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Thermal control coatings on magnesium alloys prepared by plasma electrolytic oxidation

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ABSTRACT

Four kinds of oxide coatings with different solar absorptance properties were prepared on AZ91D magnesium alloys by plasma electrolytic oxidation. They were of different colors due to the different additives in the electrolytes. The microstructure and composition were characterized by scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS) and X-ray diffraction (XRD), respectively. The optical properties were investigated by the UV-VIS-NIR spectrophotometer, and the thermal control properties were measured by solar spectrum reflectometer as well as emissivity tester. Results showed that the solar absorptance of the coatings ranged from 0.439 to 0.918 while the emittance remained unchanged.

1. Introduction

Materials with light weight are in great need for spacecraft application for the purpose of saving energy nowadays [1]. Magnesium alloys are a kind of promising materials in automotive, aerospace and electronic industries for their low density (about 2/3 that of Al) and high strength/weight ratio, etc. [2]. However, the operation of spacecraft faces great challenges. They have to experience the extreme temperature cycling between the area with direct sunlight and the shaded area with the thermal gradient of several hundred degrees, which reduces its efficiency and handicaps its normal running [3]. The temperature of the devices is passively regulated by the radiation exchange between the surface and the environment, for the absence of atmosphere [4]. It can be controlled primarily by the ratio of solar absorptance (α_s) and emittance (ε) on the surface, namely α_s/ε. Thermal control coatings are of great importance in maintaining the equilibrium temperature of the spacecraft through regulating α_s/ε ratio [5]. Lots of the thermal control coatings used in the electronic housing packages of spacecraft were conventionally fabricated on aluminum alloys through anodizing oxidation [6,7,3,8]. As one of the anodizing methods, plasma electrolytic oxidation presents some apparent advantages compared with the traditional anodizing oxidation. It is a novel technique to fabricate thick and hard functional ceramic coatings on aluminum and magnesium alloys [9]. The electrolyte for PEO is usually less toxic, the cost of the preparation process can be reduced and the process itself can be simplified [5].

Thermal control coatings prepared by plasma electrolytic oxidation bring increased interest to researchers. The study results of Wu et al. [10–12] showed that the solar absorptance (α_s) and emittance (ε) could be changed through adjusting the current density, frequency, pulse duty as well as the composition and concentration of the electrolyte. The research of Tang et al. [13] indicates that the emittance of the PEO coatings increases with the content of Fe_2O_3 in the coating, and this can be regulated through the concentration of $FeSO_4$ in the electrolyte. They pointed out that the emittance is also affected by other factors like the roughness, microcavities and thickness of the PEO coating. However, most of the researches at present focus on a kind of PEO coatings with single colors or just making a list of the thermal control properties of different coatings. The variation of thermal control properties is not obvious just through changing the concentration of additives in the electrolyte or the process parameters. To the best of our knowledge, few investigations are about the effect of colors of PEO coatings on their thermal control property, especially coatings on magnesium alloys. The current work changes the kinds of additives in the electrolyte aiming at adjusting the spectroscopic and thermal control property of the PEO coatings on magnesium alloys to vary in a wide range. The four kinds of PEO coatings with distinct colors, optical and thermal control properties are expected to be employed under different circumstances or spacecraft of

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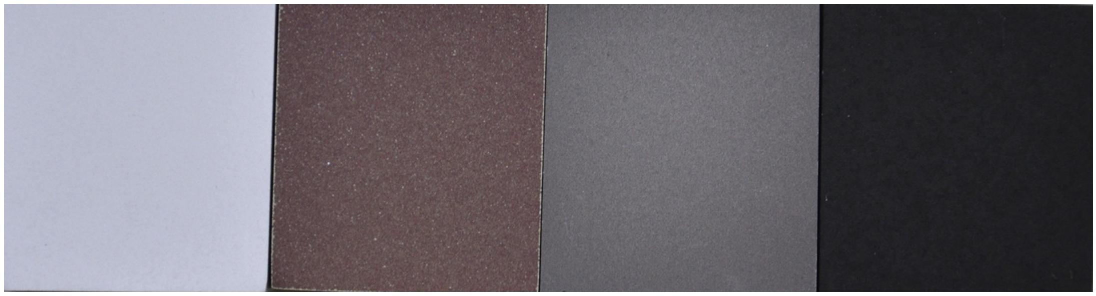

Fig. 1. Macrograph of PEO coatings prepared from different electrolytes. (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)

different parts to maintain the expected certain equilibrium temperature. The operation of spacecraft then can be normally carried on without affecting its efficiency under this circumstance.

2. Experimental details

AZ91D magnesium alloys were employed in this research. Its composition is shown in Table 1. The samples before PEO treatment were cut into a dimension of 50 mm × 40 mm × 10 mm and polished with 800 and 2000 mesh SiC abrasive papers. A pulsed bipolar power source was employed for the PEO process. Four 1.5-L baths composed of sodium silicate and potassium hydroxide with different additives were prepared. The detailed composition of the baths is shown in Table 2. The process was carried out in a stainless steel container equipped with a Cu cooling coil, and the temperature of the solutions was kept at 20 ± 2 °C through flowing water. The stainless steel acted as the cathode, while the specimens acted as the anode. All PEO processes were operated under positive current density of 4.5 A/dm^2. The negative current density in Cu0.5 electrolytes was zero while the other three coatings were prepared with negative current density of 2.3 A/dm^2. The specimens after PEO treatment were rinsed with distilled water and dried in warm air (around 40 °C). The thickness of the four PEO coatings was kept the same by modulating the deposition time. The relevant electrical parameters were also listed in Table 2.

The surface and cross-sectional appearance was characterized by JEOL JSM-5600LV scan electron microscope (SEM) equipped with energy-dispersive spectrometer (EDS, KEVER). D/Max-2400 X-ray diffractometer with Cu-Kα radiation was used to investigate the phase composition. The scanning is within $2\theta = 20^\circ$–80°, at a grazing angle of 2°. The percentage area of porosity on the surface was calculated for three times by OLYCIA m^3 image analysis software for each of the coatings, and the average values were used to represent the level of the coating porosity.

The emittance of the coating was measured by RD-1 emissivity tester at room temperature. The total solar absorptance was measured by SSR-ER solar spectrum reflectometer. The optical properties of the coatings in the 0.2–2.5 μm wavelength region were characterized by Perkin-Elmer Lambda 950 UV–VIS-NIR spectrophotometer with a barium sulfate coated integrating sphere. The theoretical value of total solar absorptance was calculated by the following equation [14].

$$\alpha_s = \frac{\int_0^\infty (1-\rho_\lambda)E_s(\lambda)d\lambda}{\int_0^\infty E_s(\lambda)d\lambda} \quad (1)$$

where α_s is the total solar absorptance. ρ_λ is the spectral reflectance at the wavelength of λ (0.2–2.5 μm). $E_s(\lambda)$ is the spectrum intensity of solar irradiance.

Table 1
Nominal composition of AZ91D magnesium alloys (wt.%).

Al	Zn	Mn	Others	Mg
8.5–9.5	0.45–0.90	0.17–0.4	0.08	Balance

Table 3
Porosity analysis results of PEO coatings prepared from different electrolytes.

Coating	Percentage area of porosity (%)
Si	1.87
Cu0.5	6.52
W2	12.72
V8	9.03

3. Results and discussion

3.1. Morphologies and structure

The macrograph of the four PEO coatings with different additives is shown in Fig. 1. It can be seen that the coatings prepared from Si, Cu0.5, W2, V8 electrolytes are white, red, gray and black in color, respectively. Fig. 2 presents the typical surface morphologies of the PEO coatings. The four coating surfaces exhibit different levels of porosity. The percentage area of surface porosity calculated by OLYCIA m^3 image analysis software measurement is listed in Table 3. It can be seen that there are less and small pores on the Si surface (Fig. 2a), while the Cu-containing surface is with pores of larger number but smaller sizes (Fig. 2b). The morphology of the W2 coating surface in Fig. 2c is poorer than the other three. It is rich in pores with large sizes, and the percentage area of porosity is the biggest among the four coatings (as high as 12.72%). The V8 surface is also with the typical porous microstructure of PEO, the pores are larger than that of the Si and Cu0.5 coating, but are still smaller and less than W2. The difference in the microstructure is decided by

Table 2
The electrolyte composition and processing parameters of different coatings.

Code	Electrolyte composition	Breakdown voltage (V)	Final voltage (V)	Deposition time (min)
Si	10.0 g/L Na_2SiO_3 + 1.0 g/L KOH	430	500	45
Cu0.5	10.0 g/L Na_2SiO_3 + 8.0 g/L KOH + 20 g/L KF + 0.5 g/L $Cu(Ac)_2$ + 100 mL $NH_3 \cdot H_2O$	380	400	10
W2	10.0 g/L Na_2SiO_3 + 1.0 g/L KOH + 2 g/L Na_2WO_4	450	490	30
V8	10.0 g/L Na_2SiO_3 + 1.0 g/L KOH + 8 g/L Na_3VO_4	430	500	40