J Mater Sci (2007) 42:7251–7255
DOI 10.1007/s10853-007-1507-z

The influence of the oxidation time on the optical properties of the ceramic thermal control coating prepared by micro-plasma oxidation

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Received: 16 September 2006 / Accepted: 9 January 2007 / Published online: 10 May 2007

Abstract The ceramic thermal control coating was produced in situ growth on the aluminum alloy by micro-plasma oxidation method. The coating possessed stable optical properties, high microhardness, and excellent adhesive power, low cost and so on, which can be widely used in the thermal control system of the spacecraft. In this article, the influence of oxidation time on the solar absorptance and emittance of the coating had been studied. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the phase composition and microstructure of the coating. The results show that the coating that is mainly composed of the α-Al_2O_3 and γ-Al_2O_3 phase has porous surface configurations. The coating can reach to a solar absorptance value higher than 0.91 and an infrared emittance value higher than 0.76, which can be used as a kind of important thermal control coating for space applications.

Introduction

A spacecraft in orbit undergoes extreme temperature cycle due to the direct sun load on one side and deep cold space on the other. This causes a large temperature change on the vehicle, which is in the range of –200 °C ~ +200 °C. So the thermal system of the spacecraft must be carefully designed to ensure the spacecraft and its parts have the fullest working efficiency. Thermal control coatings are the materials that can control the equilibrium temperature of the state by its optical properties [1]. And they play an important role on thermal control by providing suitable optical properties [2–4]. The two properties of most interest for thermal control coatings are solar absorptance (α_s) and infrared emittance (ε). The solar absorptance determines the amount of heat absorbed by the surface from the surroundings and the emittance determines the amount of heat released from the surface to the surroundings. The steady state temperature of a spacecraft far from the earth's atmosphere is directly controlled by the ratio of solar absorptance to emittance, viz. the α_s/ε value in the absence of any internal power dissipation [5, 6]. There are many kinds of thermal control coatings, like white coatings and black coatings.

Black thermal control coating has be widely used in the spacecraft, especially in some optical parts of the spacecraft to absorb the stray light and to maintain the temperature of spacecraft and its' parts at the desired operating range because its' α_s/ε ratio is about 1. Many kinds of black thermal control coatings that have a high solar absorptance and a high infrared emittance have been investigated and used in the thermal control of the spacecraft in the past. The methods for producing black thermal control coatings mainly conclude anodizing or coating the black pigment and agglomerant. But these black coatings have some limits in application.

A relatively new method, called micro-plasma oxidation (MPO) characterized by high productivity, economic efficiency, ecological friendliness, large thickness, high microhardness, good wear resistance, high insulation resistance, and excellent bonding strength with the substrate has been significantly focused on producing ceramic

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coating on some valve metals, such as Al, Mg, Ti and their alloys aiming at increasing corrosion resistance and wear resistance [7–11], as well as acquiring functional coating for special applications [12, 13]. The coating can be used in many fields, such as automotive, aerospace, medical, and textile engineering, etc. [14, 15]. Especially, the coating has the potential in using as a kind of thermal control coating for the spacecraft for their excellent optical properties. However, the study on this item is hardly reported at present.

In this paper, the optical properties of the coating prepared on the surface of aluminum alloy by pulsed bi-polar micro-plasma oxidation in the $NaAlO_2$ electrolyte system were investigated for the first time. The influences of oxidation time on the optical properties, phase composition, thickness and microstructure of the coating were studied by UV–Vis–NIR spectrophotometer, X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively.

Experimental

Foursquare samples (40 mm × 40 mm × 2 mm) which were cut from an 2024 aluminum alloy sheet (the nominal composition in weight percent: 3.8~4.9% Cu, 1.2~1.8% Mg, 0.3~0.9% Mn, 0.50% Fe, 0.50% Si, 0.30% Zn, 0.10% Ni, and 0.15% Ti and Al balance) were polished with $120^{\#}$ and $1000^{\#}$ abrasive paper and then washed in acetone. A home-made high power pulsed bi-polar electrical source with power of 5 kW was used for micro-plasma oxidation of the samples in a water-cooled electrolyser made of stainless steel, which also served as the counter electrode. The reaction temperature was controlled to below 30 °C by adjusting the flowing velocity of the cooling water. The set-up scheme used in this equipment is shown in Fig. 1. The electrolyte used in experiment was sodium aluminate with the concentration of 0.1 mol/L and sodium molybdate with the concentration of 1 g/L and the used reagents were analytical grade. The whole MPO process was carried out under both the anodic and cathode current density of 8 A/dm^2 with a fixed working frequency of 50 Hz, for 30 min (sample a), 60 min (sample b), 120 min (sample c), 180 min (sample d), respectively. Then the coated samples were flushed with water and dried in the air.

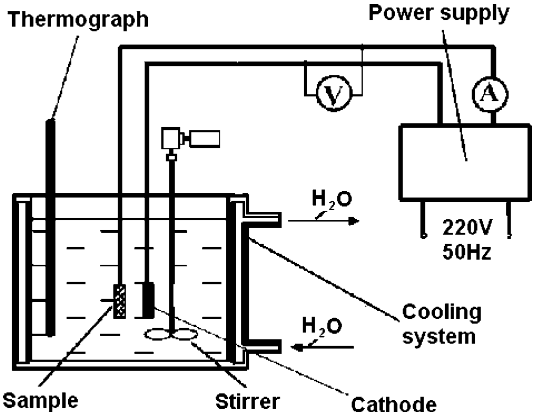

Fig. 1 Schematic view of the micro-plasma oxidation set-up

The emittance of the coating was measured by Gier-Dunkle DB-100 infrared reflectometer at 300 K. The PerkinElmer Lambda 900 UV–Vis–NIR spectrophotometer with a barium sulfate coated integrating sphere was used to measure the spectral reflectance of the coatings in the 200–2,500 nm wavelength region. Total solar reflectance (ρ_s) in the wavelength region was calculated by the Eq. 1. Total solar absorptance (α_s) was calculated by Eq. 2.

$$\rho_s = \frac{\sum_{i=1}^{n} \rho_{\lambda i} E_s(\lambda_i)\Delta\lambda_i}{\sum_{i=1}^{n} E_s(\lambda_i)\Delta\lambda_i} \tag{1}$$

$$\alpha_s = 1 - \rho_s \tag{2}$$

Where the ρ_s is the total solar reflectance, α_s is the total solar absorptance, $\rho_{\lambda i}$ is spectral reflectance at the λ_i wavelength, $\Delta\lambda_i$ is the interval of wavelength, $\Delta\lambda_i = 1/2\,(\lambda_{i+1} - \lambda_i)$, $E_s(\lambda_i)$ is the spectrum intensity of solar irradiance at the wavelength of λ_i. Its unit is W/m^2 μm, n is the number of the testing points in the 200–2,500 nm wavelength region.

Phase composition of the coating was examined with XRD (D/max-rB, RICOH, Japan) with a Cu Kα source. The thickness of the coating was measured, using an eddy current based thickness gauge (CTG-10, Time Company, China), where the minimum resolution is 1 μm with an accuracy of 0.1 μm. In this experiment, the average thickness of each of samples was obtained from 10 measurements at different positions. Surface images of the produced coating were studied with scanning electron microscopy (SEM) (S-570, Hitachi, Japan).

Results and discussion

Behavior of the MPO process

Figure 2 displays the change curve of voltage with the reaction time during the micro-plasma oxidation process. It can be seen from Fig. 2 that the anode voltage increases acutely before 3 min and then increases gently. The cathode has the same trend. But the anode voltage is much bigger than that of the cathode. At the beginning of the

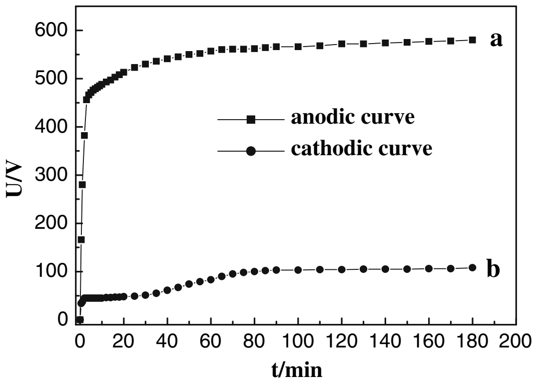

Fig. 2 Voltage–time curve in the micro-plasma oxidation process

process, a thin insulating oxide film is quickly formed on the surface of aluminum alloy in the chosen electrolyte. When the voltage reaches to a critical value, the oxide film exhibits dielectric breakdown. Then the micro-plasma discharge stage begins. In the micro-plasma discharge stage, a great number of luminescent sparks moving rapidly across the surface of the sample were observed. Usually, the lifetime of the spark is less than 1 ms, but the instantaneous temperature in micro-plasma discharge channel can reach to 2,000 K [16], which makes the coating molten near the channel. Due to the strong electric field, the anionic components are drawn into the channel. At the same time, aluminum and alloying elements are melted out of the substrate, enter the channel and get oxidized. The oxidized aluminum is ejected from the channel into the coating surface in contact with the electrolyte, which increases the thickness of the coating. Then the discharge channel gets cooled by the electrolyte and the reaction products are deposited on to its walls. All those processes repeat and the coating is formed unceasingly. So the thickness of the coating changes with the oxidation time. Table 1 illustrates the influence of oxidation time on the thickness of the coating. It is clear that the thickness of the coating increases with the oxidation time. The variety of the coating thickness as a function of oxidation time is given in Fig. 3. It can be seen from Fig. 3 that the increase of the thickness of the coating is hardly linear with the oxidation time.

Table 1 Thickness, α_s and ε values of the coatings prepared under different oxidation time

Oxidation time (min)	30	60	120	180
Thickness (μm)	24.5	43.9	66.0	77.0
Absorptance value (α_s)	0.45	0.70	0.81	0.87
Emittance value (ε)	0.08	0.56	0.65	0.73

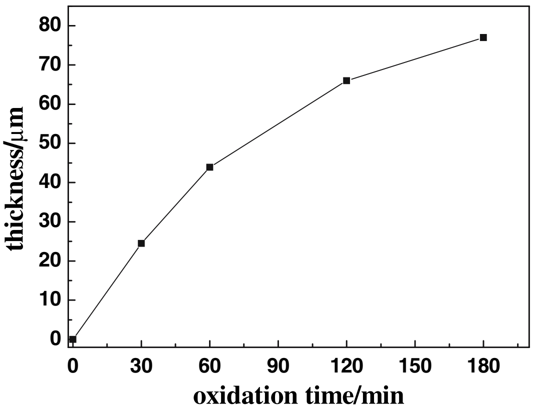

Fig. 3 Influence of oxidation time on the thickness of the coating

The influence of the oxidation time on the optical properties of the coating

Many parameters such as oxidation time, electrolyte system, current density, etc., influence the properties of the produced coating. By many experiments, oxidation time is an important parameter that influences the value of α_s and ε. The spectral reflectance (ρ) of the coatings formed for different oxidation time in the 200–2,500 nm wavelength region is shown in Fig. 4. It is clear from Fig. 4 that the spectral reflectance of the coatings reduces with the increase of oxidation time at the measurement wavelength region (200–2,500 nm). By using the spectral reflectance datum in Fig. 4 and formulas (1) and (2), the solar absorptance values of the four different coatings are gained. The curve of α_s-time is shown in Fig. 5. It is clear from Fig. 5 that the solar absorptance value increases markedly with the oxidation time when the time is less than 60 min and the increase of the solar absorptance value become slower when the time is larger than 60 min. The solar absorptance value of the

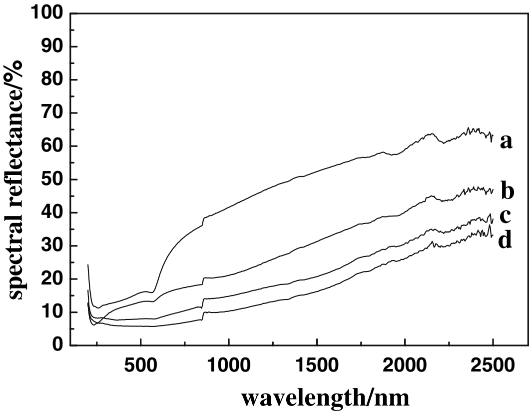

Fig. 4 Influence of oxidation time on the spectral reflectance of the coating (**a**) 30 min; (**b**) 60 min; (**c**) 120 min; (**d**) 180 min

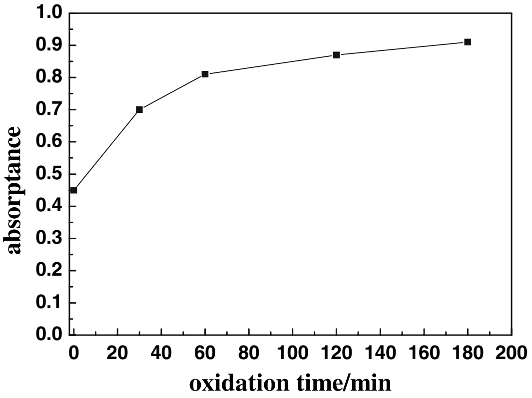

Fig. 5 The influence of oxidation time on the solar absorptance of the coating

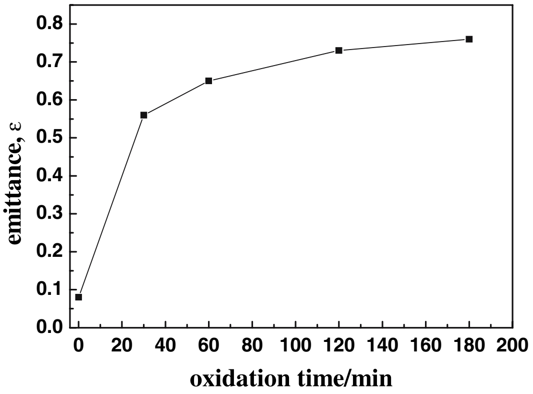

Fig. 6 The influence of oxidation time on the emittance (ε) of the coating

uncoated aluminum alloy sample is 0.45. When the sample is processed by MPO for 60 min, its solar absorptance value reaches to 0.87. The value continues increasing and it reaches to 0.91 when the sample is processed for 180 min. During the process of MPO, the color of the produced coating becomes blacker with the oxidation time. It becomes completely black coating when the sample is processed for 180 min.

The influence of oxidation time on the emittance (ε) of the coating is shown in Fig. 6. It is clear from Fig. 6 that the emittance value increases markedly with the oxidation time when the time is less than 60 min and the increase of the emittance value become slower when the time is larger than 60 min. Generally, the emittance value of the metal is very low. The emittace value of the aluminum alloy sample is 0.08. The coating produced by MPO mainly consists of all kinds of Al_2O_3 phase. Alumina has high emittance value, the emittance of the coating processed for 30 min reaches to 0.56. But the surface of the coating processed for 30 min has many pores. So the alloy substrate has not been completely covered by alumina because of those pores. Therefore, the emittance value is not very high because of the substrate effects. The increase of the thickness results in the increase of the quantity of alumina that covers the alloy substrate. So the emittance value of the coating is mainly affected by the thickness of the coating. Therefore, the emittance value increases with the thickness of the coating. The thickness of the coating processed for 180 min is 77 μm and the emittance value can reach to 0.76.

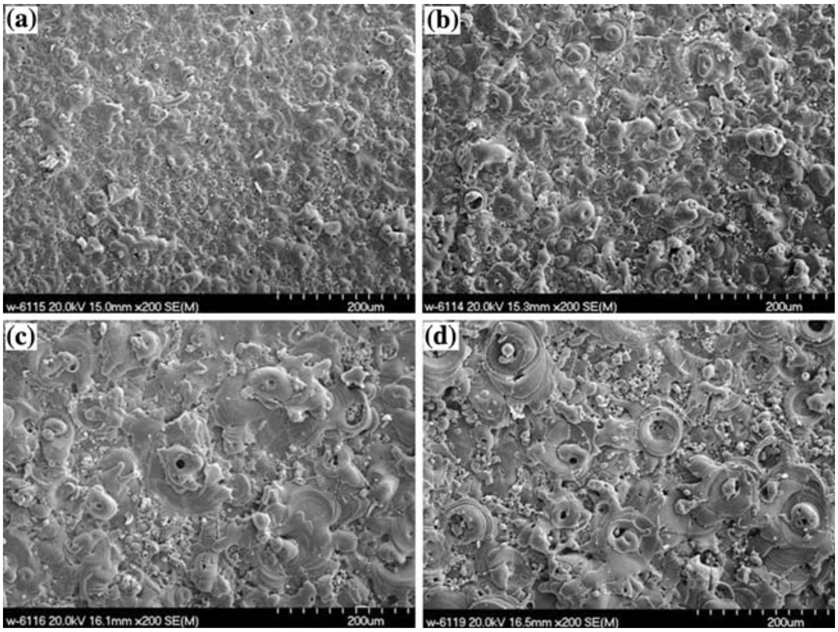

Fig. 7 SEM morphologies of surface ((a), (b), (c), (d)) of the coatings of different oxidation time. (**a**) 30 min; (**b**) 60 min; (**c**) 120 min; (**d**) 180 min

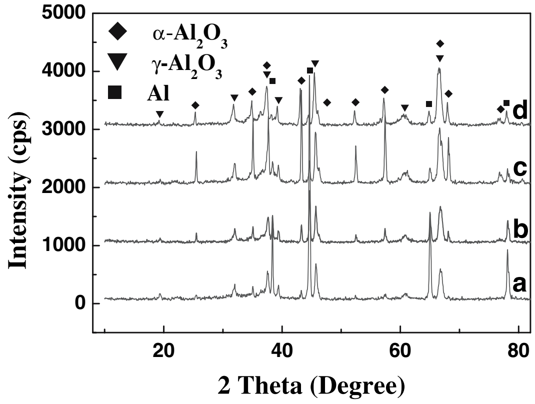

Fig. 8 XRD patterns of the coatings of different oxidation time (**a**) 30 min; (**b**) 60 min; (**c**) 120 min; (**d**) 180 min

The phase composition and the microstructure of the coatings

The surface morphologies of the MPO coatings formed for different oxidation time are shown in Fig. 7. Panels (a), (b), (c) and (d) are the surface images of the coatings prepared for 30, 60, 120 and 180 min, respectively. The coating of panel (a) has more pores than those of others. From (a) to (d), the diameter of the pores increases with the oxidation time. When the oxidation time is 120 min, the diameter of the pores (panel (c)) is about 20 μm, but the number of pores decreases. The trace of the micro-plasma discharge can also be seen in these figures, which is consistent with the solidification of molten alumina. Those traces of the micro-plasma discharge join together to form the surface of the coating. Figure 7 also illustrates that the coating formed long time is coarser, which results from the overlapping of the many pancakes produced by micro-plasma discharge. The coarser surface will be favor to absorb more light. So the solar absorptance value of the coating prepared for 180 min is highest (0.91).

X-ray diffraction study of the MPO coating processed for 30, 60, 120 and 180 min are shown in Fig. 8a–d, respectively. The results show that these coatings mainly consist of the Al_2O_3 and aluminum. Figure 8a shows that the coatings processed for 30 min mainly consist of α-Al_2O_3, γ-Al_2O_3 and aluminum whose characteristic diffraction peaks are very strong due to substrate effects. These results reveal the coating prepared under this condition is very thin and the number of the pores on the coating is large. So the aluminum substrate surface is not completely covered. When the oxidation time exceeds 30 min, the intensity of the Al_2O_3 enhances and the intensity of the characteristic diffraction peaks of aluminum reduces. Especially in Fig. 8d, the diffraction peaks of aluminum almost disappear and the coating are mainly composed of α-Al_2O_3 and γ-Al_2O_3. The content of the α-Al_2O_3 phase increases and the content of the γ-Al_2O_3 decrease in the coating with the oxidation time. This result shows the temperature that results from the plasma discharge is high enough to cause the transformation of originally formed γ-Al_2O_3 to α-Al_2O_3 phase that is more stable under high temperature. It can be concluded that the content of the Al_2O_3 phase in the coating increases with the oxidation time and the lower temperature phase γ-Al_2O_3 begins to change to the higher temperature phase α-Al_2O_3 with oxidation time.

Conclusions

The ceramic thermal control coating can be gained on the surface of the aluminum alloy in 0.1 mol/L $NaAlO_2$ and 1 g/L $NaMoO_2$ electrolyte system by MPO. The ceramic coating has a high solar absorptance value and a high emittance value. The solar absorptance and the emittance values of the coating increase with the oxidation time, which result from the increases of the surface coarseness of the coating and the content of the Al_2O_3 phase in the coating. At the same time, the lower temperature phase γ-Al_2O_3 begins to change to the higher temperature phase α-Al_2O_3 with the oxidation time. When the samples are processed for 180 min, the α_s and ε values of the coating can reach to 0.91 and 0.76, respectively.

Acknowledgments This work was achieved through the financial support of the National Laboratory of Vacuum and Cryogenics Technology and Physics (Project No. 51475020105JW2301).

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