

Corrosion resistance of micro-arc oxidized ceramic coating on cast hypereutectic alloy

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Abstract: The corrosion resistance of the micro-arc oxidation (MAO) ceramic coating on a cast Al-13Si-5Cu alloy was investigated using various electrochemical methods including electrochemical impedance spectroscopy (EIS) and polarization curves. Microstructures of MAO ceramic coating were studied by SEM, and the influence of microscopic patterns on corrosion resistance was analyzed. The corrosion resistance of the aluminum alloy can be improved significantly by MAO process owing to increasing impedance and corrosion potential and decreasing corrosion current, and the ceramic coatings are composed of loose layer, compact layer and transition layer, which improve the corrosion resistance. The corrosion resistance is determined by the thickness of the compact layer and is not proportional to the total thickness of MAO, though the latter is one of the important factors influencing the corrosion resistance.

Key words: micro-arc oxidation(MAO); Al-13Si-5Cu aluminium alloy; EIS; polarization; corrosion resistance

1 Introduction

In recent years, many efforts have been devoted to developing micro-arc oxidation (MAO) technique due to the fact that the thick and hard ceramic oxide coating fabricated by MAO treatment can surprisingly improve the wear resistance and chemical stability as well as biocompatibility of light metals such as aluminum, magnesium, titanium and their alloys[1]. For aluminum alloys, MAO process can form compact ceramic coatings showing good wear resistance, corrosion resistance, electronic insulation, high temperature shock, etc, which gives rise to the wide applications of ceramic coatings formed on aluminum alloy in many fields. Considering the wide application of MAO process to aluminum alloys, the hypereutectic Al-Si alloy treated by MAO has less been investigated. Al-Si alloy is a hypereutectic alloy which is widely used in diesel engine, with good mechanical performance and corrosion resistance[2–3]. In this work, the alloy Al-13Si-5Cu is prepared and treated by MAO process and the corrosion resistance is studied by electrochemical methods.

2 Experimental

The alloy bar with the chemical composition of Al-13Si-5Cu was cast and machined into the sample with size of $\phi 8$ mm $\times$ 3 mm. The ceramic coatings were fabricated using micro-arc oxidation device MAO200/175-II, which was developed in Xi'an University of Technology. The sample and stainless steel plate were separately used as anode and cathode. The MAO electrolyte was a mixed system including silicate and phosphate. The ceramic coatings with the thickness of 6.0, 12.1 and 17.8 μ m were separately obtained by the way of constant current, altering the treatment time, voltage and frequency, simultaneously stirring and cooling the electrolyte by air pump to keep the temperature between 20 °C and 40 °C.

Electrochemical analyses including EIS, Tafel curves and their related data-processing were carried out using an electrochemical work station, LK98C. The tri-electrode system was used, which contained working electrode of matrix alloy and ceramic coating sample by MAO, auxiliary electrode of platinized platinum and

reference electrode of saturated calomel electrode.

Electrochemical impedance spectroscopy (EIS) was carried out in a 5% sodium chloride solution at 25 °C, with the parameters of 50 mV AC signal amplitude, 500 Hz frequency and 1 times integral.

The microstructures of cross-section and surface of the ceramic coatings were observed using JEM-2021 scanning electron microscopy (SEM).

3 Results and discussion

3.1 Measurement of electrochemical impedance spectroscopy

Fig.1 shows the effect of thickness of ceramic coatings on impedance value of the samples. As illustrated in Fig.1, the values of electrochemical impedance of the samples 1, 2 and 3 is higher than that of the matrix alloy 4 significantly. It indicates that the MAO can increase the electrochemical impedance value of aluminum alloy which varies with the thickness of ceramic coating.

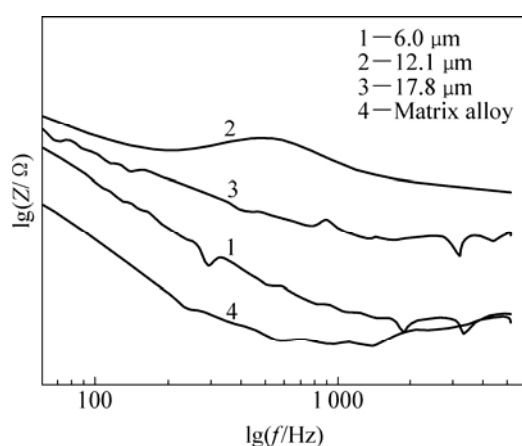


Fig.1 Impedance of matrix alloy and samples 1, 2, 3 with different thickness of MAO ceramic coatings

It can also be seen from Fig.1 that the electrochemical impedance values change with the thickness of the ceramic coating. Sample 2 achieves the highest value, while sample 1 is the lowest, which indicates that the corrosion resistance of sample 2 is the best, the next is sample 3, and the worst is sample 1. The result indicates that the corrosion resistance isn't in direct proportion to the ceramic coating thickness. The fine corrosion resistance depends on the ceramic coating compactability[4–5]. So, the corrosion resistance of sample 3 is worse than that of sample 2 because of the different compactability.

3.2 Measurement of Tafel curves

The Tafel curves gained by testing in the 5% sodium chloride solution at 25 °C with 0.2 V/s scanning

rate and open circuit potential, are shown in Fig.2. The values of self-corrosion potential (ϕ_{corr}) and corrosion current density (J_{corr}) are listed in Table 1.

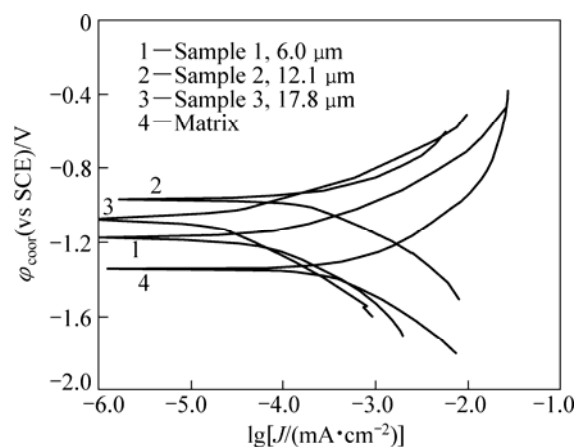


Fig.2 Tafel curves of matrix alloy and samples treated by MAO ceramic coatings

Table 1 Self-corrosion potential and corrosion current of matrix and samples treated by MAO

Sample	$\phi_{\text{corr}}/\text{V}$	$J_{\text{corr}}/(10^{-4} \text{A} \cdot \text{cm}^{-2})$
1	-1.20	2.35
2	-0.98	0.53
3	-1.03	0.92
4	-1.33	4.70

From Fig.2, we can see that the electrochemical corrosion occurs in the polarization system. The polarizability diminishes and the self-corrosion potential shifts from positive to negative. The self-corrosion potential of the samples with thickness of 12.1, 17.8 and 6.0 μm ceramic coatings, shifts from positive to negative and their corrosion current is enhanced in succession. The thickness, compactness and composition phase of the ceramic coating of the alloy influence the corrosion resistance. And a thin, uncompact and loose phase layer has poor corrosion resistance. The discharging and unsealed channels through which electrolyte can corrode the alloy surface remained in ceramic coating determined by the characteristic of the MAO[6–7]. The corrosion resistance of sample 1 is poor due to its thin, uncompact and loose phase layer. Sample 2 is better than sample 3 though its coating is thinner than sample 3, because the compactness of the sample is higher than that of sample 3.

3.3 Corrosion rate

The proof test was carried on by mass gain method in order to validate the results by electrochemical method. The mass gain method refers to the value of original mass subtracting the mass after corrosion[8–9].

$$v = \frac{m_0 - m_1}{S \cdot t} \quad (1)$$

where v is the corrosion rate ($\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$); m_0 is the original mass (g); m_1 is the mass after removing corrosion outgrowth (g); S is the alloy area (m^2); t is the corrosion time (h).

The corrosion rates of samples in 5% sodium chloride solution at 25 °C after being corroded for 168 h are shown in Fig.3. Fig.3 shows that the order of corrosion speed of the samples is $v_4 > v_1 > v_2 > v_3$, which indicates that the MAO treatment can decrease the corrosion speed of the aluminum alloy. The 5% sodium chloride solution contains chloride ions which centralized on the localize active site through selective adsorption and form chloride nucleators when their destructive action to coating surpasses the critical condition, thus the spot corrosion comes into being, which causes the corrosion pits form and continuously deepened[10–12]. Therefore, the corrosion speed of matrix alloy is faster than others. Moreover, the ceramic coating compactness difference accounts for the corrosion speed order, i.e. $v_1 > v_2 > v_3$, which was consistent with the results obtained by electrochemical method.

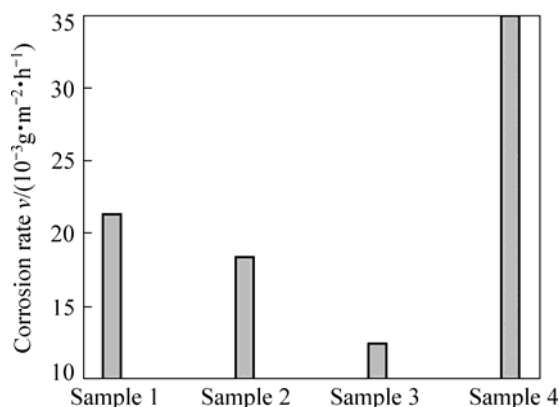


Fig.3 Corrosion rate of samples and matrix in sodium chloride solution

3.4 Micrograph of ceramic coatings

The SEM images of samples treated by MAO are shown in Fig.4. As shown in Fig.4(a), there exist plenty of tiny and “volcano” like substance, and in the center, there is one pore with diameter of 7–8 μm , i.e. the unsealed discharge channel, when the reaction happened between liquor and the matrix alloy. In the condition of existing micro-area arc, the ceramic coating is thickened and forms many small particles covering the original “volcano”. Due to the compact structure that is combined with matrix alloy by metallurgical bonding, the matrix is protected[13–14]. According to Fig.4(b), these pores exist only on the surface of the alloy, and are not through the coating. The improved corrosion resistance results from the ceramic coating structure which consists of loose layer, compact one and transition one.

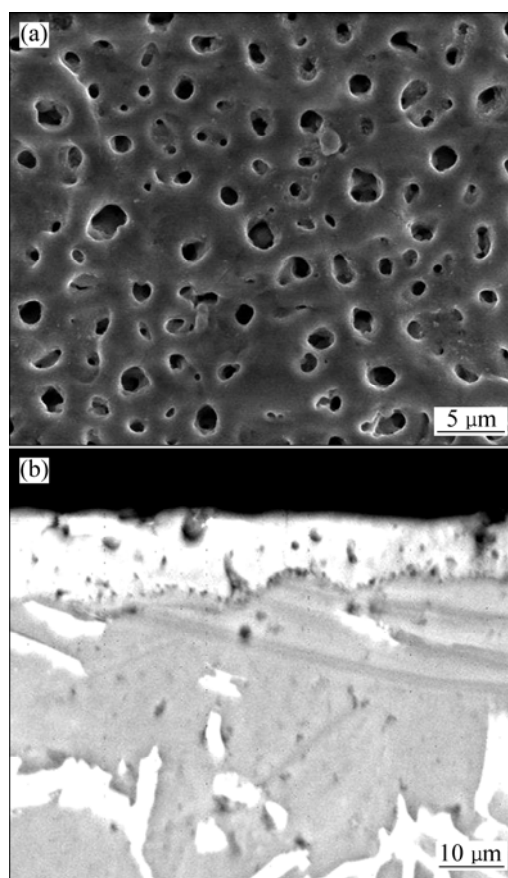


Fig.4 SEM morphologies of ceramic coating: (a) Surface; (b) cross-section

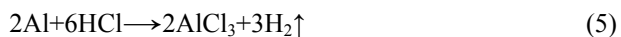
The SEM image of the samples treated by MAO and corroded in 5% sodium chloride solution at 25 °C is shown in Fig.5. We can see that a large number of corrosion products, most of which are concentrated on the orifice of discharge channel, distributed on the alloy surface after corrosion. The pitting corrosion, happens during the corrosion procedure as the following steps[15–16].

1) Al^{3+} concentrates and Cl^- transfers/concentrates in the pore with the development of corrosion.

2) Cl^- participates in the corrosion reaction and makes the solution in the pore to be acidified:



3) Acidic solution is corroded rapidly:



The hydroxide and oxide deposit and cover on the alloy surface owing to the above three stages.

The corrosion potential and EIS reach relatively steady value since the dissolved procedure of the alloy and the covering procedure occur simultaneously.

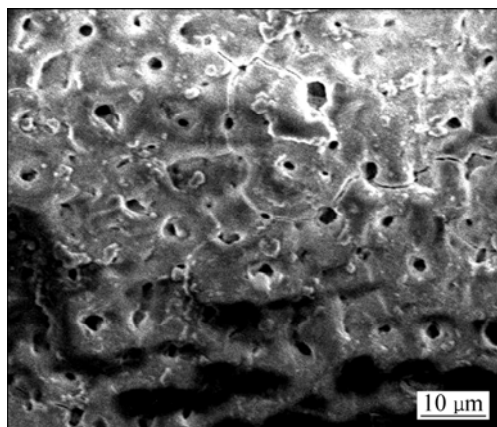


Fig.5 Surface morphology of ceramic coating after corrosion

4 Conclusions

1) The MAO treatment of Al-13Si-5Cu alloy can increase the impedance values of the alloy and increase the corrosion potential to -0.98 V, which result in great improvement of corrosion resistance of the alloy.

2) The MAO ceramic coatings on the Al-13Si-5Cu alloy consists of loose layer, compact layer and transition one. This special microstructures contribute to the high corrosion resistance.

3) The corrosion resistance of the MAO ceramic coatings is mainly determined by the compactness of the ceramic coating.

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