

# Study on Micro Arc Oxidation Coating Based on Ti-5Al-1V-1Sn-1Zr-0.8Mo Alloy with Applied Voltage in Stages

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**Abstract:** The aim of this work is to study how applied voltage in stages incorporates into the prepared micro arc oxidation (MAO) coatings on titanium and control the characteristics and resistances. The microstructure of MAO coatings were characterized by scanning electron microscope (SEM) and laser scanning confocal microscopy, and the coating composition was analyzed by energy dispersive spectrometer (EDS) and X-ray diffraction (XRD). Thickness, roughness and corrosion resistance of coatings were evaluated. Compared with the coating obtained in different applied voltage stages, the coating formed on substrate alloy with first applied voltage 320 V for 180 s and second applied stage 420 V for 720 s shows a minimal roughness. The coating with first applied voltage 320 V for 120 s and second applied stage 420 V for 780 s exhibits a dense micro structure and the best corrosion resistance. The XRD result shows that the MAO coating is composed of  $TiO_2$  and  $Ti_2O_3$  in metastable state.

**Key words:** micro arc oxidation; coating; applied voltage; Ti-5Al-1V-1Sn-1Zr-0.8Mo alloy

The micro arc oxidation technology can form an oxide coating in situ on the surface of Al, Mg, Ti, Zr and other light metals, and improve the wear resistance, corrosion resistance and other properties of the substrate alloy<sup>[1-5]</sup>. Therefore, this technology is widely used in many areas, such as biomaterial, aeronautics, astronautics, and shipbuilding<sup>[6-8]</sup>.

At the beginning of micro arc oxidation, a passivated coating is formed on the surface of the substrate alloy during the process of voltage increasing, which indicates the increased resistance of the substrate. When the voltage is high enough to breakdown the passivated coating, the molten metal starts to gush out, reacts with the electrolyte and solidifies to form a thicker coating. Since the high-temperature melt solidifies instantaneously, a large amount of stresses induce cracks and discharge channels. These locations become the weak points of the next breakdown, which make the coating grow continuously. Therefore, the intensity, location and uniformity of the discharge and breakdown will affect the distribution and release of stress in the coating, and further affect the quality and performance of the coating<sup>[9]</sup>.

At present, the common methods of power supply for micro

arc oxidation are constant voltage and constant current mode. With constant voltage mode, the current is changed passively, and this change determines the process of micro arc discharge and structure of micro holes<sup>[10]</sup>. Therefore, the discharge and breakdown of micro arc can be controlled by controlling voltage, which can reduce internal stress and the cracks. It is generally believed that the constant voltage is easy to control the thickness of the coating<sup>[11]</sup>, but the breakdown capacity is insufficient at the end of treatment process. The discharge arc and coating formation appear when the applied voltage is over arcing voltage. Due to the high energy discharge concentrating in an area, common methods using one-time applied voltage often lead to a non-uniform thickness coating. Therefore, the paper is focused on discharge and breakdown process by controlling the applied voltage, to obtain a suitable treatment method of micro arc oxidation technology.

## 1 Experiment

The substrate for micro arc oxidation is Ti-5Al-1V-1Sn-1Zr-0.8Mo alloy. The specimens were cut into the flake-like with 30 mm×20 mm×5 mm in dimension before heat treatment

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(950 °C/4 h/water quench). Then, the specimens were polished by sand paper step by step and washed with acetone. An electrolyte solution is composed of 16 g·L<sup>-1</sup> Na<sub>2</sub>SiO<sub>3</sub>, 2.0 g·L<sup>-1</sup> Na<sub>2</sub>EDTA and 10.0 g·L<sup>-1</sup> Na<sub>2</sub>HPO<sub>4</sub>. The applied forward voltage was divided into two stages by T-30b type micro arc oxidation power. The applied voltage in first stage was over the arcing voltage (315 V), and the second applied voltage was 420 V. In order to study the influences of stay time and applied voltage of first stage on MAO coatings, they were selected as shown in Table 1. Negative voltage was 80 V, and the electrolyte by circulating water cooling system controlled between 20 °C to 30 °C. The current change were recorded per second.

The thickness of the coating was measured by eddy current thickness meter (HCC-25). The morphology images of the coating were analyzed by scanning electron microscope (QUANTA FEG 650) and laser scanning confocal microscopy (LSM700). Laser confocal microscopy was also used to measure the roughness. Six equal distance locations of X-axis and Y-axis were selected for line scanning from the area of 1.3 mm×1.3 mm. To measure the roughness of coatings, the average of the data was taken as the roughness result of the coating. The X-ray diffraction (XRD) analysis was performed on an X-ray diffract meter (PW1700, Cu K $\alpha$  radiation) to identify the different phases present in the coatings. The scans were acquired from 20° to 80° at a step scan of 0.02°. The corrosion resistance of the coating was tested by electrochemical workstation at room temperature. A corrosive medium with 3.5% NaCl was used for the test. The reference electrode was saturated calomel electrode and auxiliary electrode was platinum plate. The test area was 10 mm×10 mm.

## 2 Results and Discussion

### 2.1 Discharge process with different applied voltage

According to the change trend of current with S1, it can be divided into two stages: the first stage, the forward current peaks and then falls back to the trough during 0~120 s. With the increase of forward voltage from 0 V to 420 V (0 s to 30 s), the forward current increases rapidly to the maximum value. This is because the rising of voltage is much higher than the increase of thickness of oxidation coating, which means that thin coating represents low resistance and the current in the

circuit is high. Then, due to the formation of oxide coating, resistance increases, and the forward current gradually decreases with constant voltage (420 V). In the second stage (120 s to 900 s), due to the action of voltage, discharge breakdown occurs at the weak area on the coating surface and the current increases. In this process, the thickness of the coating increases continuously and the current decreases until arc blowout. The method of applying voltage in stages can change the process of current “up-down” from two times to three times and control the growth of the coating by controlling the arc breakdown (discharge energy), which can obtain a more reasonable treatment process.

Based on the variation of current of S1, as shown in Fig.1a, at the time of 120 s of MAO process, the current curve is at its lowest, and then it starts to go up until the time of 300 s. As can be seen in Fig.1a, during 0~120 s, because the forward voltage of S2 and S3 is lower than 420 V, the current is lower, and the coating on S2 and S3 is thinner. With the 120 s stay at 340 and 360 V, the obtained coating is more likely to breakdown than S1 at 420 V, so the current increases significantly. In Fig.1b, after a stay of 180, 240 and 300 s at 320 V, the current is lower than that of the S1, which indicates that the thickness of the coating increases as the stay time increases, and the breakdown becomes difficult, so the current decreases.

### 2.2 Surface morphology of coatings

The reaction of micro arc oxidation process with one-time applied voltage is intense, the larger porosity and thicker

**Table 1 Specimen code and applied voltage process**

Specimen code	Forward voltage (treating time)
S1	0→420 V (900 s)
S2	0→340 V (120 s)→420 V (780 s)
S3	0→360 V (120 s)→420 V (780 s)
S4	0→320 V (120 s)→420 V (780 s)
S5	0→320 V (180 s)→420 V (720 s)
S6	0→320 V (240 s)→420 V (660 s)
S7	0→320 V (300 s)→420 V (600 s)

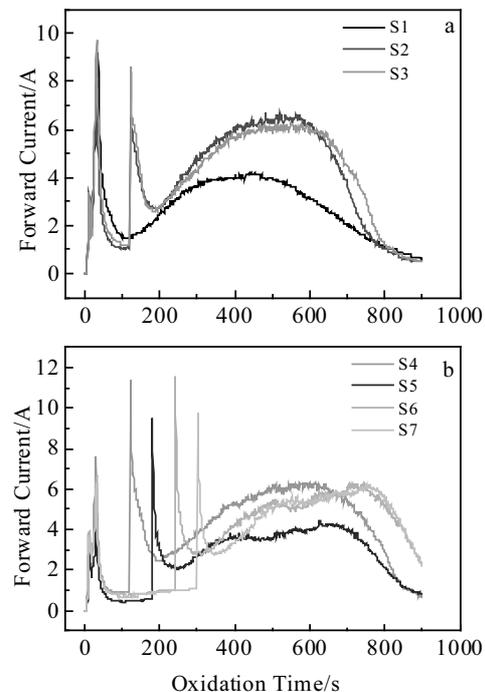


Fig.1 Variation of current with oxidation time at different applied voltages in stages: (a) S1~S3 and (b) S4~S7

coating is obtained, and there are many cracks on the surface, as shown in Fig.2a. There are a lot of raised melt oxides with irregular shape after solidification which are the result of intense discharge. It is proved that the coating formed at the end of the process is only broken down by partial discharge. The coating in Fig.2b is relatively flat, and the circular hole diameter distributed on the surface is basically the same. There are a large number of cracks in Fig.2c. The coating formed on S3 after the transition voltage from 360 V to 420 V is not different from that of S1 significantly. A few micro cracks can be seen in Fig.2d, and there is also a large amount of melt oxides in the holes, but they do not erupt with the completion of the discharge arc. It is

indicated that the strength of discharge on the coating of S4 is appropriate. The holes distributed on the coating of S5 have the smallest diameter and the most uniform distribution, as shown in Fig.2e. As can be seen in Fig.2f and 2g, the diameters of the discharge holes are uneven, which means that there are large irregular holes and small micro holes. This is the result of the micro arc oxidation reaction which is not uniform with first applied voltage stage over 180 s.

Fig.3 shows the 3D morphology and line scanning analysis of the coatings which are formed by different applied voltage processes. As can be seen from the figures, the surface of the coating is a three-dimensional structure with ups and downs,

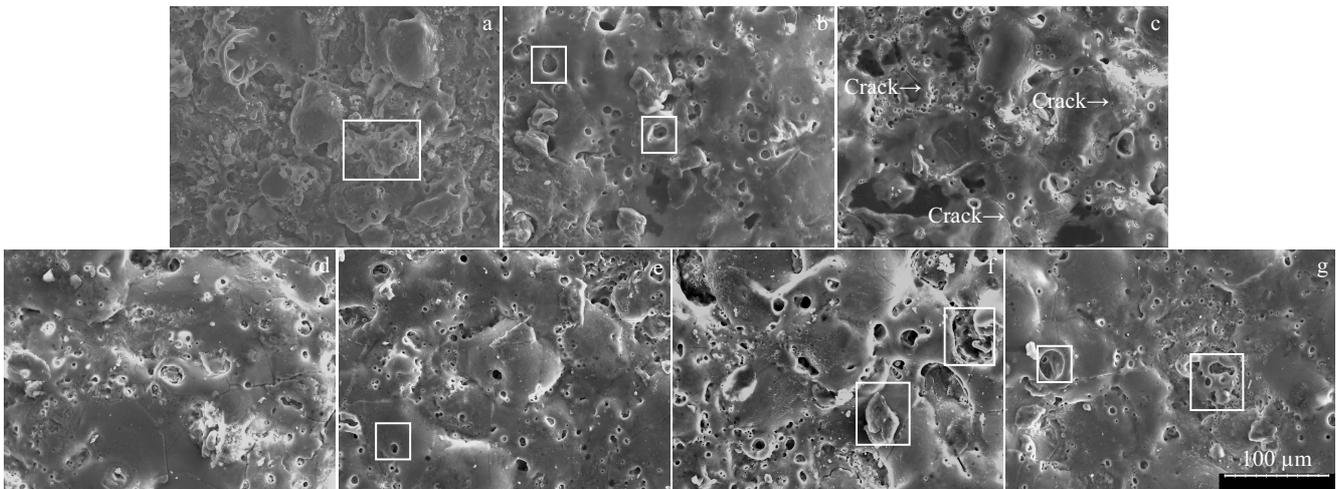


Fig.2 SEM images of MAO coatings: (a) S1, (b) S2, (c) S3, (d) S4, (e) S5, (f) S6, and (g) S7

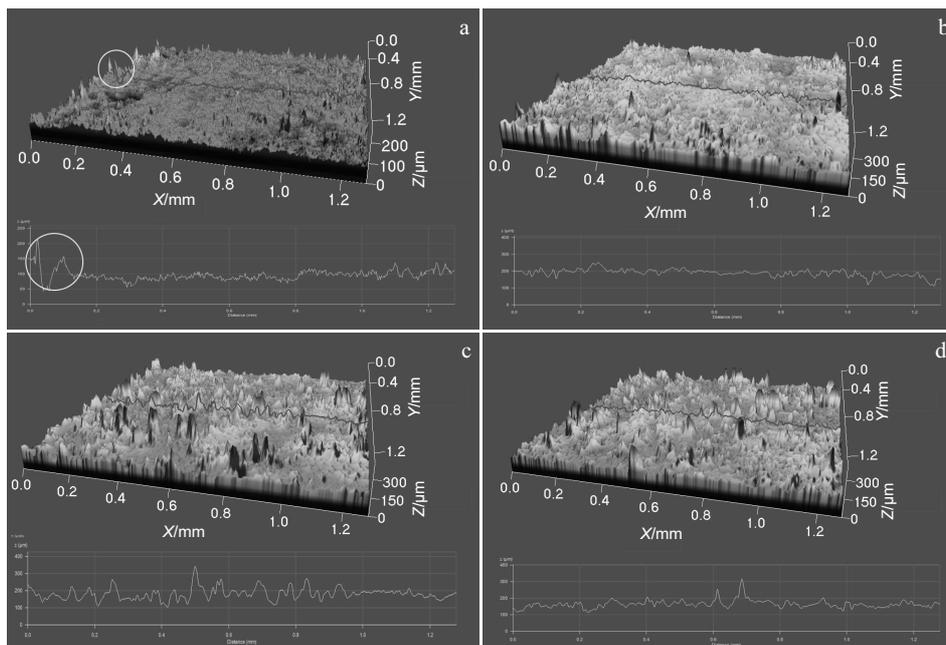


Fig.3 3D morphologies and line scanning analysis of MAO coatings: (a) S1, (b) S2, (c) S3, and (d) S4

and the convex part is the melt oxide particles observed in the surface morphology. When the voltage is loaded at one time, there are individual “high-altitude” area and concave area below coating surface, as shown in Fig.3a, with one-time applied voltage. This position is caused by local peeling during high-energy breakdown. When the applied voltage process is sectional, the first stage applied voltage is lower (320 and 340 V), the coating is smooth relatively, as shown in Fig.3b and Fig.3d. When the first applied voltage is 360 V, as shown in Fig.3c, the fluctuation and unevenness of the coating are obvious, but the distribution of the bulge is more uniform than that of S1 surface.

### 2.3 Thickness and roughness of coatings

Fig.4 shows the thickness and roughness of the micro arc oxide coatings obtained by different applied voltage process. As can be seen from the figure, the thickness is affected by the voltage obviously, and the thickest coating of 87  $\mu\text{m}$  is obtained by the one-time applied voltage. When the voltage is applied in subsection, the coating is gradually thickened with the increase of the first stage applied voltage. High voltage makes the discharge more energetic and the reaction more intense, so a thicker coating is obtained. When the first stage applied voltage is 320 V, the thickness of the coatings is almost not affected by prolonging the time of first stage. This phenomenon is the result of two reasons. Firstly, the current before 120 s falls off obviously, which means that the first stage applied voltage (320 V) is not enough to breakdown the dense coating. Secondly, the next stage applied voltage for all is 420 V, which means the effect of second stage applied voltage for thickness is almost ignored.

It also can be seen from Fig.4 that the roughness of the coating decreases significantly with subsection applied voltage process. A comparison of roughness of the three coatings with different first stage applied voltages (S2, S3 and S4) indicates that the roughness of coating increases with the rising of the first stage applied voltage. The reason is that the thinner coating was obtained with lower first stage applied voltage (320 V), and the smooth and uniform coating was formed by more weeny discharge arc at the second stage (420 V). However, when the

first stage applied voltage is too high, because of the positive feedback effect<sup>[12]</sup>, the growth of coating can only be carried out by the breakdown of discharge arc at a few weak positions, which will lead to the increase of the coating roughness. By comparison of coatings with the low first stage applied voltage (320 V), the lowest roughness of the coatings is detected on S5 which was loaded for 180 s at first stage. This result corresponds to the surface morphology. According to the current curve of S5, as shown in Fig.1b, its current is minimal with slight change during the second applied stage. It indicates that the micro arc oxidation reaction on the surface of S5 is not intense, and the growth of the coating is uniform, so the roughness of the coating is minimal.

### 2.4 Coating composition

The elemental composition and phase composition of the coating on the surface of the substrate alloy staying at first applied stage of 320 V for different oxide time are compared, and the results are shown in Table 2 and Fig.5. The main component elements of the coatings are O, Na, Si, Ti and Al, among which Na, Si and O are from the electrolyte. Ti and Al are the main components of the substrate which all exist in the form of their oxides. With the one-time applied voltage, the contents of Al and Si in the coating of S1 are more than others, which should be the amorphous mullite form and it is not detected in the XRD result of Fig.5. Content of Ti in the coating of S4 is the highest, and the result in Fig.5 shows that there is  $\text{Ti}_2\text{O}_3$  in metastable state besides  $\text{TiO}_2$ . In addition, the anatase  $\text{TiO}_2$  phase content is also higher than that in other coatings. This is due to the lack of complete reaction of the melt in the pores of the coating of S4. With extending the

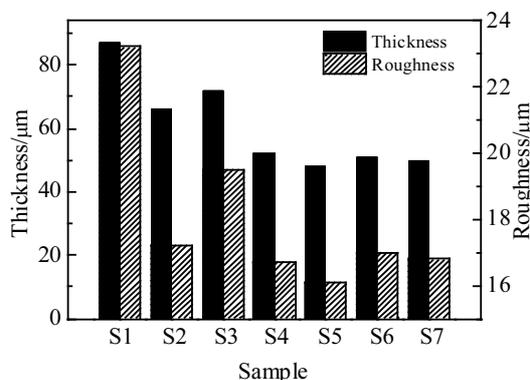


Fig.4 Thickness and roughness of MAO coatings

Specimen code	O	Na	Si	Ti	Al
S1	54.33	4.92	25.24	12.97	2.54
S4	54.76	4.97	20.13	19.05	1.09
S5	59.46	2.20	22.79	14.50	1.05
S6	58.59	2.23	21.73	15.68	1.77
S7	57.48	2.68	23.26	15.21	1.37

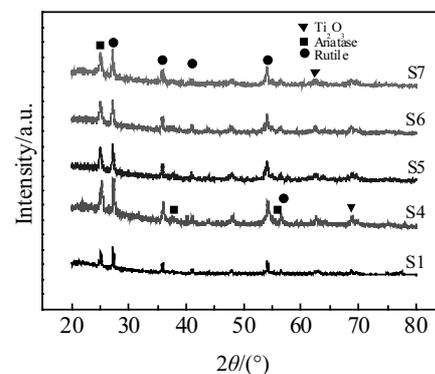


Fig.5 XRD patterns of MAO coatings

first stage of applied voltage, the content of O element in coatings of S5, S6 and S7 decreases slightly. This indicates that the reaction is fully carried out and the diffraction peak of  $T_2O_3$  decreases.

## 2.5 Corrosion resistance of coatings

The polarization curves are shown in Fig.6, and the calculated values of corrosion potentials ( $E_{\text{corr}}$ ) and corrosion current density ( $I_{\text{corr}}$ ) are shown in Table 3. The results mainly indicate the corrosion resistance of all coatings are affected by applied voltage process.

In thermodynamics,  $E_{\text{corr}}$  is mainly determined by the properties of the material itself. A higher  $E_{\text{corr}}$  causes a decrease in tendency of corrosion occurrence. Compared to other coatings,

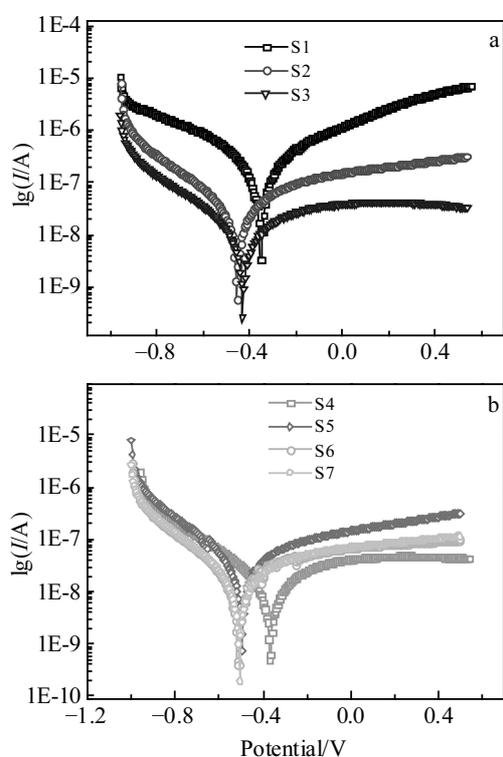


Fig.6 Polarization curves of MAO coatings with different applied voltage processes: (a) S1~S3 and (b) S4~S7

**Table 3 Corrosion potentials and corrosion current density of MAO coatings**

Specimen code	Corrosion potential, $E_{\text{corr}}/V$	Corrosion current density, $I_{\text{corr}}/nA \cdot cm^{-2}$
S1	-0.3569	12.8
S2	-0.4689	4.78
S3	-0.4345	15.4
S4	-0.3904	2.45
S5	-0.5027	3.62
S6	-0.51	7.95
S7	-0.5111	8.66

the corrosion potentials ( $E_{\text{corr}}$ ) of the coating on S1 and S2 surface are positive shift slightly, which means a decrease in thermodynamic tendency of corrosion occurrence. As the time of first stage of applied voltage (320 V) increases,  $E_{\text{corr}}$  tends to be similar. However,  $E_{\text{corr}}$  can only show the corrosion tendency, while the corrosion resistance depends on the corrosion current density in the specific corrosion environment.

The corrosion resistance of micro arc oxidation coating is mainly dependent on the thickness, microstructure and surface defects of the coating. Thereinto, the microstructure is mainly reflected by the number of micro pores and porosity, while the surface defects are mainly about the microcracks. In the case of MAO process of S1, although the coating is thicker than others, its surface is not smooth and dense. The thicker coating is due to the large amount of melt oxides and means that there are amount of surface defects. Therefore, the corrosion resistance of the coating on S1 is worse. As the applied voltage in the first stage is higher (S3, 360 V), the corrosion medium can easily penetrate the coating and corrode the substrate due to a large number of cracks, as shown in Fig.2c. Therefore, compared with other coatings, its  $I_{\text{corr}}$  is the largest and the coating has poor corrosion resistance. Applied voltage is lower in the first stage (320 V), the effect of treating time in first stage on its thickness is small, and the main affecting factors of the corrosion resistance are the microstructure and surface defects. As can be seen in Fig.2d, the dense coating is obtained with the melt oxide in the micro pores. Thus, it can prevent the corrosive  $Cl^-$  into the coating, resulting in the lowest corrosion current density, and corrosion resistance improves. After the first stage time is prolonged, such as the coating of S6 and S7, cracks and irregular discharge channels appear, resulting in poor corrosion resistance.

## 3 Conclusions

- 1) The applied voltage in stages can change the process of current "up-down" from two times to three times and control the growth of the coating by controlling the discharge energy.
- 2) The dense coating is obtained with the melt oxide in the micro pores on the coating surface with the first stage applied voltage 320 V for 120 s. The holes distributed on the coating with the first stage applied voltage 320 V for 180 s have the smallest diameter and the most uniform distribution.
- 3) The thickest coating of 87  $\mu m$  is obtained by the one-time applied voltage. The minimal roughness of coating is obtained with the first stage applied voltage 320 V for 180 s.
- 4) The coating with first stage applied voltage 320 V for 120 s exhibits the lowest corrosion current density and the best corrosion resistance.

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## 基于 Ti-5Al-1V-1Sn-1Zr-0.8Mo 合金的分段电压微弧氧化膜层的研究

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**摘 要:** 主要研究分段电压对于钛合金表面所制备的微弧氧化膜层特性的影响。利用扫描电子显微镜(SEM)和激光扫描共聚焦显微镜对 MAO 膜层的结构进行了表征, 利用能谱分析(EDS)和 X 射线衍射(XRD)对膜层成分进行分析。对比评价了不同分段电压模式下膜层的厚度、粗糙度和耐蚀性。结果表明, 第 1 阶段电压为 320 V 氧化时间 180 s 与第 2 阶段电压为 420 V 氧化时间为 720 s 相比, 所形成的膜层粗糙度最小。第 1 阶段外加电压 320 V 氧化时间 120 s 与第 2 阶段外加电压 420 V 氧化时间 780 s 相比, 膜层最为致密, 耐腐蚀性最好。XRD 结果表明, 膜层是由 TiO<sub>2</sub> 和亚稳态 Ti<sub>2</sub>O<sub>3</sub> 组成。

**关键词:** 微弧氧化; 膜层; 外加电压; Ti-5Al-1V-1Sn-1Zr-0.8Mo

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