Minireview Article

Investigation of the Influence of Two Different Surfactants on the Frictional Properties of Micro-Arc Oxidation Coatings on Titanium Alloys

ABSTRACT

The micro-arc film-forming mechanism leads to a large number of holes, cracks and protrusions in the ceramic-like oxide film, which makes the compactness and wear resistance of the film less than ideal. By adding anionic surfactant, the microstructure of the film is improved and the friction performance of the film is improved. Methods The micro-arc oxide film layer on the surface of TC4 titanium alloy was prepared by adding AES fatty alcohol sodium ethoxyethylene ether sulfate and SDBS sodium dodecylbenzene sulfonate to the electrolyte. The thickness and hardness of the coating layer were measured by digital eddy current coating thickness gauge and computerized digital microscope Vickers hardness tester, the surface and cross-sectional morphology of the film were observed by scanning electron microscope (SEM), and X-ray diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS) combined with X-ray energy spectroscopy (EDS) were used to jointly analyze the phases contained in the film. The types and contents of the elements were determined, the tribological properties of the film were tested by the friction and wear testing machine, and finally the incorporation mechanism and anti-friction mechanism of the particles were analyzed. Results The thickness of the micro-arc oxide coating with SDBS and AES increased significantly, and the friction performance of SDBS was better, with a friction coefficient of about 0.18, and the film was uniform and dense, with strong adhesion and strong anti-wear and anti-friction properties. Conclusion Micro-arc oxidation with appropriate addition of SDBS can improve the friction performance of the film and enhance the adhesion of the film.

Keywords: titanium alloy, micro-arc oxidation, film layer, friction properties, AES, SDB

1. INTRODUCTION

As a medium strength α-β titanium alloy, TC4 has the advantages of high specific strength, low density, good corrosion resistance, excellent toughness and weldability, and has been well applied in aerospace, petrochemical, shipbuilding, automotive and other fields [1-5], and is the most widely used titanium alloy at present. However, TC4 titanium alloy has low hardness and poor wear resistance, which seriously affects the range of use of titanium alloy. Surface treatment technology can significantly improve the hardness and wear resistance of titanium alloys, and commonly used surface treatment technologies include ion implantation, thermal spraying, anodic oxidation, micro-arc oxidation, etc. [6-9].

Compared with ordinary anodic oxidation, micro-arc oxidation has the advantages of economy, high efficiency and environmental protection, and metallurgical bonded ceramic oxide can be in-situ grown on the surface of Al, Mg, Ti and other valve metals [10-12]. In the process of micro-arc oxidation, the anode substrate is introduced into the high-pressure discharge area, and with the instantaneous high temperature and high pressure generated by arc discharge, the molten material on the surface of the substrate can interact with the components of the electrolyte solution to form a ceramic coating dominated by matrix metal oxides [13-17]. However, in the process of micro-arc oxidation, due to spark discharge, gas precipitation, rapid cooling of molten material and other factors, a large number of micro-pores and micro-cracks will be formed in the film layer [18-20]. These defects will form loose layers with poor bonding force on the surface of the film layer, which will easily peel off under external forces and cause serious abrasive wear on the surface of the film layer, thus leading to the failure of the film layer. Studies have shown that adding solid particles as additives to the electrolyte can achieve the effect of filling micro-pores and micro-cracks, thereby improving the corrosion resistance and wear resistance of the micro-arc oxidation film [21-25].

Shen[26-27] et al. used micro-arc oxidation technology to prepare micro-arc oxidation ceramic layer on the surface of aluminum alloy, and studied the influence of surfactant (sodium dodecyl benzene sulfonate (SDBS)) on the structure and properties of micro-arc oxidation ceramic layer. The results show that with the addition of SDBS, the number of micropores on the surface of the micro-arc oxidation ceramic layer decreases, the size decreases to a certain extent, the density increases, the film formation rate of the electrolyte accelerates, and the thickness of the ceramic layer increases. After adding SDBS, the corrosion resistance of the ceramic layer is improved to some extent. Therefore, in this paper, micro-arc oxidation coating containing nano-Cu particles was formed on the surface of TC4 titanium alloy by micro-arc oxidation treatment method, and the effects of different surfactants on the morphology, phase structure, elemental composition, hardness and tribological properties of micro-arc oxidation coating were studied.

1.Experiment

1.1 Sample pretreatment

The experimental material was TC4 titanium alloy (Ti-6Al-4V) with dimensions of 20 mm × 20 mm × 4 mm. Before micro-arc oxidation, the samples were pre-treated. They were successively ground with 180#, 400#, 600# and 800# sandpapers to remove the rough and uneven parts on the surface of the test blocks and the oxide film layer. The samples were then washed in an ultrasonic cleaner to remove oil stains and impurities on the surface. After the samples were dried, they were placed in a glass cover and set aside for use.

1.2Preparation of the film layer

The MAO device mainly includes power supply (JX-MAO, Lanzhou Jingxin Power Co., LTD.), electrolytic cell, stirrer, circulation cooling system and other components. During the experiment, the TC4 sample was placed in the anode, and the stainless steel plate was used as the cathode. The agitator continued to stir during the energized period, and the temperature of the electrolyte was not higher than 25℃. In the process of micro-arc oxidation, the unipolar constant current control mode is adopted, the current density is 8.0A /dm2 (effective value), the frequency is 300 Hz, and the duty cycle is 25%. The basic electrolyte is composed of $(NaPO_3)_6$ (10 g/L), $Na_2B_4O_7$ (8 g/L), Na_2SiO_3 (2 g/L) and NaOH (4 g/L). Nano-ni particles (diameter about 200 nm) were added to the configured basic electrolyte and continuously stirred for more than 30 min to make it fully dispersed.

1.3Membrane characterization and performance test

The microstructure of the MAO film surface and cross section was analyzed by SEM (TESCAN VEGA), the element content on the film surface was detected by EDS, and the phase composition of the coating was analyzed by XRD (Rigaku/SmartLab SE, Japan - Rigaku). The element composition of the film was analyzed using XPS (Thermo SCIENTIFIC ESCALAB Xi+, USA - Thermo Field) combined with the peak fitting results of XPSpeak41. MAD-1000JMT2 computer digital micro Vickers hardness tester was used to measure the hardness of the micro arc oxide film. The load and retention time were 50 g and 10 s, respectively. The tribological properties of the coating were evaluated under dry friction conditions using a multifunctional friction and wear testing machine (MFT-50000). The friction pair was a 440c stainless steel ball with a diameter of 4 mm and the load, frequency, amplitude and friction time were 1 N, 5 Hz, 10 mm and 600 s, respectively

2.Results and analysis

2.1Effect of different surfactants on the surface morphology of the film

Figure 1 shows the surface microstructure of the micro-arc oxidation film prepared by micro-arc oxidation under two different surfactants for 20min. It can be seen in the figure that the irregular micropores on the surface of the film layer, whose maximum pore size can reach 15 μm, are formed by the discharge channel or the gas escape of molten material too late to fill the cooling, and are restricted by the mechanism of micro-arc oxidation. In contrast, the surface of the SDBS film has fewer bumps, and the number and size of micropores are reduced, and the flatness is better.

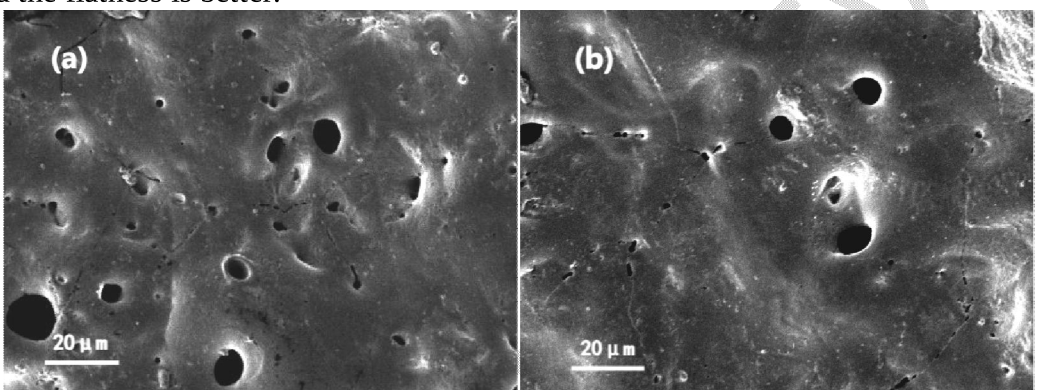

Figure 1: Surface topography using different surfactant layers AES（a）SDBS（b）

2.2Effects of different surfactants on the composition of the film

Table 1 shows the EDS analysis results of the film prepared under different surfactants. It can be seen that the elements in the film layer are mainly composed of O, Ti and a small amount of Cu. This indicates that the anions and Cu particles in the electrolyte also participate in the film formation reaction, and the Cu content in the film prepared by SDBS is higher than that of AES.

Table 1: Elemental content of the film using different surfactants

	MAO	Element content of ceramic film /at.%					
	time/min	O	Al	Ti	Si	P	Cu
AES	20	69.18	1.28	16.97	1.05	9.39	2.14
SDBS	20	65.68	1.57	15.56	0.80	9.92	4.47

2.3The effect of different surfactants on the morphology of film cross section

Figure 2 shows the cross section morphology of the film prepared by micro-arc oxidation of different surfactants for 20min. It can be seen from the figure that the interface between the film layer with SDBS added and the matrix is well bonded, and there are a few microholes and cracks in some film sections. AES was scanned by EDS, and the elements were O, Al, Ti, P, S, etc. Cu was distributed in sparse star spots, which indicated that the element content of Cu was low. When SDBS is used, the scanning results show that the star-dot distribution is gradually dense, and the element content of Cu is increased. When different surfactants were used, the thickness of the prepared film did not change much under the same micro-arc oxidation time, but the number and size of defects in SDBS film decreased significantly.

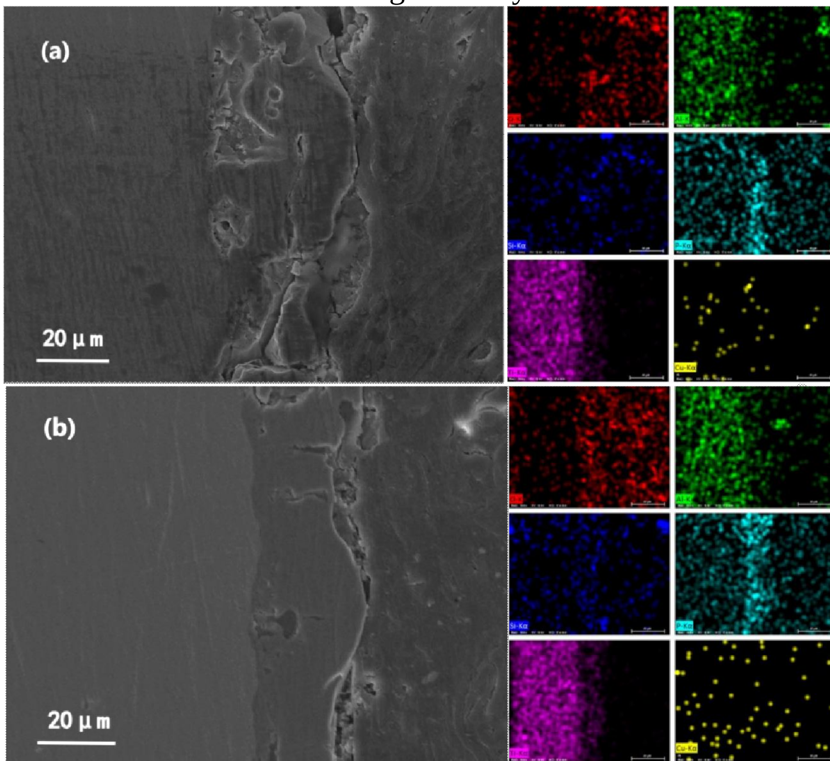

Figure 2: Cross-sectional morphology of different surfactant layers AES（a）SDBS（b）

2.4Effect of different surfactants on the phase composition of the membrane

Figure 3 shows the X-ray diffraction pattern of the film prepared by micro-arc oxidation of different surfactants for 20min. After detection and analysis, the results show that the main phases in the prepared film layer are anatase phase and rutile phase.

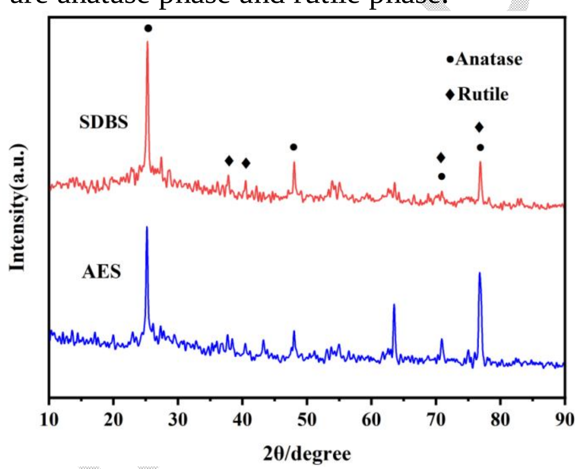

Figure 3: X-ray diffraction patterns of different surface-active prepared coatings

In order to clarify the existence form of Cu particles in the film layer, XPS was used to further analyze the element composition in the film layer. Figure 4(a) shows the XPS full spectrum of the membrane prepared by different surfactants. In the full spectrum, Na, O, Ti, P and other elements from the basic electrolyte were observed, in addition, Cu was also observed. Combined with the EDS scanning results, it was proved that Cu particles successfully entered the membrane. Figure 4(b) shows the high-resolution spectrum of Cu. Cu has two characteristic peaks at the 2p1/2 and 2p3/2 orbits, and the binding energies are 952 eV and 933 eV respectively.

Cu entering the film layer mainly exists in the form of elemental Cu and CuO, among which the content of elemental Cu in the film prepared by SDBS is higher.

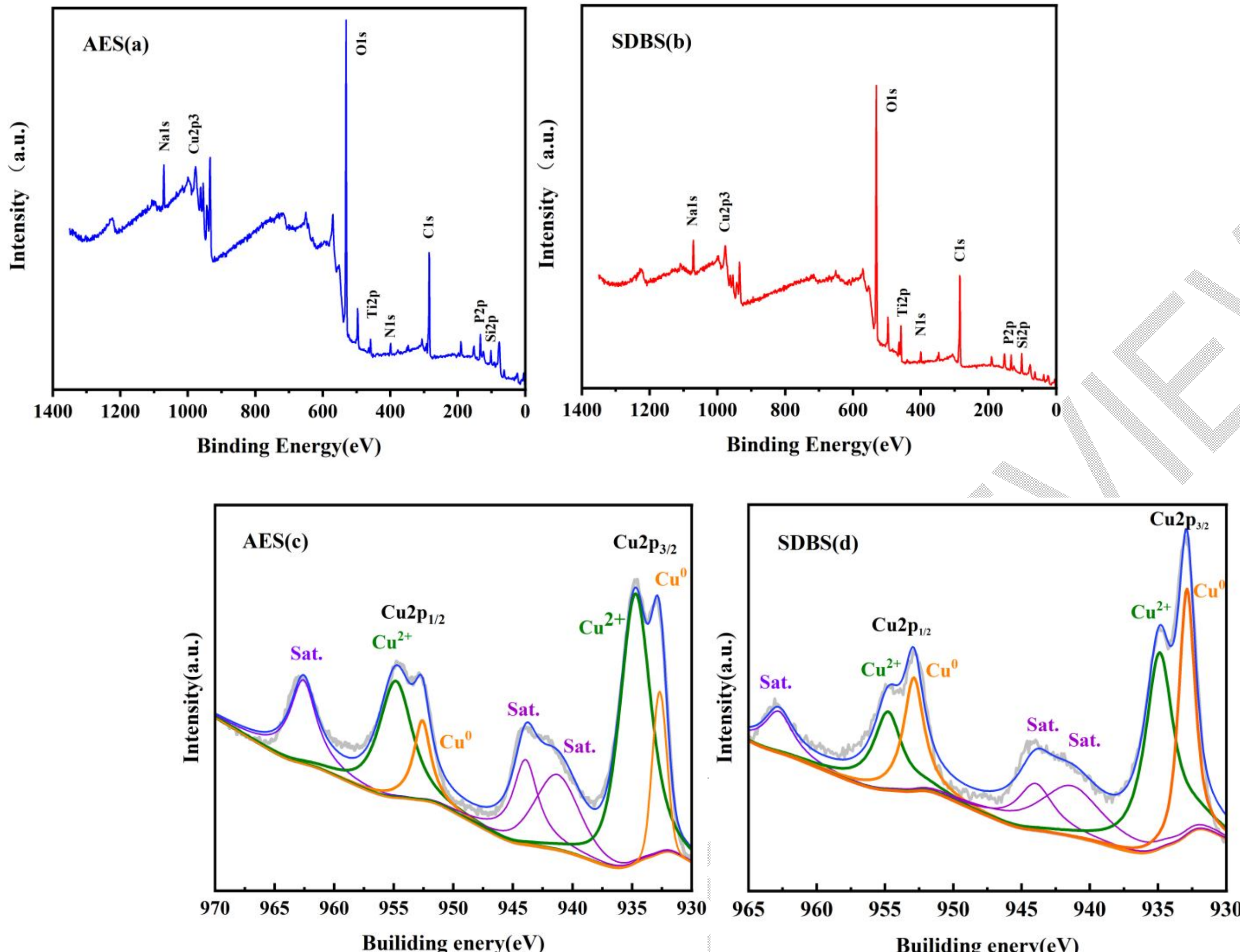

Figure. 4: XPS spectra (a/b) of different surfactants, full spectrum (c/d) of the coatings, and high-resolution spectra of Cu2p

2.5Effect of different surfactants on the hardness of the film

Table 2 shows the hardness of the prepared film under different surfactants. It can be seen from the figure that the hardness of the film layer is improved, and the hardness of the film layer prepared by adding SDBS is about 659HV, which is about 240HV higher than that of the basic film layer.

Types	1	2	3	4	5	6	7	8	Average
Basics	402	397	418	430	427	411	434	422	418
AES	490	542	468	531	506	452	477	524	499
SDBS	614	657	645	721	608	697	625	704	659

Table 2: Hardness of film layers prepared using different surfactants

2.6 Effect of different surfactants on wear resistance of the film

Figure 5 shows the change curve of the friction coefficient of the film prepared by different surfactants in 1200 s. It can be seen from the figure that the friction coefficient of the film prepared by AES is stable at about 0.5 at 900 s, the film is not damaged, and the average friction coefficient is 0.266. The friction coefficient of the film prepared with SDBS tends to be stable around 0.3 at 900s. The average friction coefficient of the film is

0.203. The SDBS friction coefficient curve is relatively stable, which indicates that the surface of the film is denser, the friction pair only plays a slight cutting role in the friction and wear process, and the fine debris of the film can be filled in the microholes to prevent further damage to the film. At the same time, combined with the high resolution spectrum of Cu2p of XPS, the content of Cu in the film prepared by SDBS is higher, and it has better wear and wear reduction.

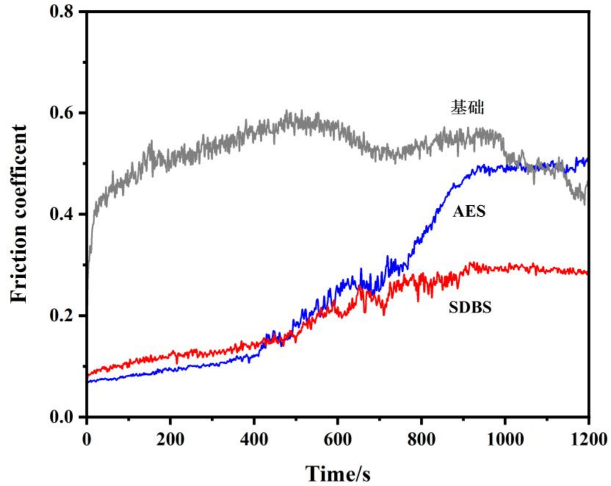

Figure 5: Coefficient of friction of the prepared film under different surfactants

Figure 6 shows the surface abrasion pattern of the film layer. It can be seen from the figure that the mechanical plow gully caused by the grinding pair can be seen on the surface of AES, and its main wear form is abrasive wear, so the friction coefficient curve of the AES film layer increases first and then becomes stable. However, the SDBS film maintained the integrity of the structure after the wear test. In general, the surface state of the film using SDBS was better, and the surface of the film was not damaged, indicating that SDBS had a better strengthening effect on the structure of the film, and the film was more uniform and dense, with stronger bonding force and stronger anti-wear and anti-friction ability.

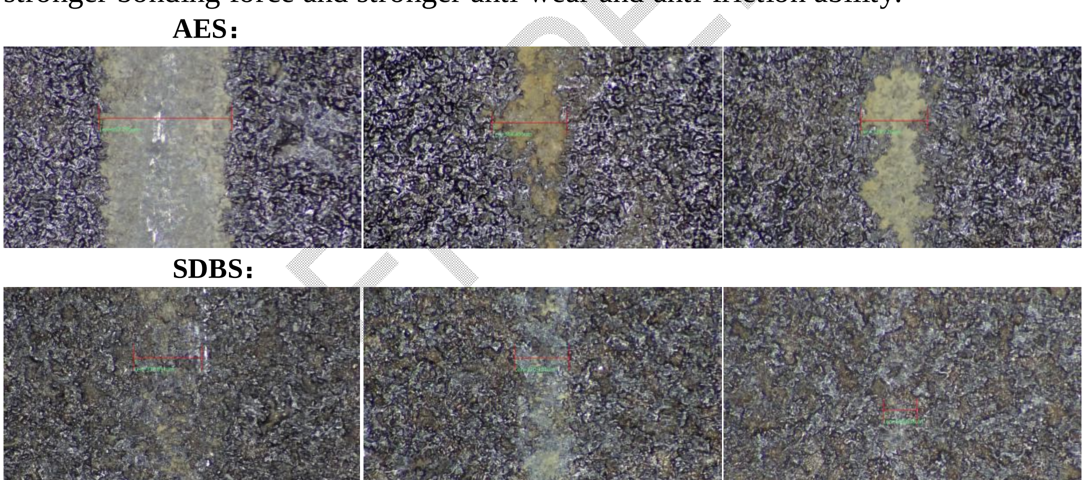

Figure 6: Pattern of abrasion marks of a film prepared using different surfactants

7 CONCLUSIONS

(1)The addition of the two surfactants can improve the film forming quality, and the surface pores of the micro-arc oxidation film prepared by SDBS are reduced, and the pore size is reduced, and the smoothness is better. The film layer is more uniform and dense, and the binding force is stronger.

(2)The microarc oxide film prepared by AES and SDBS is mainly composed of rutile phase and anatase phase, and Cu is detected in the film, and the Cu entering the film mainly exists in the form of Cu and CuO, among which the content of Cu in the microarc oxide film prepared by SDBS is higher, and the anti-friction property is better than that of the film with AES.

(3)The hardness and wear resistance of the micro arc oxidation film prepared by AES and SDBS are improved, and the performance of the film prepared by SDBS is better. The hardness of the film prepared by SDBS is 659HV, which is about 240 HV higher than that of the base film, and the friction coefficient is 246% lower than that of the base film

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