Journal of Ceramic Processing Research. Vol. 7, No. 4, pp. 359~362 (2006)

J O U R N A L O F
Ceramic Processing Research

A study of the corrosion resistance of a micro-arc oxidation coating on a cast aluminum-copper alloy

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Protective coatings have been successfully prepared on a high strength aluminum-copper alloy ZL205 using a micro-arc oxidation (MAO) method. The influence of the oxidation time and current density on the thickness and corrosion resistance of MAO coatings has been studied. The thickness of MAO coating increases linearly with an increase of oxidation time. When the oxidation time is shorter than 20 minutes, the coating improves the corrosion resistance of ZL205 alloy quickly with an increase of oxidation time, which is confirmed by 5% salt spray test. When the oxidation time is longer than 20 minutes, the corrosion resistance of the MAO coating increases slowly with an increase of oxidation time. For a fixed oxidation time, the thickness of the MAO coating increases with an increase of current density and the corrosion resistance can also be improved. SEM and XRD analysis show that the surface morphology and phase of the MAO coating change with an increase of the oxidation time, which results in different corrosion resistance of the MAO coating.

Key words: micro-arc oxidation, casting aluminum-copper alloy, ceramic coating, corrosion resistance.

Introduction

Aluminum and its alloys are known to be relatively resistant to corrosion. However, such materials are susceptible to corrosion when exposed to acids and halides. For example, aluminums and its alloys deteriorate rapidly when exposed to sea water. Traditionally, there have been two common ways of increasing the corrosion resistance of aluminum alloys: anodizing and passivation with chromate solutions. Neither of these two ways, however, is wholly satisfactory. Anodizing involves a complex and expensive multi-step procedure. Chromate passivation does not provide long-term corrosion protection and is harmful to the environment.

The micro-arc oxidation (MAO) method is a new anodizing technology for nonferrous alloys to improve their corrosion resistance and wear behavior [1-5]. This method is a breakthrough for the traditional technique of anodic oxidation. Coatings obtained by this method are crystalline and have good corrosion resistance, wear resistance and an excellent adhesion to the substrate. Furthermore, the electrolytes used in the MAO process are weak alkaline solutions and are friendly to the environment. Also, pretreatments except for water rinses are not strictly necessary for the MAO method. According to a recent study [6-8]. Many investigations have focused on the treatment of 2024 aluminum alloy and cast aluminum-silicon alloy using the MAO method. Little research has been done on cast aluminum-copper alloy using this method. Cast aluminum-copper alloy has good strength and poor corrosion resistance among all cast aluminum alloys because of the presence of copper. Therefore, the improvement of corrosion resistance of cast aluminum-copper alloy will extend its application. In the study reported here, a protective coating was successfully prepared on cast high strength aluminum-copper alloy by the MAO method. The corrosion resistance of the coatings was tested by a 5% salt spray test. The microstructure and phase composition of the coatings were investigated using a scanning electron microscope(SEM) and X-ray diffraction (XRD) methods.

Experimental Details

Column samples (Φ 40×12 mm) of cast aluminum-copper alloy ZL205 were used as substrates. The nominal composition of this alloy is 4.6-5.3% Cu, 0.3-0.5% Mn, 0.15-0.35% Ti, 0.15-0.25% Cd, 0.05-0.3% V, 0.05-0.02% Zr, 0.005-0.06% B (in wt%) and Al balance. The MAO process was carried out with a 75-kW source power instrument which consists of a special high voltage AC power supply with asymmetric potential peak wave form at anode and cathode and a stainless steel bath with a stirring and cooling system. In the experiment, the samples and the stainless steel walls of the bath were used as the two electrodes. The electrolyte was prepared from a solution of sodium silicate in de-ionized water with some additives such as sodium tungstate and sodium tartrate. The electrolyte temperature was controlled to remain lower than 45 °C

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during the oxidation process. After the MAO process, the samples were rinsed in distilled water and dried in hot air.

The thickness of the coating was measured using a German ISOCOPE MPOD eddy-current thickness tester according to the GB 4957-85 standard. The corrosion resistance of the coated and uncoated ZL205 substrates were evaluated by exposing the substrates to a salt fog atmosphere generated by spraying a 5 wt.% aqueous NaCl solution at 35 °C for 120 hours according to the GB/T 10125-1997 standard. The corrosion rate ΔW was used to evaluate the corrosion resistance of the coated and uncoated ZL205 alloy. The corrosion rate is defined by $\Delta W=(W_1-W)/W\times100\%$, where W stands for the sample mass before the salt spray corrosion test and W_1 stands for the sample mass after test. The phase composition of MAO coatings were investigated by an automatic Rigaku D/Max2200 X-ray diffractometer (Cu target, 40 kV, 40 mA). The morphology and micro-structure of the MAO coatings were observed by a JSM-5800 scanning electron microscope (SEM). The samples were sputter-coated with gold prior to SEM observation because of the low conductivity of the MAO coatings.

Results and Discussion

Influence of oxidation time and current density on the growth and corrosion resistance of MAO coatings on ZL205 alloy

Figure 1 shows the variation of thickness and corrosion rate of MAO coating with oxidation time. It is found that the MAO coating thickness increases linearly with an increase of oxidation time, and the corrosion rate of MAO coatings decreases in a salt fog atmosphere at the same time. The corrosion resistance of a MAO coated alloy treated only for 5 minutes is about 3 times higher than that of uncoated ZL205. When the oxidation time is about 100 minutes, the corrosion rate of MAO coatings is about 23 times lower than that of uncoated substrate. It is obvious that MAO coatings can improve the corrosion resistance of ZL205 greatly. When the oxidation time is shorter than 20 minutes, the MAO coating improves the corrosion resistance of ZL205 alloy rapidly with an increase of oxidation time. When the oxidation time is longer than 20 minutes, the corrosion resistance of a MAO coating increased only slightly with an increase of oxidation time.

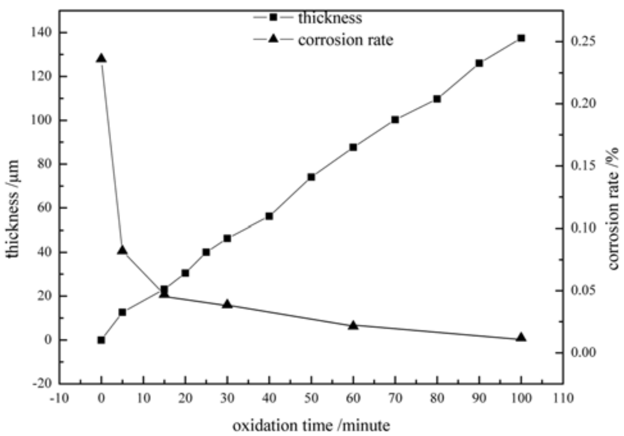

Fig. 1. Variation of thickness and corrosion rate of MAO coating on ZL205 with oxidation time.

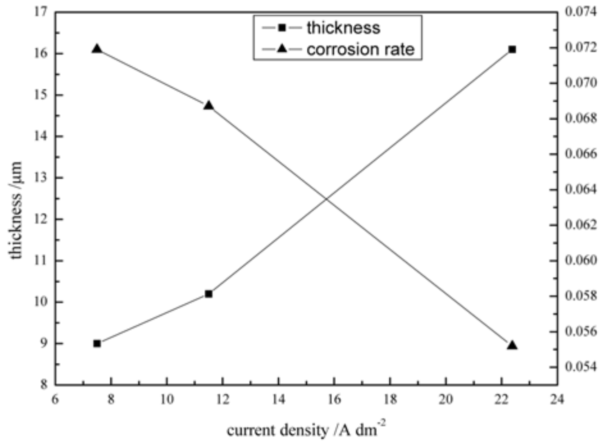

Fig. 2. Variation of thickness and corrosion rate of MAO coatings on ZL205 as a function of current density.

When the oxidation time is fixed at 10 minutes, the variation of thickness and corrosion rate of MAO coating on ZL205 as a function of current density is shown in Fig. 2. It can be seen that the MAO coating thickness increases with an increase of current density and the corrosion rate decreases at the same time.

Characteristics of MAO coating

Figure 3 shows the surface morphologies of MAO coatings with different oxidation times. The surfaces are porous and rather rough. Discharge channels which are caused by the micro-sparks during the MAO process are the main characteristics of MAO coatings. Traces of melting can be found around the discharge channels. There are more discharge channels on the MAO coating surfaces when the oxidation time is shorter, and the diameter of these discharge channels is also smaller. With an increase of oxidation time, the surface of MAO coatings becomes rougher and the diameter of discharge channels is also larger. For example, the diameter of a discharge channel can reach about 20 micrometers when the oxidation time is 100 minutes (Fig. 3d). If pores caused by discharge channels on the surfaces of MAO coatings are deep, the MAO coatings on ZL205 cannot inhibit the contact of the corrosive medium with the substrate and the substrate metal will be corroded slowly. As far as pores in the MAO coatings are concerned, MAO coatings created with a short oxidation time should have a good corrosion resistance. However, the thicknesses of MAO coatings made with a short oxidation time are usually thin and therefore coatings made with this way do not have good corro-

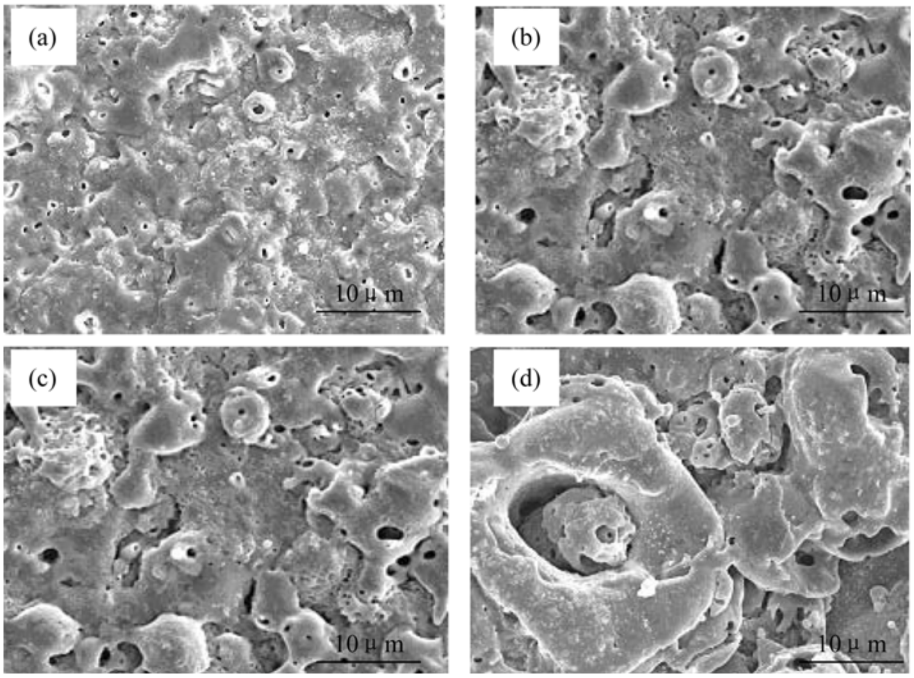

Fig. 3. Surface morphologies of MAO coatings on ZL205 with different oxidation times. (a) 5 minutes; (b) 20 minutes; (c) 60 minutes (d) 100 minutes

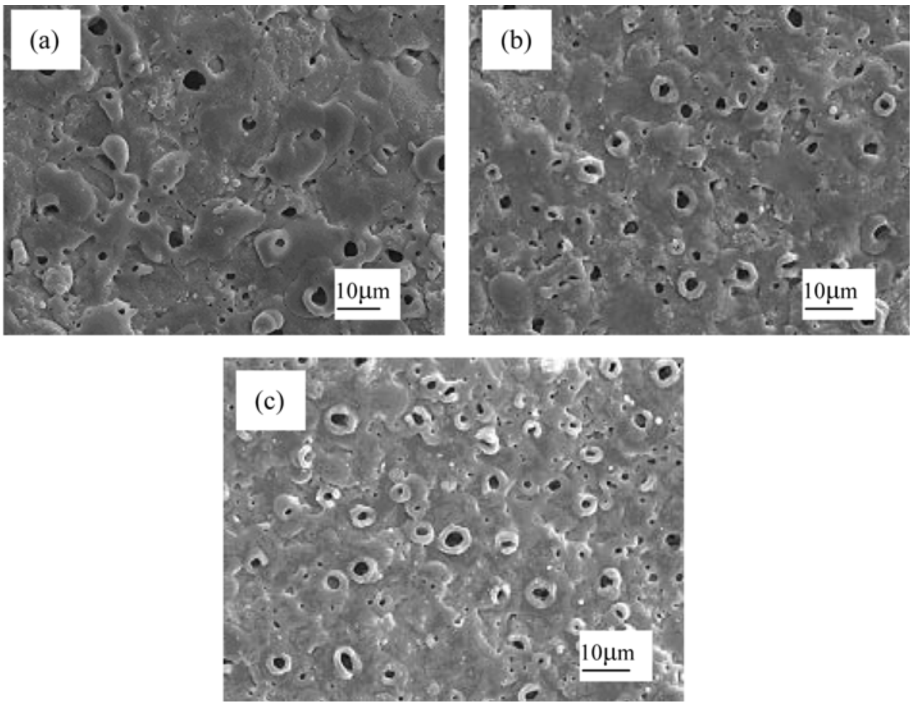

Fig. 4. Surface morphologies of MAO ceramic coatings on ZL205 with different current densities. (a) 22.38 A/dm^2; (b) 11.5 A/dm^2; (c) 7.5 A/dm^2.

sion resistance. Although discharge channels of MAO coatings with long oxidation time are large, these channels overlap with each other and melted substances caused by discharge sparks block the channels, which inhibits the contact of the corrosive medium with the substrate. Thus, MAO coatings made using a long oxidation time give good corrosion resistance.

Figure 4 shows the surface morphologies with different current densities when the oxidation time is fixed at 10 minutes. Because of the short oxidation time, these MAO coatings are relatively thin and therefore the porosity in the MAO coatings is the main factor that influences the corrosion resistance. It can be seen that the porosity in the MAO coatings is relatively small

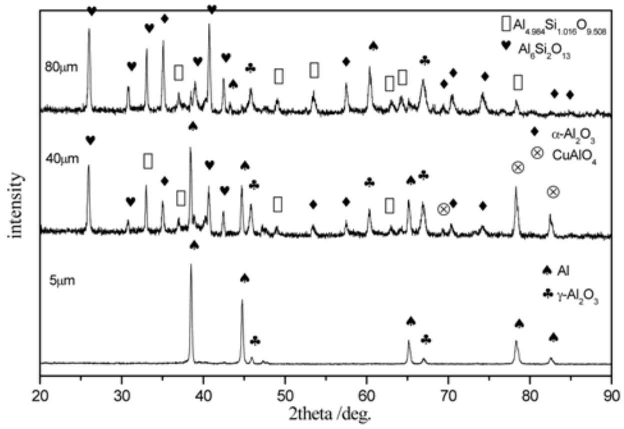

Fig. 5. XRD patterns of MAO coatings on ZL205 with different thickness.

when the current density is larger, which is the reason why MAO coatings made with a larger current density have a better corrosion resistance.

Phase composition of MAO coatings

The corrosion resistance of MAO coatings is affected not only by porosity on the surface but also by its phase composition. XRD patterns of MAO coatings with different thicknesses are shown in Fig. 4. This indicates that the MAO coating is crystalline and consists of α-Al_2O_3, γ-Al_2O_3 and mullite. The appearance of mullite, such as $Al_6Si_2O_{13}$ and $Al_{4.984}Si_{1.016}O_{9.508}$, proves that the electrolyte incorporates a reaction. It also proves that the reactions during the MAO process are very complex. When the oxidation time is longer than twenty minutes, the thickness of the MAO coatings is greater than 30 μm, and the coatings mainly consist of α-Al_2O_3 and mullite. Both α-Al_2O_3 and mullite are stable ceramic phases, and have good wear resistance and corrosion resistance. This is the real reason why MAO coatings made using long oxidation times have good corrosion resistance. When the oxidation time is shorter than 20 minutes, the MAO coatings are thin and the coating is mainly composed of γ-Al_2O_3 and amorphous aluminum oxides. Here the corrosion resistance of these MAO coatings is relatively poor and the porosity in these MAO coatings is the main factor that influences the corrosion resistance of them.

Conclusions

1) Protective coatings were successfully prepared on high strength aluminum-copper alloy ZL205 using a MAO method. MAO coatings can greatly improve the corrosion resistance of ZL205 which was confirmed by a 5% salt spray test.

2) Both oxidation time and current density influence the thickness and corrosion resistance of MAO coatings. The thickness and corrosion resistance increase with an increase of oxidation time and current density.

3) Surface morphologies and phase composition of MAO coatings change with an increase of oxidation and current density. This is the main reason why MAO coatings made with different oxidation times and current densities have different corrosion resistances.

Acknowledgements

This work is supported by the fund of Beijing Jiaotong university.

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