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Influence of Surfactants on Microstructure and Properties of MAO Coated on Aluminum Alloy in Marine Construction

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Abstract. The ceramic oxide coatings on aluminum alloys for marine construction were formed through micro-arc oxidation (MAO) process with CTAB and SDBS surfactants in the original electrolyte solution. The composition, structure and some properties such as tribological behaviour and corrosion of alumina coatings were studied with different SDBS concentration varying from 0 to 0.2g/L (0, 0.05,0.1,0.2g/L) in the electrolyte. The results show that the concentration of SDBS surfactant greatly influences the properties of MAO coating. The alumina coating surface becomes denser and thicker by adding SDBS surfactant in the electrolyte. Besides, the optimum concentration of the SDBS surfactant in the electrolyte to achieve the ceramic coating with a desirable thickness and consequently a desirable corrosion performance is 0.1 g/L.

Keywords. Aluminum alloy, micro-arc oxidation, microstructure, corrosion resistance

1. Introduction

With the development of science and technology, aluminum alloys have been developed rapidly, especially in the application of marine construction [1-2]. Aluminum alloys are light in weight and possess many outstanding mechanical properties. For these reasons that aluminum alloys can be widely used in marine engineering, which is beneficial to the design of marine engineering structures with high speed, long life, high recovery value, higher payload and low maintenance cost [3]. Marine structures are subjected to various complex loads in ocean environments. However, aluminum alloys have some undesirable characteristics including low hardness, poor resistance to wear and a reduction of corrosion performance in marine

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environments, which severely limit their application in the marine industry [4]. So far, it has been reported that the properties of aluminum alloys including anodizing, chemical conversion, organic coating, gas-phase deposition, electroplating and surface laser treatment technology can be significantly improved by surface treatment [5].

At present, it has been proved that MAO treatment process can greatly improve the properties of the aluminum alloys by MAO technology [6]. To date, most of the studies are concerning the influence of electrical parameters during MAO process [7-10]. However, only a few investigations found that the incorporation of surfactants in the electrolyte plays an important influence during the process of MAO. In this paper, 2Al2 aluminum alloy was used as the matrix to reveal the influence of surfactant addition amount on the microstructure, wear resistance and corrosion performance of MAO coatings.

1.1. Experimental Procedure

The substrates used in the experiment were 2Al2 aluminum alloys. The samples were cut into the sizes of 17mm×17mm×4mm by wire cutting machine [11].

A micro-arc oxidation device equipped with the bipolar pulse power supply (MAO-30KW) was used and the pulse mode was adopted in the experiment. The electrical parameters including voltage, current, duty cycle and frequency have been illustrated in table 1. The samples were synthesized for 40 minutes and the temperature of electrolyte was maintained at 5±1°C during MAO process.

Table 1. Electrical parameters in the MAO process.

	Voltage/V	Current/A	Duty cycle/%	Frequency /Hz	Oxidation time /min	Temperature of electrolyte /°C
Positive pulse	400	3.5	45	300	40	5±1
Negative pulse	60	3		100		

MAO coating samples were prepared in the alkaline electrolyte of silicate system which was composed of NaOH (1.5g/L), Na_2SiO_3 (8g/L) and NaF (0.5g/L). The total amount of the electrolyte was 8L. According to previous experimental results [6], it can be found that MAO coating possesses the better corrosion resistance with 2.0 g/L MoS_2 nanoparticles and 0.1g/L cetyltrimethyl amine bromide (CTAB) surfactant in electrolyte than that of the coating without nano-MoS_2 and CTAB. Sodium dodecyl benzene sulfonate (SDBS) surfactant is an anionic surfactant with a yellow oily appearance, which is not easy to be oxidized and has strong foaming power. In order to further reduce the agglomeration of MoS_2 particles, both 0.1g/L CTAB and the amount of SDBS surfactants were added in the original solution. The additive formulation including 2.0 g/L MoS_2, 0.1g/L CTAB and different concentration of SDBS (0, 0.05,0.1,0.2g/L respectively) in the base electrolytic solution has been shown in table 2.

Table 2. The additive formulation of the electrolyte.

Sample Number	MoS_2 (g/L)	CTAB (g/L)	SDBS (g/L)
1	2	0.1	0
2	2	0.1	0.05

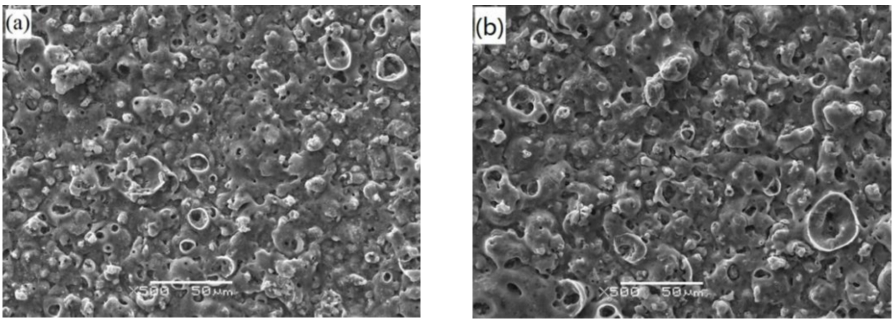
3	2	0.1	0.1
4	2	0.1	0.2

The phase characterization of MAO coating was investigated using X-ray diffraction (XRD) (Model D/Max2500PC Rigaku). The morphology and thickness of film was observed by a Scanning Electron Microscope (SEM) (JSM-6360LV). The friction coefficient of MAO coating was measured by a Multi-Function Tribometer (MFT-3000, Rtec). The sample was performed using a GCr15 steel ball (diameter 4mm, hardness 63-65HRC) and the applied load was 16N for 30min. The corrosion resistance of the ceramic coating was analyzed using an electrochemical workstation (PARSTAT2273) at room temperature.

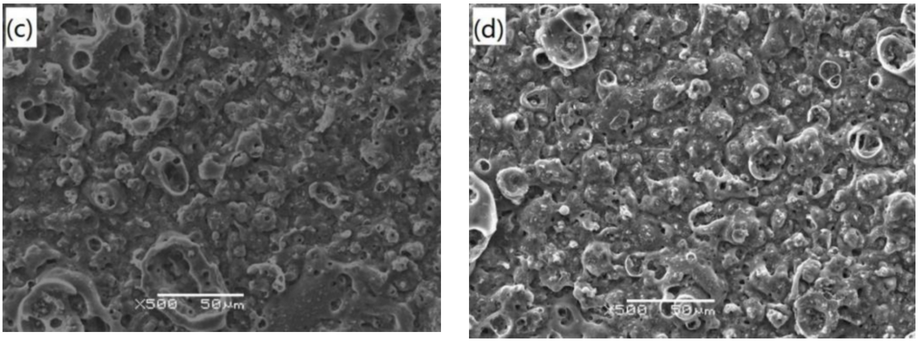
2. Results and Discussion

2.1. Effects of SDBS on the Surface Morphology of MAO Coating

Figure 1 shows the surface morphologies of ceramic coatings by adding various contents of SDBS surfactant in the base electrolyte. From figure 1(a), a large number of micropores can be observed on the coating surface in the absence of SDBS in base electrolyte and the size of the micropores was large. With the addition of SDBS, the number and size of micropores gradually decreased and the density of MAO coating is improved. These results are due to the existence of SDBS, which can effectively eliminate the repulsion between the same charges, form the attraction between positive and negative charges, increase the surface activity of the surfactant and therefore improve its hydrophobicity. On the other hand, the addition of SDBS in the electrolytes could enhance the adsorption capacity of the surface on the aluminum alloy and reduce the surface tension so that more nano-MoS2 particles can be adsorbed into the surface of the aluminum alloy. In such conditions, a denser ceramic coating can be obtained [12-13]. It can thus be concluded that the presence of SDBS surfactant contributes to shaping of dense MAO coatings.



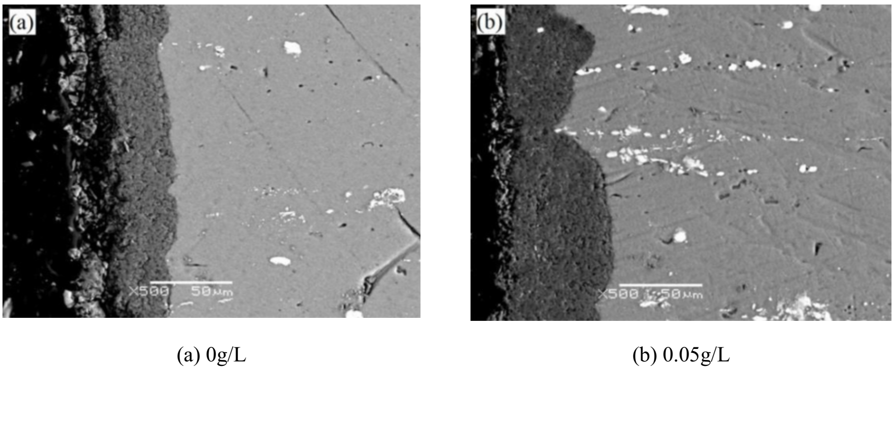
(a) 0g/L (b) 0.05g/L



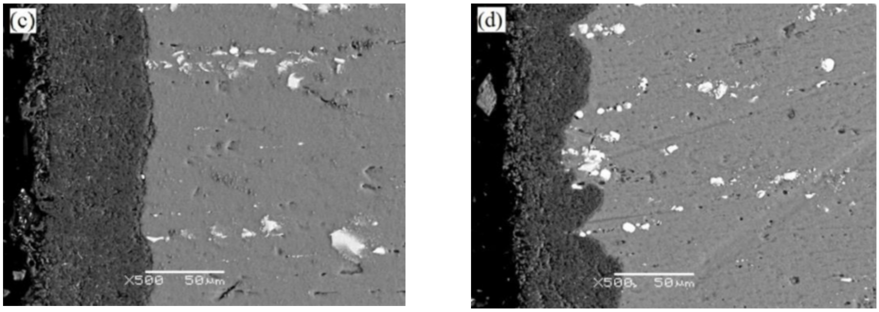
(c) 0.1g/L (d) 0.2g/L

Figure 1. Surface morphologies of MAO coatings with different concentrations of SDBS.

Figure 2 indicates the cross-sectional microstructure of MAO coatings containing different contents of SDBS surfactant. The ceramic coatings formed with the addition of SDBS surfactant is thicker than that obtained without SDBS, which reveals the coating is denser. As shown in figure 2(a), the thickness of the film is very thin without SDBS surfactant in the base electrolyte. When the concentration of SDBS is increased (from figure 2(b) to figure 2(c)), the ceramic oxidation coating is thickened, the micropores on the surface are reduced and the density of the ceramic coating is greatly improved. However, when the amount of SDBS is up to 0.2 g/L, the thickness of MAO coating decreases. This is the consequence of too much SDBS which can hinder the transport of anions to the anode surface and thus make it difficult for the anode to form and maintain the oxide coating. In addition, too much SDBS can increase the dissolution rate of the ceramic coating, so that ceramic oxidation coating can not be further thicken [14-15]. Therefore, when the amount of SDBS added is at 0.1 g/L, the thickest ceramic oxidation coating can be produced on the substrate surface.



(a) 0g/L (b) 0.05g/L

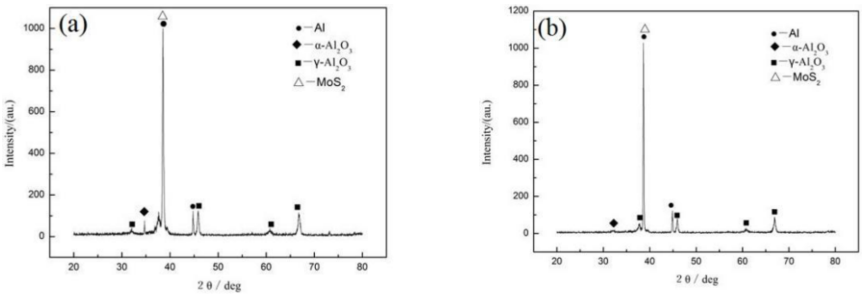


(c) 0.1g/L (d) 0.2g/L

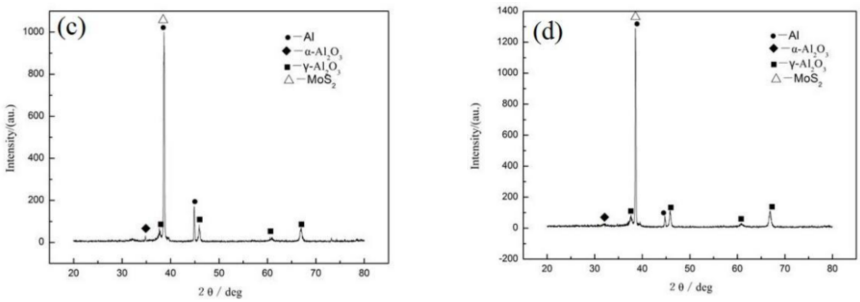
Figure 2. SEM images of the cross sections of MAO coating with different concentrations of SDBS.

2.2. Effects of SDBS on Phase Composition of MAO Coating

Figure 3 illustrates the XRD pattern of ceramic coatings at various SDBS concentrations in the electrolyte. As shown in figures 3(a)-(d), the Al peaks correspond to the matrix, while the characteristic peaks of nano-MoS_2 appear at the same positions of Al peaks in the spectrums. It can be observed that aluminum (Al), γ-Al_2O_3, α-Al_2O_3 and a small amount of nano-sized MoS_2 particles are present in all coated specimens. From this, it can be concluded that the addition of SDBS surfactant hardly influences the phase composition of coated samples.



(a) 0g/L (b) 0.05g/L



(c) 0.1g/L (d) 0.2g/L

Figure 3. XRD patterns of MAO coating with different concentrations of SDBS.

2.3. Effects of SDBS on Tribological Performance of MAO Coating

Figure 4 exhibits the friction coefficient curves of above-mentioned specimens in the process of wear test, and figure 5 displays SEM topographis of all worn surfaces after wear test. It can be seen from the figure that the addition of SDBS is correlated to the friction performance of MAO coating.

When SDBS is not added to the electrolyte, the friction coefficient of the film is small, the curve is relatively flat during the wear test and the friction performance of the coated specimen is better as shown in figure 4. However, with the addition of SDBS in the origin electrolyte, the friction coefficient of the coated samples increases instead. It is not easy to explain the reasons for this. When the micro-arc discharge occurs in the discharge channel of the film surface, the adjacent area is heated violently, the electrolyte entering the channel and the base metal undergo an electrochemical reaction under the action of thermodynamics and the molten oxide forms, which then flows to the external surface along the channel. During this process, CTAB particles adsorbed on the surface of the electrode forms "magma" together with the ejected molten oxide and a microscopic "volcanic cone" shape is formed after cooling, which this results in uneven surface. For this reason, the friction coefficient of the film layer is increased.

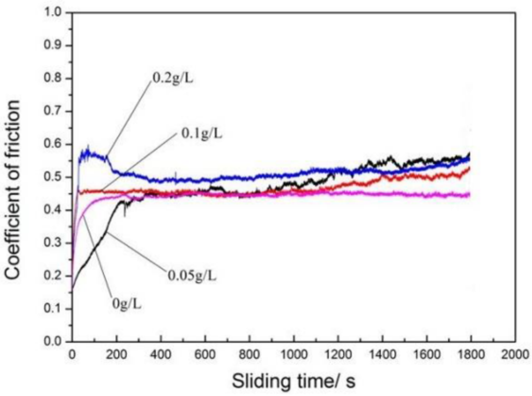
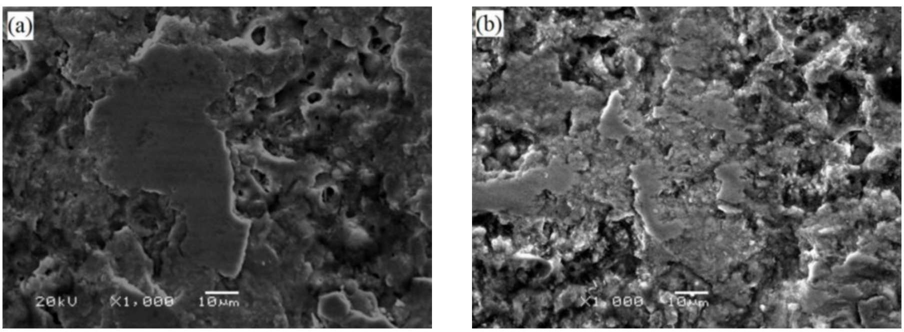
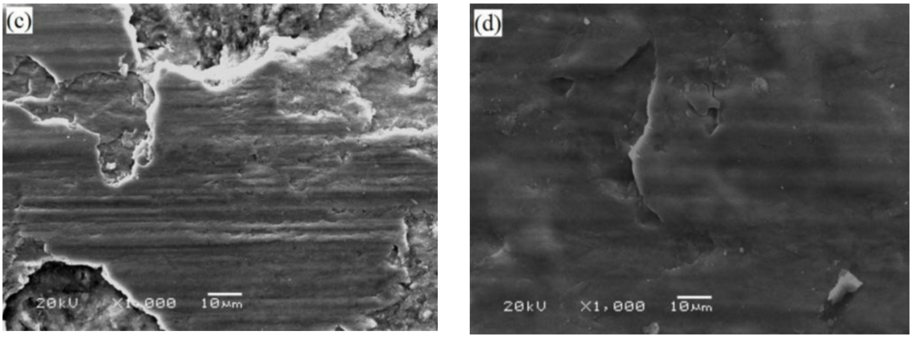


Figure 4. Coefficient of friction of coated specimen with different concentrations of SDBS.



(a) 0g/L (b) 0.05g/L



(c) 0.1g/L (d) 0.2g/L

Figure 5. SEM morphologies of the wear tracks for coated samples with various concentrations of SDBS.

2.4. Effects of SDBS on Corrosion Performance of MAO Coating

Figure 6 displays the potentiodynamic polarization curves of all above prepared samples in NaCl solution (3.5 wt. %). As observed from the figure, the coated specimen without adding SDBS in the electrolyte exhibits lower the corrosion potential and the higher corrosion current, which means the anti-corrosion property of the coated sample is worse.

With the increasing SDBS concentration in the electrolyte, the corrosion potential (E_{corr}) of coated sample firstly increases and then decreases, while the self-corrosion current (i_{corr}) is lower than that without SDBS. In a word, the addition of SDBS can reduce the interfacial tension of the solid-liquid interface and the liquid-gas interface, which makes it easier for the bubbles adsorbed on film surface to detach from the metal surface, so that the ceramic coating becomes denser and the anti-corrosion performance of ceramic coating is better [16-17] with 0.1 g/L SDBS in the base electrolyte. With the further increase of SDBS content (0.2 g/L SDBS), the corrosion resistance of the film decreases instead. The conductivity of the electrolyte is improved with the further increase of SDBS addition and the current on the surface of the aluminum alloy also increases. As a result, the energy generated at the moment of the breakdown discharge is too large so that the breakdown damage occurs in the micro-melting zone. After cooling and solidification, the pores formed by these failures cannot heal, which provides a channel for corrosive medium, making the micro-arc oxidation coating more easily corroded. As mentioned previously (figure 2(c)), when the addition of SDBS is at 0.1 g/L, the thickness of cross-sectional coating is the maximum. So the anti-corrosion performance of ceramic oxide film can be improved by adding 0.1g/L SDBS surfactant in the electrolyte.

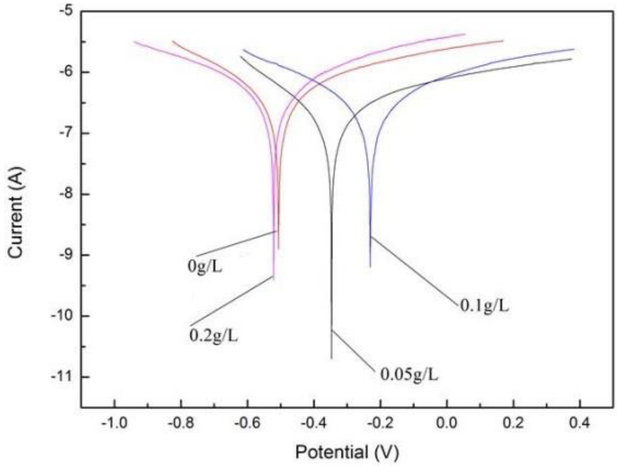


Figure 6. Polarization curves of coated specimens with various concentrations of SDBS.

3. Conclusion

The microstructure and properties of MAO coatings prepared with the addition CTAB and SDBS surfactants in the base electrolyte have been characterized. The results show that the concentration of SDBS surfactant paly an importance role in the preparation of MAO coating. The surface of ceramic oxidation coating becomes compacter and smoother with the increase of SDBS concentration. When the SDBS concentration is at 0.1 g/L, the thickness of the coating reaches the highest and the best corrosion resistance can be obtained with 0.1 g/L SDBS surfactant in base electrolyte.

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