



Preparation of ceramic coatings on an Al–Si alloy by the incorporation of ZrO₂ particles in microarc oxidation



Chia-Jung Hu ^{*}, Ming-Han Hsieh

Department of Materials Engineering, Tatung University, 40 Chungshan N. Road, 3rd Sec., Taipei 104, Taiwan

ARTICLE INFO

Article history:

Received 19 May 2014

Accepted in revised form 8 September 2014

Available online 16 September 2014

Keywords:

Microarc oxidation

Al–Si alloys

Friction coefficient

ZrO₂ particles

ABSTRACT

Ceramic coatings containing ZrO₂ were prepared on ADC12 aluminum alloys using microarc oxidation (MAO) in aqueous silicate solutions containing various amounts of ammonium metavanadate (NH₄VO₃) and 0.2 μm of solid ZrO₂ powder. A bipolar rectangular pulse with a frequency of 1000 Hz was galvanostatically used in this study. The morphologies and friction coefficients of the MAO coatings were investigated using scanning electron microscopy and a CSM tribometer, respectively. The results indicated that NH₄VO₃ electrolytes facilitate the formation of a smooth dark oxide film on Al–Si alloy because of the existence of vanadium oxide, resulting in a favorable appearance but poor tribological behavior. The introduction of ZrO₂ powder preserved the favorable and uniform dark appearance of the MAO coating on the ADC12 aluminum alloy. The uniform incorporation of monoclinic/tetragonal zirconia nanoparticles into MAO coating will reduce surface roughness and enhance hardness. These were beneficial to the tribological properties.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Cast Al–Si alloy is an essential material used in automobile manufacturing because of its high strength-to-weight ratio and excellent castability and mechanical properties [1,2]; however, its poor wear and corrosion resistance often restrict its applications. Traditional hard anodic coatings that are used to enhance the wear resistance of aluminum cannot be used on cast Al–Si alloys. Microarc oxidation (MAO), a plasma electrolytic surface processing technique, has attracted interest as an effective method to improve the wear and corrosion resistance of aluminum alloys through the creation of a thick ceramic coating [3–6]. Although the hard ceramic coating can be prepared using MAO in a basic aqueous solution containing silicate electrolytes [7–9], the gray-white nonuniform appearance of the casting structure is unfavorable. Dark coating has been suggested to avert this problem. Several reports have indicated that ammonium metavanadate is a promising candidate for the fabrication of dark or black MAO ceramic coatings [10,11]. VO₃[−] can be spontaneously reduced to V₂O₃ when Gibbs energy change of reaction, ΔG(T), is less than zero above 1825.11 K [11]. Because the temperature around the discharge channels can reach 1600–2000 K [12], V₂O₃ can be formed during the MAO process, leading to black appearance, and further oxidized and turned into V₂O₅ [13]. Few reports have focused on cast aluminum alloy substrates with a silicon content of more than 10 wt.% [14]. Although a favorable appearance can be achieved using MAO on Al–Si alloys with high Si content in an aqueous solution containing ammonium metavanadate, such V-containing MAO

coatings have a thick porous layer and coarse surface [14]. This rough and brittle surface is detrimental to tribological performance. Several reports have determined that ZrO₂ can be embedded in porous ceramic coatings on Al or Mg alloys. The introduction of ZrO₂ in MAO coatings enhances corrosion resistance as well as hardness, improving tribological performance [15–17]. In this study, a conformal oxide layer on an Al–Si alloy with high Si content (Al–10.1 wt.% Si alloy) was effectively synthesized using a MAO process in an aqueous silicate electrolytic solution, both with and without the addition of ammonium metavanadate and ZrO₂ powders (0.2 μm). The variation of the microstructure according to the deposition conditions was investigated.

2. Experimental procedure

Rectangular samples (with dimensions of 80 mm × 25 mm × 1 mm) composed of ADC12 aluminum alloys were used as working electrodes. The composition of the alloy was 10.1% Si, 1.6% Cu, 0.97% Zn, 0.9% Fe, 0.25% Mg, 0.17% Mn, and balanced Al. The samples were mechanically polished using waterproof abrasive paper up to 1200 grit, then ultrasonically degreased in acetone and distilled water. Various amounts of NH₄VO₃ and monoclinic ZrO₂ powders of 200 nm in size were added to the aqueous electrolytic solution (9 g/L of Na₂SiO₃·5H₂O + 5 g/L of NaOH). The temperature of the electrolytic solution in the stainless steel container (counter electrode) was maintained below 30 °C using a chiller during the MAO process. To maintain the suspension of the solid ZrO₂ powder in the electrolytic solution, continuous stirring was required. A pulsed bipolar electrical source with a power of 12 kW was used for the experiment. The treatment was conducted at a constant current mode; the 6 A/dm² of current density for the anode and

^{*} Corresponding author. Tel.: +886 2 21822928x6228.
E-mail address: cjhu@ttu.edu.tw (C.-J. Hu).

cathode, and the fixed electrical parameters were bipolar rectangular pulses with a frequency of 1000 Hz, a duty ratio of 0.4, and treatment times of 5, 10, and 15 min.

The surface morphology of the coatings was characterized using scanning electron microscopy. The chemical state of vanadium in ceramic layer surfaces was investigated using X-ray photoelectron spectroscopy (XPS). The microhardness (Hv) was measured using a microhardness tester (Fischerscope HM 2000S) with a maximum indentation depth of 1 μm at 5 selected points on the coating surface, and the average value of the 5 measurements was recorded. The thickness and arithmetic mean surface roughness (Ra) of the coating were measured using an eddy current coating measurement gage (Fisher Isoscope MP10-E) and a surface profilometer (Mitutoyo SJ-201), respectively. The friction coefficients were measured using a computer-controlled oscillating ball-on-disk tribometer (CSM TRN 01-05600) equipped with an Al_2O_3 ball of 6-mm diameter. The measurement was conducted at a linear speed of 5 cm/s, a track radius of 5.1 mm, and a load of 2 N. After the tribological tests, the images of the wear tracks were analyzed using SEM. Surface profiles on the samples were measured by a stylus profiler (Veeco Metrology, Dektak 150) with a load of 3 mg. The wear volume was determined by using the profiles from the wear track cross-section, and the specific wear rate K_s was calculated using the formula: $K_s = \Delta V / (P \cdot d)$, where P is the normal load of 2 N, d is the sliding distance of 40 m, and ΔV is the wear volume which can be obtained by multiplying wear depth, wear width, and the track radius of 5.1 mm.

3. Results and discussion

3.1. Phase formation of the MAO coatings on Al–Si alloy

Results of XRD revealed peaks of $\gamma\text{-Al}_2\text{O}_3$ appearing in the coating formed in the silicate electrolyte (Fig. 1a). No peaks of $\alpha\text{-Al}_2\text{O}_3$ were found in the coating due to an insufficient oxidation time of 15 min. Metastable $\gamma\text{-Al}_2\text{O}_3$ may transform to stable $\alpha\text{-Al}_2\text{O}_3$ at a longer time than 15 min. In comparison, $\alpha\text{-Al}_2\text{O}_3$ was found in the coatings by treating Al alloys for 40–60 min in silicate electrolyte in other PEO studies [18]. Addition of 3 g/L of NH_4VO_3 to the silicate electrolyte enhanced

the transformation of $\alpha\text{-Al}_2\text{O}_3$ in the coating (Fig. 1b). Monoclinic zirconia was found in the coatings formed in zirconia-containing electrolyte, which retains the same structure as the original zirconia particles. The monoclinic zirconia in the coating may be resulted from either the untransformed zirconia particles in the suspension or from the product of transformation on cooling from higher temperature. Addition peaks of tetragonal zirconia were also found in Fig. 1c, which was obtained by transforming from monoclinic phase at above $\sim 1240^\circ\text{C}$, with the reverse transformation taking place at $\sim 1170^\circ\text{C}$ [19]. However, the absence of the cubic form of zirconia suggests that the temperature for the tetragonal-to-cubic transformation at 2370°C has not been reached in this experiment. Comparing the peak intensities of the $\gamma\text{-Al}_2\text{O}_3$ at $\sim 46^\circ$ in Fig. 1b and c, the peak was reduced for the coating containing zirconia; some $\gamma\text{-Al}_2\text{O}_3$ may transform to $\alpha\text{-Al}_2\text{O}_3$. The incorporation of the ZrO_2 in the coating seemingly facilitated the formation of $\alpha\text{-Al}_2\text{O}_3$, which suggests that the local temperature of the coating formed in zirconia-free electrolyte be lower than that in zirconia-containing electrolyte.

3.2. Microstructure and composition of the MAO coatings on Al–Si alloy

Fig. 2 shows scanning electron micrographs of cross-section of the coating formed in zirconia-free NH_4VO_3 electrolyte for 15 min, revealing micron-sized pores. The coating thickness is in the range of 13–17 μm with the outer surface (20–40% of the coating thickness) appearing to be more compact. A barrier-like region of thickness $\sim 1 \mu\text{m}$ is present next to the interface. EDX analysis indicated that aluminum and oxygen are the primary constituents of the coating, with relatively low concentrations of silicon and vanadium in most regions. Point analyses of EDX showed that atomic ratios of V:Al equal to 0.007, 0.04, and 0.05 were found at locations near the inner, middle and outer regions of the coating respectively, in contrast to a value of 0.11 from an area analysis on the coating surface (Table 1). From these results, it is concluded that vanadium element was present in most regions of the coating with less vanadium in the inner coating.

Fig. 3a reveals the cross-section of the coating formed in the zirconia-containing NH_4VO_3 electrolyte. In these pictures, the coating

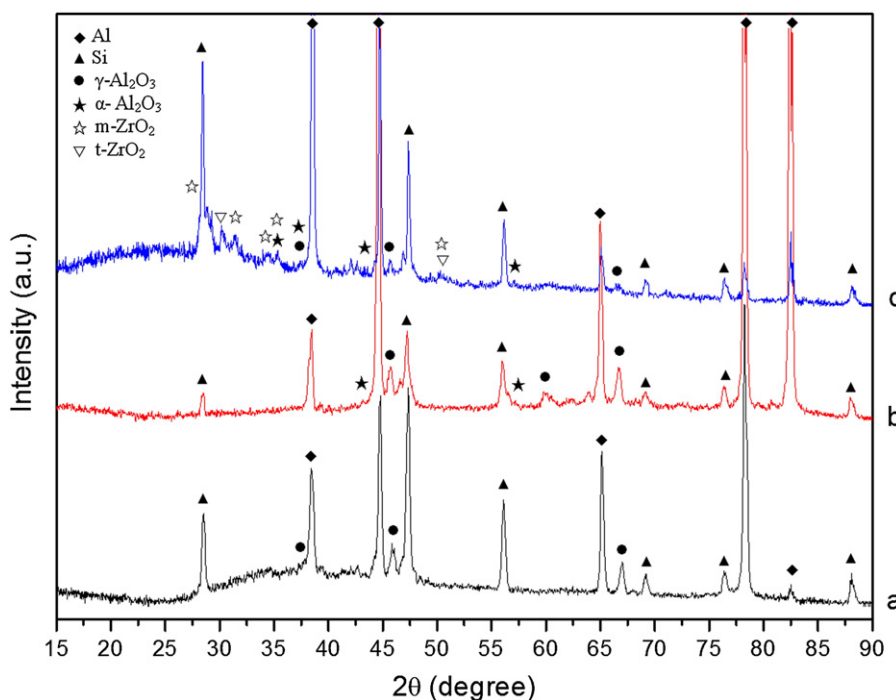


Fig. 1. XRD patterns of coatings treated for 15 min in the electrolyte containing (a) 9 g/L of Na_2SiO_3 , (b) 9 g/L of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 3 g/L of NH_4VO_3 , and (c) 9 g/L of $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$, 3 g/L of NH_4VO_3 and 6 g/L of ZrO_2 .

Download English Version:

<https://daneshyari.com/en/article/8027260>

Download Persian Version:

<https://daneshyari.com/article/8027260>

[Daneshyari.com](https://daneshyari.com)