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Aqueous solution-chemical derived Ni—Al_2O_3 solar selective absorbing coatings. 2. Wetting agents and spreading of aqueous solutions on aluminum substrate

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ABSTRACT

Wettability of aluminum substrate by the aqueous solutions containing ethoxylated alcohol nonionic surfactants $C_{12}E_n$- or Triton X-series was studied using dynamic contact angle measurements. The efficiency of wetting was found to strongly depend on the length of polyoxyethylene (POE) chain of $C_{12}E_n$- or Triton X surfactants. For $C_{12}E_4$ that has a very short POE chain, it hardly made the aqueous solution spreading over aluminum. The others with a long POE chain were indeed very efficient in promoting the solution spreading. Moreover, all the spreading process could be completed within 10 s. The single-layer Ni—Al_2O_3 coatings were fabricated from the precursor solutions containing $C_{12}E_n$- or Triton X surfactants and the reflectance spectra were measured by a UV/vis spectrophotometer equipped with an integrating sphere. The results indicated that the precursor solution with a long POE chain surfactant as wetting agent favored to fabricate a uniform film on the aluminum substrate and therefore to get a high solar absorptance.

1. Introduction

Al_2O_3-based cermet coatings have excellent optical properties and thermal stability, and have been widely used as solar absorber surfaces [1–7]. Recently, the solution chemical method for fabricating Al_2O_3-based cermet coatings has attracted much attention [8–16] since this method is very simple and easy to perform and also has a considerably low cost in comparison with the usual sputtering preparation. Westin et al. reported a solution-chemical method to fabricate Ni—Al_2O_3 coatings, in which aluminum isopropoxide (AIP) was used to form alumina precursor solution in polar organic solvent such as methanol, ethanol and isopropanol and this solution was mixed with the Ni-salt solution, after the coating formed on aluminum substrate the Ni-salt was reduced into nano-sized nickel particles under 500–600 °C and N_2 atmosphere [8]. Subsequently Boström et al. also studied the methanol-based solution-chemical method [9–12]. After Boström's work, we prepared the Ni—Al_2O_3 coatings with promising optical properties according to a similar procedure but using ethanol as solvent [13,14]. Very recently, we further developed the solution-chemical method in water to fabricate Ni—Al_2O_3 coatings [15,16]. In this approach, the nitrate salts of aluminum and nickel and a chelating agent (citric acid) were used to produce homogeneous precursor solution. Of course, a wetting agent is also necessary so as to well spread the aqueous solution over aluminum substrate. Under 500–600 °C and N_2 atmosphere, aluminum ions were converted into Al_2O_3 matrix [17] and nickel ions were in situ reduced into nano-sized nickel particles embedded in Al_2O_3 matrix [15]. The optimum single layer attained a high total solar absorptance of 0.85 and a total thermal emittance of 0.03 [15]. Furthermore, a practical three-layer coating, i.e. double absorption layers together with one top anti-reflection layer was fabricated, the solar absorptance of which was as high as 0.93 [15].

For an optical absorbing coating, its homogeneity is of utmost importance because it can induce significant interference-induced absorption. In the solution-chemical method, the homogeneity depends on the homogeneous dispersion of solute in the solution and its matching with the substrate, in which the former has been achieved by introducing suitable chelating agent in the formula. Aluminum has high infrared reflectance, high thermal conductivity and low cost and hence was often used as the substrate of solar absorbing coatings. Most metals and their oxides have high surface free energies ranging from several thousand to several hundred mN/m [18]. This seems to indicate that the spreading of aqueous solution over aluminum metal substrate is very easy and, however, the fact is not as simple as imagined. Many authors found that the wetting behavior of aqueous solution on the high energy surface of hydrophilic solid such as quartz was even rather complex [19,20]. The pioneer investigations have revealed that a water film was first formed on the solid surface by water vapor adsorption or water

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molecules diffusion when water drop was settled on [19]. This decreased solid surface free energy to a low level and yielded a finite contact angle for water drop, which hindered the following spreading of aqueous solution over it. In other words, the wetting ability of aqueous solution does not well match the aluminum substrate, resulting in defects (unhomogeneity) in the coating. Therefore, the wetting agent which can promote spreading is essential for the fabrication of a fine coating. Nonionic surfactants, polyoxyethylene alkyl ethers, were commonly used as wetting agents [19,21]. The molecular structure of the nonionic surfactants such as the length of hydrophilic chain as well as the branching or not in the hydrophobic part has been known to significantly affect their adsorption and spreading on the solid surface [18,21]. The purpose of this work is to understand the wettability of aluminum substrate by aqueous solutions containing different nonionic surfactants. This is an important basis for developing the aqueous solution-chemical method in the fabrication of Al_2O_3-based cermet coatings.

2. Experimental

2.1. Materials

Ethoxylated alcohol surfactants $CH_3(CH_2)_{11}(OCH_2CH_2)_n$—OH (EO number n = 4, 10, 23, respectively, referred below as $C_{12}E_4$, $C_{12}E_{10}$, $C_{12}E_{23}$) and $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_n$—OH (average EO number n = 10, 30, referred below as Triton X-100 and Triton X-305) were purchased from Sigma and Merck, respectively, and used as received. All the surfactant solutions were prepared with Milli-Q water (resistivity = 18.2 MΩ cm^{-1}).

The aluminum plates used as the substrates were treated by ultrasonic wave in a bath filled with phosphoric acid solution of 1.5 mol L^{-1} at 50 °C for 20 min to etch away Al_2O_3 layer on the aluminum. Then the substrates were rinsed thoroughly in distilled water and dried by blowing with N_2. In order to inhibit from oxidation, the contact angle measurements were performed immediately after the substrates were treated.

2.2. Coating procedure

The precursor solution preparation was described in our previous work in detail [15]. The coatings were prepared by a spin coater KW-4A manufactured by Institute of Microelectronics, China. The precursor solution was dispensed onto the center of the aluminum substrate (35 mm × 35 mm) and spun on it at a slow spin rate of 500 rpm. After the substrate was covered with precursor solution, the spin rate of the substrate was increased to 2000 rpm and the spinning process was continued for 30 s, during which the excess solution was forced off and a uniform wet coating was formed. The wet coating was dried at 80 °C and heat-treated at 600 °C under N_2 atmosphere for 1 h. The coating thickness was controlled by the total metal ion concentration in the precursor solution which determined the solution viscosity.

2.3. Measurements

Dynamic contact angles were measured by the sessile drop method in an optical angle meter OCA-20 equipped with a video camera which collects up to 50 images per second (Dataphysics Instruments GmbH, Germany). The measuring chamber was kept at a constant temperature of 25 ± 0.1 °C and about 45% relative humidity. Drop of water or aqueous surfactant solution of accurate 2 μL was dosed by electronic syringe and hung on the needle tip, and then the substrate was carefully moved up until the drop set down to the substrate, by which the inertial effects can be minimized. The whole dynamic process was recorded by the video camera. By the method, the calculation of contact angle was done after the movie was stored, which allowed us to analyze the whole wetting process. Deposited drop of 2 μL was considered small enough for gravitational effect in wetting to be negligible. At the same time, since equilibrium contact angles were reached within 10 s at these experimental conditions (see the discussion in Section 3.2), no notable evaporation took place. Therefore, the contact angles used here were directly deriving from measurement results without correcting. The accuracy of the measurements was ±1°.

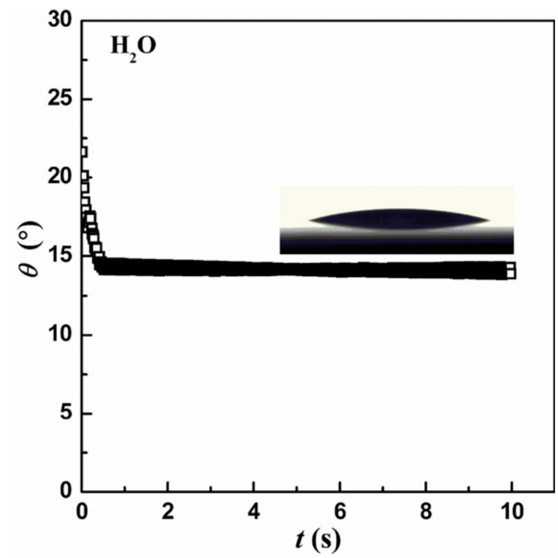

Fig. 1. Dynamic contact angles for pure water on hydrophilic aluminum surface and the appearance of water drop at equilibrium state.

Reflectance in the wavelength interval 0.3–2.5 (m was measured by a PerkinElmer Lamda 900 UV/vis/NIR double beam spectrophotometer equipped with an integrating sphere. The data were used to calculate the total solar absorptance according to Eq. (1) defined as

$$\alpha_s = \frac{\int_{0.3}^{2.5} I_s(\lambda)(1 - R(\lambda))d\lambda}{\int_{0.3}^{2.5} I_s(\lambda)d\lambda} \quad (1)$$

where I_s (λ) is the solar spectral radiation of AM 1.5, $R(\lambda)$ is the measured reflectance at a specific wavelength λ.

3. Results and discussion

3.1. Contact angles of water on aluminum substrate

Although most metals and their oxides belong to high-energy hydrophilic solids, it is still hard to guarantee the good spreading of water over the metal substrate. For example, the contact angle of water on aluminum even attains 14° (Fig. 1). As revealed in the pioneer works, this is attributed to the water film formation on the hydrophilic solid surface before the spreading of water through water vapor adsorption or water molecules diffusion from the water drop [19]. The water film covered on solid surface reduces the surface-free-energy of the solid to a low level and hinders the following spreading. This is why we have to add a wetting agent into the solution for the fabrication of Al_2O_3-based cermet coatings. Apart from promoting spreading, wetting agent also favors to produce a crack-free coating since it decreases surface tension of solution.