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Formation of uniform passive oxide layers on high Si content Al alloy by plasma electrolytic oxidation

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ABSTRACT

In this research, we demonstrated the successful fabrication of conformal passive oxide layers on a high Si content Al alloy by a plasma electrolytic oxidation (PEO) process. The PEO process of Al–12 wt%Si alloy was performed in an electrolyte containing sodium hexametaphosphate ($(NaPO_3)_6$) and ammonium metavanadate (NH_4VO_3), and the variation of the morphology of the electrochemically generated oxide layer was investigated. When NH_4VO_3 was added to electrolyte, the oxide layer uniformly covered the entire surface of Al–12 wt%Si alloy, and the synthesized oxide layer was confirmed to be a mixture of Al_2O_3, V_2O_3 and V_2O_5. In addition, the oxide layer exhibited a uniform black color, and this is expected to solve the problem of non-uniform colorizing caused by different oxidation behaviors of Si-rich phases during surface treatment.

1. Introduction

Al–Si alloys are one of the most attractive light metal alloys for use as die casting materials owing to their unique characteristics such as excellent cast-ability, high strength-to-weight ratio, low coefficient of thermal expansion, and good thermal conductivity [1].

Despite such significant advantages, application of these alloys has been limited by difficulties in forming thin and uniform passive oxide layers on the surface, caused by differences in the oxidation behaviors of the Si-rich phase and Al-rich phase in the alloy matrix [2]. Several studies attempted to produce thin, uniform oxide layers on Al–Si alloys with conventional anodizing or PEO processes from an electrolyte containing silicate [2–5]. Nevertheless, researchers have yet to produce a uniform oxide layer that is free of appearance problems. Wang and Nie [2] reported an Al–Si–O compound, which is formed on a Si-rich region. However, this compound had a lower melting point than the Al oxide formed on the Al matrix, thus caused a more porous structure in Al–Si–O compound phases. Consequently, more discharge spots arose on the Si-rich regions due to accumulation of the Al–Si–O compound.

The structures of the oxide layer produced by the PEO process depend on various processing conditions, including chemical additives, the concentration of the electrolyte, the applied bias, and the substrate composition [6–13]. In particular, application of chemical additives to the electrolyte exerts a considerable influence on the properties of the anodically formed oxide layer on Al–Si alloys. It is therefore imperative to select a suitable electrolyte composition for obtaining a thin and uniform oxide layer.

In this research, a conformal oxide layer on an Al–Si alloy with high Si content (Al–12 wt%Si alloy) was effectively synthesized with a PEO process from an electrolyte containing NH_4VO_3, and the variation of the microstructure according to the deposition conditions was investigated.

2. Experimental

Die-casted Al–12 wt%Si plates of size 30 mm × 50 mm × 2 mm were mechanically polished with 1000 grit emery paper and rinsed with de-ionized water. The samples were then ultrasonically cleaned in ethanol. The PEO process was performed with a 20 kW power supply using a glass-vessel container as the electrolyte cell [13]. Stainless steel was used as a counter electrode, and a cooling system was installed to maintain the electrolyte temperature at 300 K. The applied current density was fixed as $100\,mA/cm^2$. The coatings by PEO process were formed in the sodium hexametaphosphate ($(NaPO_3)_6$) electrolyte, either without (bath A) or with the addition of ammonium metavanadate (NH_4VO_3).

For the microstructural analysis, the surface morphology of the oxide layer was investigated with FESEM (HITACHI, S-4800). The components of the oxide layer were inspected by EDS. Also, X-ray photoelectron spectroscopy (XPS) was performed with an ESCA (PHI 5800) system for a surface chemical analysis.

3. Results and discussion

Optical micrograph of die-casted Al–12 wt%Si alloy shows the α-Al dendrites embedded in the Al–Si eutectic compounds (Fig. 1). It is difficult to form the uniform coating layers on die-casted Al

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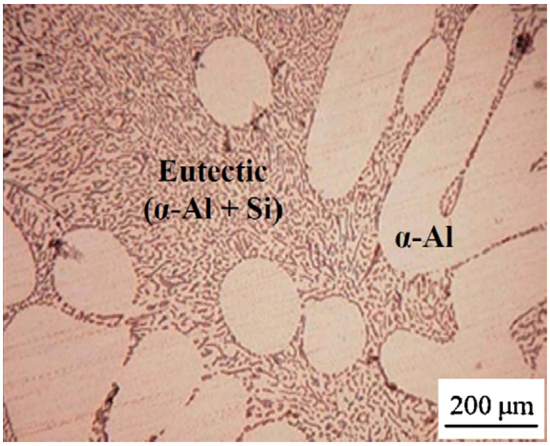

Fig. 1. Optical micrograph of die-casted Al–12 wt%Si alloy.

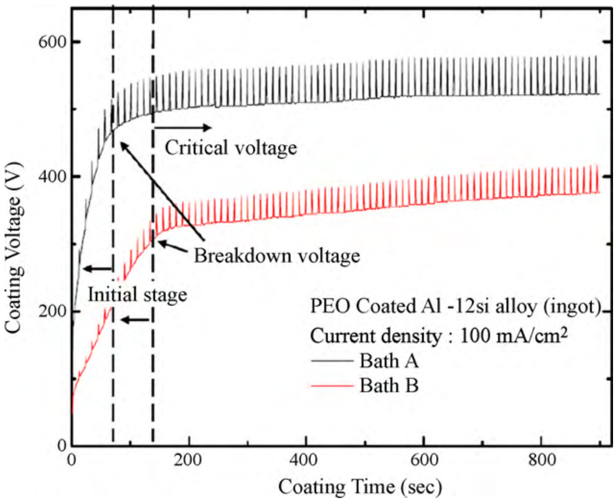

Fig. 2. The variation of voltage responses during PEO process (bath A: without NH_4VO_3; bath B: with NH_4VO_3).

alloys by conventional anodizing process [14] due to the different oxidation behaviors of Al-rich phase (α-Al) and Si-rich phase (α-Al + Si eutectic mixture).

Fig. 2 shows the time-transient behaviors of the voltage responses of the Al–12 wt%Si alloy in electrolyte with and without NH_4VO_3, respectively. The voltage responses of the PEO process for the Al–12 wt%Si alloy processed in the electrolyte without NH_4VO_3 (bath A) was higher than that with NH_4VO_3 (bath B). The critical voltage at which the responses reach a constant level was not obtained, and the voltage responses increased continuously in bath B. The difference of the final voltages between bath A and bath B might be due to the incorporation of vanadium salt in the bath, as it affects the difference of size and duration time of micro arcs at the substrate and the electrolyte interface. In order to investigate the growth behavior of the oxide layer, specimens were treated in an electrolyte with and without NH_4VO_3 for processing time of 250 and 900 s, respectively. Fig. 3 shows the surface morphologies of the oxide layers on Al–12 wt%Si alloy according to the coating time. When the process time was 250 s without NH_4VO_3, the surface mainly remained in an uncoated state (Fig. 3(a)). In case of the addition of NH_4VO_3, the oxide layer started to form appreciably on areas where α-Al and Al–Si intermetallic compounds were located (Fig. 3(b)). When the coating time was increased in the electrolyte without NH_4VO_3 to 900 s, two different types of non-uniform coating layers formed as shown in the enlarged figure (Fig. 3(c)). In contrast, a uniform oxide layer was formed on both α-Al and Al–Si

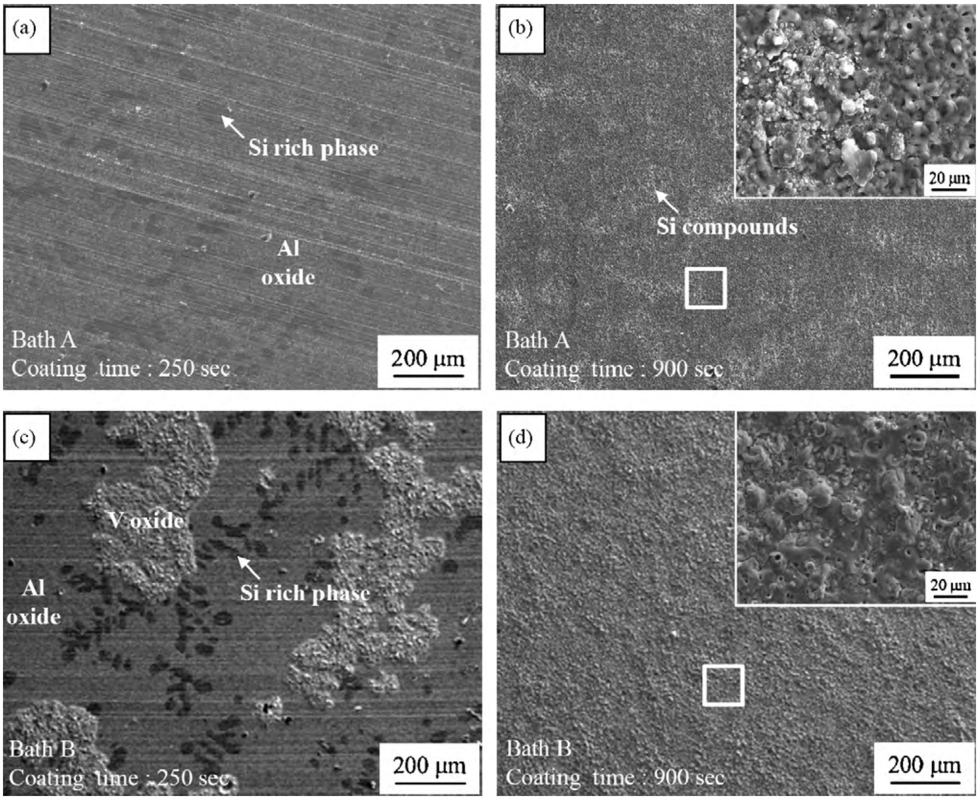

Fig. 3. Surface morphology of the oxide layer on Al–12 wt%Si alloy formed by the PEO process: (a) 250 s without NH_4VO_3, (b) 250 s with NH_4VO_3, (c) 250 s without NH_4VO_3, and (d) 900 s with NH_4VO_3.

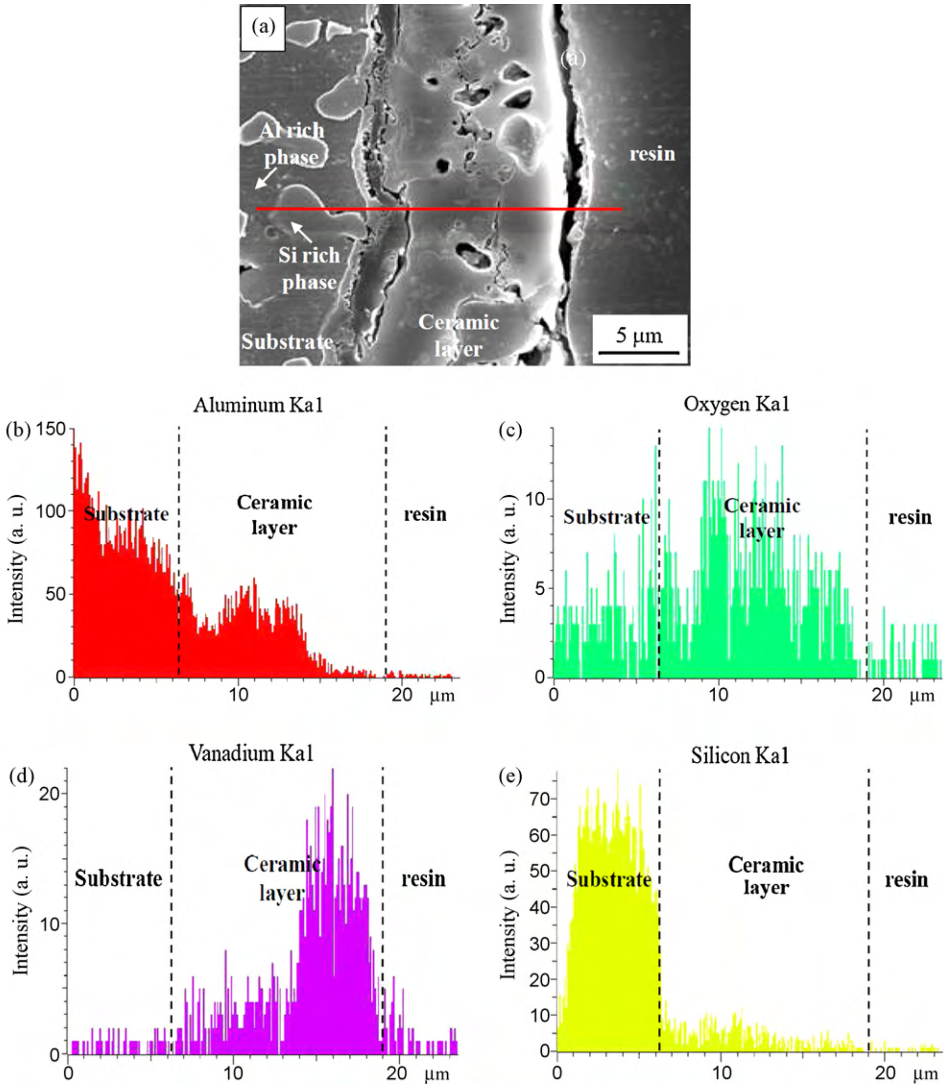

Fig. 4. Cross-sectional SEM image (a) and EDS line scanning ((b) aluminum, (c) oxygen, (d) vanadium, and (e) silicon) results of oxide layer on Al–12 wt%Si alloy coated to 900 s in bath B containing NH_4VO_3.

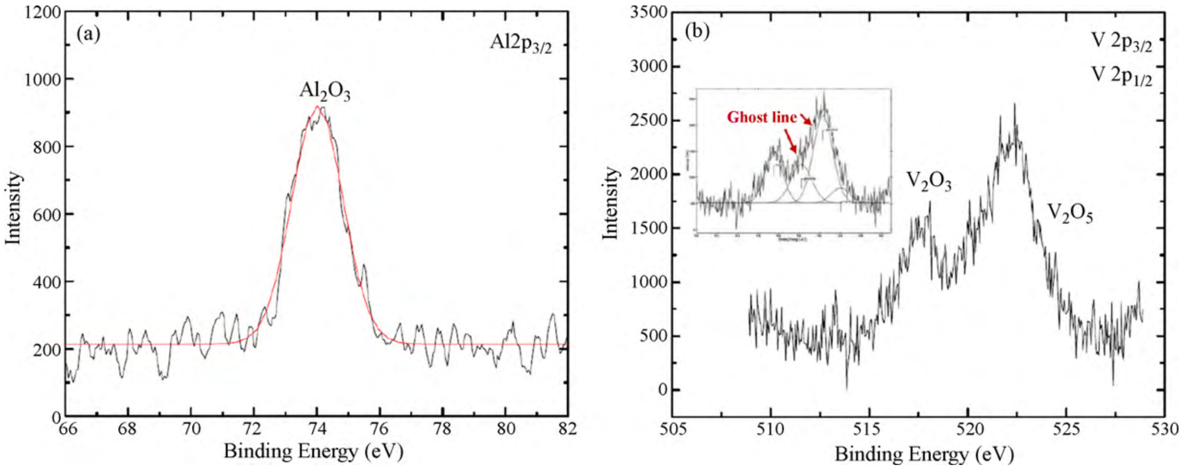

Fig. 5. XPS analysis of V $2p_{1/2}$ and V $2p_{3/2}$ for the oxide layer on Al–12 wt%Si alloy processed in bath B containing NH_4VO_3.

intermetallic compound areas in the electrolyte with NH_4VO_3. At this time, the surface was uniformly black, and the morphology at a micro-scale was also conformal. Compared to the oxide layer obtained from the electrolyte without NH_4VO_3 (Fig. 3(c)), for which notably irregular marks could be found on the surface, a conformal black coating with a uniform appearance could be obtained from PEO treatment with NH_4VO_3 (Fig. 3(d)).

Depth profiling of the composition of the oxide layer synthesized by the PEO process with NH_4VO_3 was performed by EDS (Fig. 4). The analysis results clearly show that a vanadium-rich region formed at the upper region of the oxide layer. This strongly suggests that the incorporation of vanadium in oxide layer might initiate when the oxidation overpotential exceeds that of Al.

The oxidation states of vanadium oxide were verified with a XPS analysis (Fig. 5). The individual spectrum was analyzed for V $2p_{3/2}$ and V $2p_{1/2}$, respectively, to clarify the oxidation products in the oxide layer obtained from the electrolyte in the case of 900 s process time (Fig. 3(c)). The binding energy of 516.82 eV ($2p_{3/2}$) and 524.57 eV ($2p_{1/2}$) from XPS spectra indicated the formation of V_2O_3 and V_2O_5. The existence of V_2O_3 clearly accounts for the black color of the oxide layer formed on Al–12 wt%Si alloy [15,16].

4. Conclusions

A conformal, black oxide layer on an Al alloy with high Si content was successfully obtained by PEO process from an electrolyte with NH_4VO_3. It was confirmed from EDS analysis that the vanadium oxide was dominant component at the outer region of PEO generated oxide layer, which could effectively cover both α phase and Si-rich phase, resulting the formation of conformal black coating on the entire surface of high Si content Al alloys. Such a black oxide layer is expected to solve the non-uniform problems on the surface of high Si content Al alloys after electrochemical passivation treatment.

Acknowledgement

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