

Oxide Based Ceramic Coating on Al–4Cu Alloy by Microarc Oxidation

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In this study the Al–Cu aluminum alloy with 4 wt% Cu was prepared under controlled atmosphere and coated by microarc oxidation technique for the durations of 40, 80, and 120 min. The phase composition, surface roughness and hardness of the coating were characterized by X-ray diffraction, scanning electron microscopy, profilometry. The outer region contains larger sized porosities while fine porosities were formed in the inner dense region of the coating. The longer coating duration resulted in dense inner region with finely distributed α -Al₂O₃ precipitates. The presence of Cu in the outer region is not significant while the presence of Si in inner region was lower than in the outer region. Mullite and γ -Al₂O₃ phases were formed for 40 min and α -Al₂O₃ phase was additionally formed for 80 min and 120 min coating time. The coating thickness increased from 38 μ m (40 min) to 115 μ m (120 min) while the surface roughness (R_a) increased from 5 μ m (40 min) to 9 μ m (120 min).

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1. Introduction

Aluminum and its alloys are extensively used as engineering materials because of their important properties of high strength/density ratio and recyclability [1, 2]. Copper has been the most common alloying element for aluminum alloys. Copper-containing Al alloys are one of the promising materials for many industrial application such as aerospace and automotive [3, 4]. However, their weak tribological properties and low corrosion resistance in some environment reduce their usage. Many of surface modification methods either changes or affects adversely the bulk properties of the materials, as they need high temperature. Therefore the methods applied at high temperature are not suitable for the materials like aluminum and its alloys.

The anodic oxidation is extensively used surface modification technique for aluminum and its alloys. But, as the obtained coating thickness (maximally 50 μ m) and hardness (maximally 800 HV) is very low and the process is not eco-friendly due to the acidic solutions used, which limits the usage of the process [5, 6]. Furthermore, the fatigue strength decreases significantly after anodization due to the dissolution of the Cu-rich intermetallics during the anodizing process of Cu containing Al alloys [7]. Microarc oxidation (MAO) coating is a promising technique to Al and its alloys due to its application at room temperature in eco-friendly solutions and resultant properties of coating such as high corrosion resistance, wear resistance, hardness, thickness and well adherence to the substrate [5, 8–10].

Most of the widely used 2xxx series of Al alloys contains approximately 4 wt% Cu. Therefore, in this study

the surface of the Al-4 wt% Cu (Al-4Cu) alloy was coated by MAO technique for the durations of 40, 80 and 120 min. The coatings were characterized by X-ray diffraction (XRD), scanning electron microscopy–energy dispersive spectroscopy (SEM–EDS), profilometry.

2. Experimental

Al–Cu alloy ingots were prepared by melting of commercially pure Al (99.8%) and Cu (99.99%) pieces and solidification in water cooled copper mold under controlled atmosphere. The samples with the dimensions of 50 mm \times 25 mm \times 4 mm were sliced from the ingot. The plate shaped substrates were ground using 1200 grit SiC paper, polished using 3 μ m alumina and ultrasonically cleaned in ethanol for 5 min. The profilometry (Veeco Dektak 8) was utilized to analyze the surface topography of the substrates prior to MAO process. The MAO coating process was carried out by means of an asymmetric AC power supply. An electrolyte for MAO coating was prepared by dissolving of 12 g/l Na₂SiO₃ and 2.5 g/l KOH in distilled water. The samples were coated for the durations of 40, 80, and 120 min by keeping the bath temperature at 20 °C using the same electrical parameters. The coated samples were rinsed in distilled water and then cleaned using ethanol. The surface roughness of the MAO coated samples was determined by means of the same profilometer using the same parameters used for bare substrates. Rigaku D-MAX 2200 X-ray diffractometer (40 kW, 40 mA), with a Cu K_α radiation over a $2\theta = 20^\circ$ to 90° , was employed for the characterization of MAO coated Al–4Cu alloy substrates.

Further XRD scans of the 120 min MAO coating of Al–4Cu were carried out after removing approximately half of the coating thickness by conventional grinding. The surfaces of gold coated samples were examined by XL30 FEG ESEM. Then the samples were cut, mounted

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into epoxy resin, ground and polished to expose the cross-section of the coatings. The microstructural examination and determination of the chemical composition of the MAO coated Al–Cu alloy were performed by cross-sectional SEM–EDS analysis. The samples exposing the cross-section of the coating were gold coated before the SEM analysis.

3. Results and discussion

3.1. XRD

The XRD patterns obtained from the surface of MAO coated Al–4Cu alloy for the durations of 40, 80, and 120 min are shown in Fig. 1. The figure also shows the pattern obtained from the surface scan of 120 min. MAO coated Al–4Cu after removing approximately half of the coating thickness by conventional grinding. The peaks belong to mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and $\gamma\text{-Al}_2\text{O}_3$ phases are seen for all coating durations and for ground sample. The presence of the mullite phase was attributed to the complex chemical reactions between electrolyte constituents and substrate during microarc formation [1, 5, 10, 11]. $\alpha\text{-Al}_2\text{O}_3$ was not formed in the duration of 40 min but it started to form in the coating duration of 80 min. The existence of $\alpha\text{-Al}_2\text{O}_3$ phase with higher intensity was detected at 120 min coating time. The increase in the intensity of $\alpha\text{-Al}_2\text{O}_3$ is further clearly confirmed from the ground surface of 120 min coated sample's XRD pattern. The increase in the intensity of $\alpha\text{-Al}_2\text{O}_3$ phase by coating time can be attributed to the increase in the coating thickness. The aluminum peaks originated from the substrate are also seen on the pattern of 40 min coated sample and ground sample.

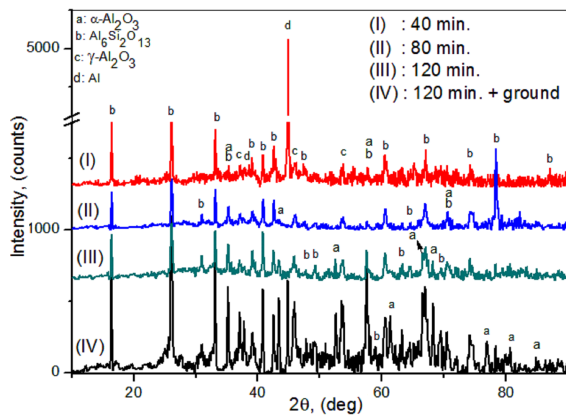


Fig. 1. XRD pattern from the surface of MAO coated Al–4Cu for 40, 80 and 120 min and from the ground surface of 120 min coated Al–4Cu.

3.2. SEM analysis

Figure 2 shows the SEM micrographs of coating surfaces of MAO coated Al–4Cu alloy. The small porosities are distributed randomly for the duration of 40 min

(Fig. 2a). However, the number of small porosities decreases relatively and the number of bigger sized porosities increases and the microcracks are evident for the sample coated for 80 min (Fig. 2b). As shown in the SEM micrograph (Fig. 2c) of 120 min coated sample, the size of microcracks increases significantly and the surface of this sample is rougher than the samples coated for 40 and 80 min. The surface of the samples coated for 40 min and 80 min was covered by melted and solidified features and contained sphere like solid features. The surface of the sample coated for 120 min has coarse surface with spongy-form spheroid features. Furthermore, the typical MAO surface is seen on the surface of the coatings with semi-sphere like features the center of which was filled with porous material for 120 min coating. These spheroids which burst by the rapid cooling effect of cold electrolyte, contained some small porous features on their bottom center which resulted in material that transferred to the surface through microarc channels. A part of the molten metal and oxide mixture coming out of microarc channels spread and partly splashed on the surface of coating and then solidified by rapid cooling in the electrolyte. In the first 40 min of the coating time, the melted and rapidly solidified mullite phase was seen as covering the surface and the formation of this phase developed independently of cooling rate. Similar case was valid for the formation of $\gamma\text{-Al}_2\text{O}_3$ phase. The formation of cracks on the surface of MAO coated samples is attributed to low thermal shock resistance of oxide based ceramic coating by rapid cooling and high pressure created by sequential material transfer through microarc channels. The crack formation was less evident because of the high amount of sponge like features created on the coating with longer MAO time.

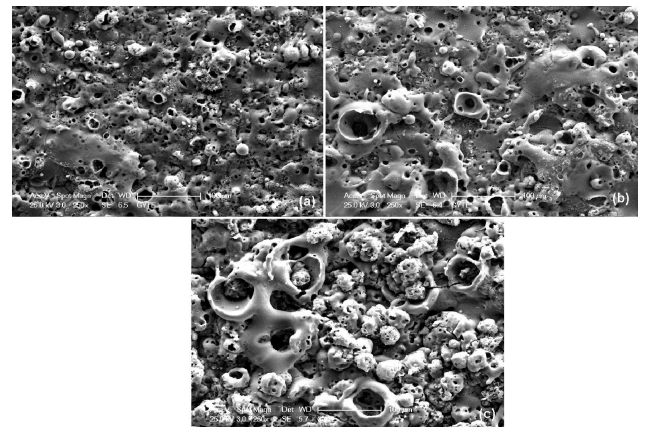


Fig. 2. SEM micrographs of coating surfaces of MAO coated Al–4Cu alloy: (a) 40 min, (b) 80 min, (c) 120 min.

Figure 3 shows the cross-sectional SEM micrographs of the samples coated for 40, 80, and 120 min. The figures show that the coatings adhered to the substrate perfectly and the interface is wavy in nature for 40 and

80 min (Fig. 3a,b). The microcracks were seen in the cross-sectional views of the MAO coated samples for all coating durations. The detailed examination of the cross-sectional views showed that there were porosities with various sizes for all coating times. As the coating time increases, the size and amount of the porosities increases. While the bigger sized porosities were present in the other region (region I) of coating, the fine porosities were formed in the inner region (region II) of the coating. The thicknesses of both regions increase when the coating duration increases. However, the coating obtained for 120 min has relatively dense inner region with finely distributed precipitates (Fig. 3b).

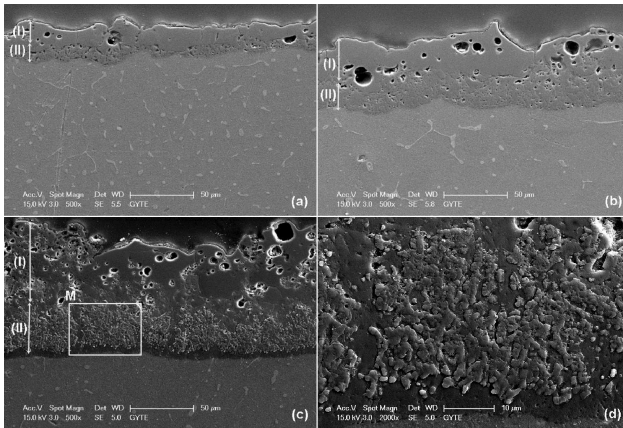


Fig. 3. Cross-sectional SEM micrographs of the samples coated (a) 40 min, (b) 80 min, (c) 120 min, and (d) magnification of region "M" in (c).

The irregular shaped precipitates are more clearly seen in the magnified SEM micrograph of the dense region marked as "M" in Fig. 3c (Fig. 3d). These precipitates have much higher wear resistance than the surrounding matrix. As the XRD spectrum of the 120 min coated sample showed that the intensity of the α - Al_2O_3 significantly increased when the approximately half of the coating ground was removed, it can be easily concluded that these precipitates are α - Al_2O_3 phase. Similar findings were reported for some other MAO coated Al based alloys [1, 11]. α - Al_2O_3 phase precipitates in the dense region of the MAO coating is more stable than γ - Al_2O_3 , as metastable γ - Al_2O_3 phase can transform to α - Al_2O_3 at temperatures higher than 1000°C [12]. The thicker MAO coating result in γ - Al_2O_3 phase in the inner regions transform to α - Al_2O_3 due to the low thermal conduction of oxide based ceramic coating [8, 13].

The typical regional SEM-EDS spectrum obtained from regions I and II for the coating time of 120 min is illustrated in Fig. 4. The spectrum shows that Al, O, Si and Cu are present in both regions. However, the presence of Cu in the region I is not significant while the presence of Si in region II is higher than in region I. The presence of Si was attributed to the sodium silicate in the electrolyte and its infiltration through microarc channels.

As Cu concentration is higher in region II than region I, the difference might be attributed to the sequential formation and dissolution of Cu-O since Cu-O is not very stable.

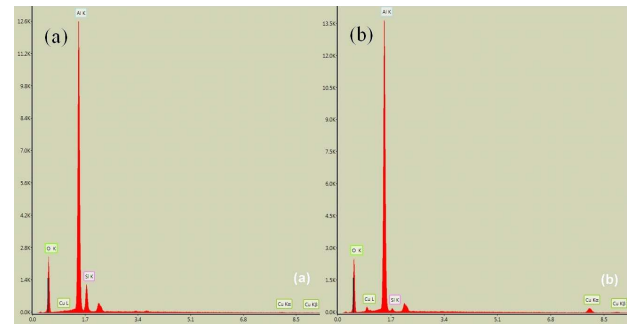


Fig. 4. The regional SEM-EDS spectrum obtained from 120 min coating of Al-4Cu: (a) regions I and (b) regions II (Fig. 3c).

3.3. Coating thickness and surface roughness

Figure 5 shows the change in coating thickness and surface roughness with MAO process time. As it is seen in Fig. 5 the coating thickness increases approximately linearly with the MAO coating time. The coating thickness is $38\ \mu\text{m}$ for the coating time of 40 min and it increases to $115\ \mu\text{m}$ for the coating time of 120 min.

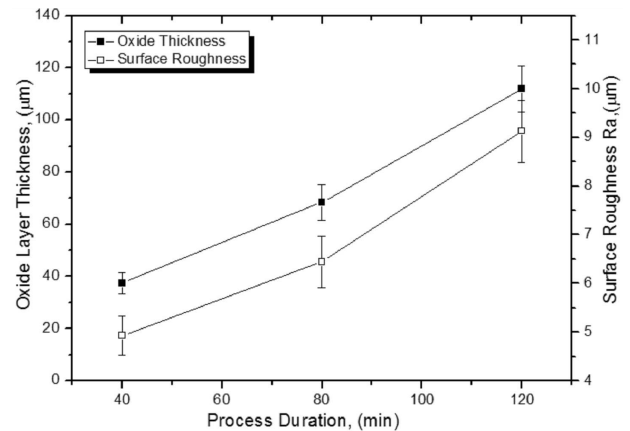


Fig. 5. The change in coating thickness and surface roughness with MAO process time for Al-4Cu alloy.

The surface roughness of the Al-4Cu alloy substrates were measured as approximately $0.30\ \mu\text{m}$ before MAO coating. The surface roughnesses of the samples were also increased approximately linearly with MAO process time. The surface roughness was measured as $5\ \mu\text{m}$ and $9\ \mu\text{m}$ for coating time of 40 min and 80 min, respectively. The thickness increase is a natural result of the oxide material accumulation on the surface during MAO process. Increase in the thickness with MAO time resulted in increase in breakdown voltage and it intensified

microsparks and consequently the surface roughness increased by coating time [14].

4. Conclusions

The coating by MAO adhered very well to the substrate. The coating is characterized as two main regions. While the bigger sized porosities were present in the outer region (region I) of coating, the fine porosities were formed in the inner region (region II) of the coating. The thicknesses of both regions increase when the coating duration increases. However, the coating obtained for 120 min has relatively dense inner region with finely distributed α -Al₂O₃ precipitates. Al, O, Si and Cu are present in both regions. The presence of Cu in the region I is not significant while the presence of Si in region II is higher than in region I. The coating contains the mullite and γ -Al₂O₃ phases for 40 min coating and α -Al₂O₃ phase was also obtained for 80 min and 120 min coating time. The coating thickness increased linearly with coating duration from 38 μ m (40 min) to 115 μ m (120 min). MAO coating process duration increased the surface roughness (R_a) from 5 μ m (40 min) to 9 μ m (120 min).

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