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Preparation of black PEO layers on Al–Si alloy and the colorizing analysis

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ABSTRACT

Uniform black ceramic coatings were successfully fabricated on the surface of hypoeutectic Al–Si alloy by a plasma electrolytic oxidation (PEO) technology. The coloring additives were NH_4VO_3 and Na_2WO_4. The positive voltage was controlled to increase from 0 to 400 V by nine steps. SEM, EDS, XPS and XRD were used to study the characteristics of the black coatings. It is found that the distribution of the pores left by the discharge channels became more and more uniform with the processing time. The color of the layer changed from gray to brown gradually, and finally turned to black. The layer looks black mainly for the existing of vanadium oxides and tungsten oxides on its surface, and VO_3^- plays a more important role than WO_4^{2-} in the colorizing.

1. Introduction

Al–Si die casting alloys own some prominent properties, such as excellent castability, low thermal expansion coefficient, etc., they are now widely used in the manufacturing industry [1]. Some of their products, especially electronic devices, need surface coloring treatment for decoration demands. One of the common coloring technologies for aluminum alloys is electrolytic coloring after the anodic oxidation process, but this coloring craft is a bit complicated and inefficient [2,3]. Moreover, for the aluminum alloys with high silicon content, is hard to obtain an anodic oxidation film with uniform nanopores, which will make the colorant difficult to enter the layer and get a uniform color by the following electrolytic coloring process [2,4].

As a simple and eco-friendly technique, plasma electrolytic oxidation (PEO) can produce a ceramic coating on the surface of aluminum alloys fast, and the PEO layer possesses a series of performance that are much better than the anodic oxidation film, like, high adhesion strength, good corrosion and abrasive resistance [5,6]. This technology can also be used to prepare a colored film when adding some metal salt into the electrolyte. Actually, the black, gray, green, umber, etc., layers have been successfully synthesized on aluminum alloys by PEO in one step [7–9]. However, such black coatings were just mentioned qualitatively, there was no quantitative data to describe the characteristics of the coating, for example, the color itself and the layer surface condition. In addition, the PEO colorizing mechanism of Al–Si alloy still needs further study.

In this research, NH_4VO_3 and Na_2WO_4 were both selected as the coloring additives to deposit a black ceramic coating on the surface of hypoeutectic Al–Si alloy by plasma electrolytic oxidation. The effects of the colorant concentration on the properties of the PEO layers were determined, the formation process of the black coating was analyzed, and the coloring mechanism was also specifically discussed.

2. Experiment

2.1. Coating fabrication

The material used in this study was a Al–Si casting alloy with silicon content of 6.5–7.5 wt.%. The size of the samples were 15 mm × 10 mm × 4 mm, they were polished by 800 grit water proof sand paper, degreased in 1 mol L^{-1} NaOH and then rinsed with distilled water. The electrolyte was mainly composed of Na_3PO_4 (0.04 mol L^{-1}), and different concentration of NH_4VO_3 and Na_2WO_4, some NaOH (0.06–0.08 mol L^{-1}) was also added to keep its pH value around 10.0. The power supply used for oxidation was WHD60 (Harbin, China), a bipolar pulse power. The positive voltage was controlled to increase from 100 to 400 V by nine steps, and the negative voltage was fixed at 30 V. The impulse frequency was 1 kHz, and the duty ratio was 30%. All the samples were PEO treated for 14 min.

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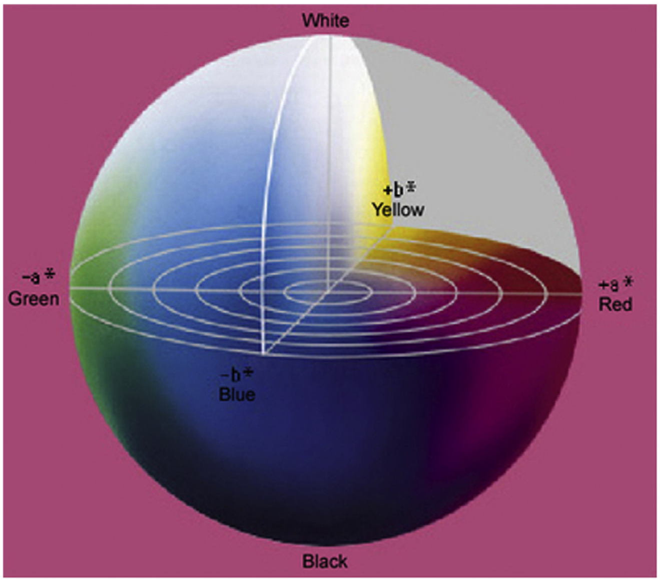

Fig. 1. CIELAB color space model.

Table 1
L^*, a^* and b^* values of the PEO layers with different additive concentration.

NH_4VO_3/mol L^{-1}	Na_2WO_4/mol L^{-1}	L^*	a^*	b^*	ΔE_0
0.05	0.06	32.48	2.00	1.89	32.60
0.06	0.05	31.51	1.37	0.5	31.54
0.07	0.04	30.74	0.67	0.48	30.75
0.08	0.03	32.83	0.69	−0.35	32.84

2.2. Coating characterization

The color of the coating was evaluated with a CIELAB color space model. And the L^*, a^* and b^* of the color were the average value of two tested points, obtained by a spectrophotometer (CM-2300D). The surface roughness (Ra) was the mean value of four tested positions, acquired by a surface plasmon resonance analyzer (D-150), with a scan range of 6 mm and a scan frequency of 200 points mm^{-1}. The morphology and element distribution of the coating were investigated by a scanning electron microscope (Quanta 200) equipped with an energy disperse spectroscopy (INCA). The oxidation state of the elements on the layer surface was analyzed by a X-ray photoelectron spectroscopy (AXIS ULTRA). The phase composition was studied by a X-ray diffraction (Philips X' pert MPD).

3. Results and discussion

3.1. Characterization of the PEO coating

3.1.1. PEO coating and the CIELAB color space model

NH_4VO_3 and Na_2WO_4 were both added into the electrolyte to deposit the black PEO layers in this research, which was different from the single additive [8]. To get a proper proportion of the two colorants, their total concentration was kept constant. The content of NH_4VO_3 was increased from 0.05 to 0.09 mol L^{-1}, while Na_2WO_4 was decreased from 0.06 to 0.02 mol L^{-1}.

As the color of the PEO coatings all looked black, it is difficult to distinguish the difference among them by naked eyes. Hence, a CIELAB color space model was introduced to describe the blackness of the PEO coatings. This model is a three-dimensional model with three parameters, namely, L^*, a^* and b^*. A group of (L^*, a^*, b^*) value corresponds to a certain color as shown in Fig. 1 [10,11]. And the difference between any two colors can be calculated by a ΔE ($\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$), which means the smaller of ΔE value of a color and the black color, the deeper blackness this color will be [10]. As the (L^*, a^*, b^*) value of the black color is (0, 0, 0), the blackness of the PEO layer can be quantificationally evaluated by the value of ΔE_0, which is deduced by the following formulas:

$$\Delta L = L^* - 0 = L^* \quad (1)$$

$$\Delta a^* = a^* - 0 = a^* \quad (2)$$

$$\Delta b^* = b^* - 0 = b^* \quad (3)$$

$$\Delta E_0 = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{1/2} = \left[(L^*)^2 + (a^*)^2 + (b^*)^2\right]^{1/2} \quad (4)$$

where L^*, a^*, b^* are the values of the layer color. It is to say, the smaller of the ΔE_0 value, the blacker the PEO coating will look.

Table 1 is the L^*, a^*, b^*, and ΔE_0 values of the color of the PEO layer. The L^*, a^* and ΔE_0 values all decreased at first with the increasing of NH_4VO_3 and decreasing of Na_2WO_4, then them increased in stead when NH_4VO_3 was above 0.07 mol L^{-1} and Na_2WO_4 was below 0.04 mol L^{-1}, yet the b^* value decreased all the time. Moreover, the absolute values of a^* and b^* are both small

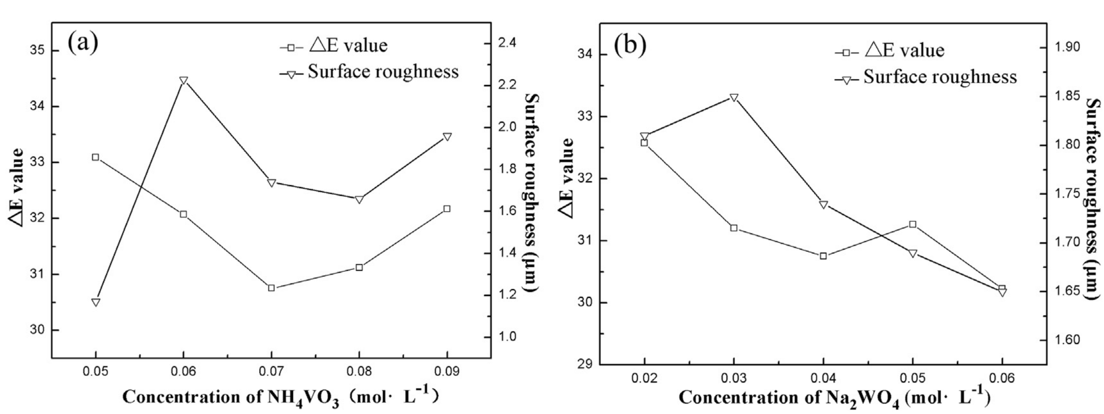

Fig. 2. ΔE_0 value and surface roughness of the PEO layers varied with additive concentration: (a) 0.04 mol L^{-1} Na_2WO_4 with different NH_4VO_3 and (b) 0.07 mol L^{-1} NH_4VO_3 with different Na_2WO_4.