₂O₄ hybrids deposited in anodic aluminum oxide (AAO) on aluminum substrate has been prepared through an electrochemical process. The structure, clarified by computer modeling, featured graded layers with increasing refractive index from the surface to the bottom, of which an overall optical performance of absorptance ($\alpha = 0.923$) and emittance ($\varepsilon = 0.06$) was achieved. The stability of the absorber was tested at high temperature and condensation at high humidity. While $\alpha$ decreased after annealing at 200 °C in air for 24 h, $\varepsilon$ was slightly influenced; the absorber showed high selectivity ($\alpha/\varepsilon$) of 0.87/0.04. Even after exposing to 300 °C for 48 h, the optical property did not change. XRD analysis showed that crystalline structure of the hybrids did not change after annealing treatment; probable reasons for the optical degradation are presented. Condensation also caused a decrease of absorptance by cracking the surface, but a good selectivity of 0.86/0.03 was obtained.

In addition to the metal–ceramic composites, metal–semiconductor absorbers are also applicable for selective coating. Of this class, black copper coating [6,7] is very attractive for solar thermal application. The band-gap energy of cupric oxide ($E_g = 1.45$ eV) is closer to the optimum cut-off wavelength of an ideal collector ($E_g = 0.5$ eV) compared to other semiconductors [8]. The coating is generally described as two layers: a dense copper oxide layer with metallic copper inclusion next to the substrate and a porous outer layer of copper oxide dispersed in air. This structure could realize a high solar absorptance of 0.98 and a relative low emittance of 0.3; however, a substantial decrease of absorptance to 0.8 was found when the coating was exposed to temperatures above 150 °C in air, which is mainly caused by the decreased surface roughness [9].

Our strategy was to take advantage of the considerable optical characteristics of black copper absorber and porous alumina as an ideal low refractive-index matrix, and to generate a low-cost, structurally stable selective solar absorber of desirable selectivity. This could be realized by depositing copper into the AAO nanotubes with optimized depth indicated by computer modeling. When exposed to high temperature, metal component adjacent to air could be oxidized to cupric oxide (CuO) in this case, resulting in black-copper-like absorbing composites in the alumina matrix. As presented in this paper, a metal–semiconductor composition of CuAl₂O₄–Cu hybrids was finally fabricated in the AAO nanotubes. Optical characteristics of the hybrids deposited AAO exhibited desirable selectivity ($\alpha/\varepsilon = 0.923/0.06$). Structural stability concerning the oxidation of metallic Cu at high temperature was observed in the presence of CuAl₂O₄.

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1. Introduction

Spectrally selective absorbers used in solar collector are known to improve the efficiency of solar–thermal conversion. A desirable selective absorber is characterized by maximum absorptance ($\alpha$) over the solar spectrum (0.3–2.5 μm) and low thermal emittance ($\varepsilon$) at the operating temperature. This is realized by 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 reason, a good selective coating features optical properties of $\alpha > 0.9$ and $\varepsilon < 0.2$ [1].

Most of the successful selective absorbing surfaces are metal–ceramic or metal–semiconductor composites. Electrochemical approach is commonly used to fabricate the metal–dielectric composites. The common design of a selective solar absorber is based on the deposition of metal particles into a porous substrate, such as anodic aluminum. The porous alumina provides an ideal dielectric matrix for the nano-sized metal particles, which provides a major absorption in the solar region. Ni [2], Cr [3] or Co [4] pigmented porous alumina is a well known selective absorber for its high absorbance and low emittance at low temperature ($T < 100$ °C). However, degradation tests show a significant decrease of solar absorbance mainly due to oxidation of metal particles at high temperature and humidity [5].
2. Experimental work

2.1. Porous alumina preparation

The procedures for producing porous alumina have been reported elsewhere [10]. Briefly, aluminum foil (99.9%) was first annealed in air at 500 °C for 4 h in a furnace. Then Al piece, 3 cm × 3 cm in size, was degreased by acetone in ultrasonic for 5 min, rinsed in distilled water and electropolished in a mixture of ethanol and perchloric acid. Anodization was carried out in a 2.5 M phosphoric acid at 20 °C for 20 min under a voltage of 15 V against a graphite counter electrode. This procedure produced a porous aluminum oxide layer of pore fraction about 30% by volume. The alumina thickness was about 700 nm with pore diameter of approximately 40 nm.

2.2. Electrodeposition

The electrolyte consists of 35 g/L CuSO₄, 20 g/L MgSO₄, and boric acid. Magnesium sulphate has been found to improve the stability of anodic oxide film by preventing the breakdown of barrier layer. The solution was buffered with boric acid during electrodeposition to maintain a pH value of 3–4. Electrodeposition was carried out under a voltage of 13 V a.c. and frequency of 200 Hz, and the duration was varied to achieve the desired length of deposited composites.

3. Characterization

Phase identification was performed by means of X-ray diffraction (XRD) using a D8 ADVANCE X-Ray Polycrystalline Diffractometer (Bruker, Germany) with Cu Kα radiation (λ = 0.154056 Å). Scanning electron microscopy (SEM) images were acquired on a SIRION 200 scanning electron microscope (FEI, USA) equipped with an INCA energy dispersive Spectrometer (EDS) system (Oxford Instrument, UK).

The optical measurements in the wavelength range 0.3–2.5 µm were made in a Perkin–Elmer λ = 950 double-beam spectrophotometer equipped with an integrating sphere. The total reflectance was measured relative to a BaSO₄ reference and the solar absorptance was calculated using ISO standard 9845-1, normal radiance, AM1.5.

The infrared near normal specular reflectance was measured between 2.5 and 25 µm with a Bruker Equinox 55 double-beam spectrophotometer. An evaporated gold mirror was used as reference. Thermal emittance was calculated from the reflectance measurements using a surface temperature of 100 °C.

4. Computer modeling

A structural mode was established to calculate the optical properties of CuAl₂O₄–Cu deposited AAO on aluminum substrate. Generally, the optimized film can be divided into three layers: close to the Al substrate is a barrier layer composed of dense Al₂O₃ with a thickness less than 10 nm, which is insufficient to play a very subordinate role with regard to the optical performance; the barrier layer is coated with an absorbing layer composed of CuAl₂O₄–Cu and Al₂O₃ matrix; on top is a layer of porous Al₂O₃ as antireflection layer.

The reflectance spectra were calculated using a computer program called CODE [11]. Bruggeman (BR) model [12] was applied to calculate the dielectric function of composites. Since the dielectric function of CuAl₂O₄ was unavailable yet and the main component of the hybrids was metallic Cu, the CuAl₂O₄–Cu deposited AAO was approximately regarded as a binary composition of Cu and Al₂O₃ in optical modeling. This settlement was found reasonable by comparing the calculated and experimental results.

5. Results and discussion

5.1. Sample characterization

From the SEM image (see Fig. 1) of Cu–CuAl₂O₄ hybrids deposited AAO, the overall thickness of deposited hybrids was not uniform, ranging from 300 to 500 nm, which could be explained with an uneven distribution of electric field caused by asymmetric depth of barrier layer and pore size during electrodeposition.

The crystalline characteristic of electrodeposited porous Al₂O₃ was investigated through XRD. As shown in Fig. 2, the XRD pattern of as-synthesized sample showed that the deposited particles were composite of spinel CuAl₂O₄ and Cu, apart from pure metallic Cu. The probable mechanism for the evolution and growth of the hybrid structure was discussed in the previous work [13]. After annealing at 300 °C for 24 h, the main peaks changed merely, and no apparent peaks corresponding to CuO arise, indicating that the Cu particles are oxidation resistant in the presence of CuAl₂O₄. It has been reported that the spinel CuAl₂O₄
could prevent noble metal from sintering under high temperature [14]. In this case, it seems that CuAl₂O₄ plays a role of protecting Cu against oxidation.

5.2. Optical characterization

The optical reflectance spectra of the simulated and experimental samples are shown in Fig. 3. Similar to the simulation result, the Cu–CuAl₂O₄ hybrids deposited alumina exhibited a good selectivity (α/ε) of 0.923/0.06 at 100 °C. As suggested by the SEM image, the thickness of Cu–CuAl₂O₄–Al₂O₃ layer was not strictly in accordance with the simulation setting, and rather thicker than what supposed to be; however, the unexpected increase of absorber layer thickness was not consecutive in 3D view. Actually, the Cu–CuAl₂O₄–Al₂O₃ absorber layer could be divided into two sub-layers: densely and loosely filled porous Al₂O₃ above, which can be described as low metal volume fraction (LMVF) and high metal volume fraction HMVF absorbing layer. The structure of two absorbing layers [15] is believed to reduce reflectance significantly and, moreover, improve the selectivity. The result of Fig. 3 proved the reasonability of this explanation, significant increase of thermal emittance brought by increase of thickness was suppressed.

Fig. 4 shows reflectance spectra of a sample after exposure to high temperature annealing. Reflectance of the sample in the visible region did not show any change after annealing at 200 °C for 24 h, while the onset of reflectance obviously shifted toward the lower wavelength in the near-infrared region compared with the original sample, resulting in a reduced absorptance of 0.86 at emittance of 0.04. When the temperature was increased to 300 °C for 24 h more, obvious changes of reflectance were not observed anymore. This result is somewhat consistent with the original assumption that high temperature may cause limited optical changes, but in a totally different way. Since oxidation of Cu was restrained, the optical changes were not caused by composite transformation—metallic Cu to Cu/CuO. Instead, the as-synthesized composite has been already of metal/semiconductor nature by itself, which was stable during annealing at 300 °C. Although adequate evidences are not available yet, possible explanation may involve the slight structure changes caused by transformation of poorly crystalline pseudo-boehmite to Al₂O₃ [16].

5.3. Accelerating test

It has been shown that degradation of the solar absorptance occurs after hours of annealing at 200 °C. A decrease of absorbance from 0.92 to 0.87 was observed for a sample after 24 h annealing, and the thermal emittance was decreased from 0.06 to 0.04. When the temperature was increased to 300 °C, which was the stagnation temperature for most domestic solar collector, both absorptance and emittance changed slightly. Even after 48 h of continued annealing, the optical performance of the sample was not altered anymore, implying that the coating surface can endure at a temperature of 300 °C.

Condensation also caused decrease of solar absorptance by cracking the surface, as the cases for most of the metal pigmented Al₂O₃. After being exposed to 100 °C hot water for 24 h, reflectance spectra were found to blue-shift, as shown in Fig. 5, leading to decreased solar absorptance. As a result, a reduced selectivity of 0.86/0.03 has been obtained. The vulnerability of Al₂O₃ to humidity at high temperature shall be tackled by applying a layer of protective layer [17].

6. Conclusion

A new selective solar absorber was prepared through electrodeposition into AAO of Cu and CuAl₂O₄. XRD of the sample showed that the hybrids were composite of spinel CuAl₂O₄ and
crystalline Cu. While optical performance mainly depended on the intrinsic absorption of Cu nanoparticles, CuAl₂O₄ played a role of protecting Cu from oxidation at high temperature. The as-synthesized sample showed an excellent selectivity \( \frac{\alpha}{\varepsilon} \) of 0.923/0.06, which was consistent with the computer simulation. When annealed at high temperature, the absorptance decreased to 0.87 to a maximum extent at 300 °C, while emittance was slightly reduced, indicating the potential use of this absorber at the working temperature of 300 °C.

Condensation also caused absorption loss to the sample by cracking the Al₂O₃ surface, which was a common problem for other metal pigmented Al₂O₃. This could be prevented by applying a protective layer on the surface. Optimization of the Cu–CuAl₂O₄ deposited AAO is expected to promote its optical performance and anti-corrosion at high temperature and humidity.

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References