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ARTICLE

# Influence of Nano-zirconia on Micro-arc Oxidation Film of TC4 Titanium Alloy

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**Abstract:** With the multifunctional micro-arc oxidation power source, the micro-arc oxidation was conducted on TC4 titanium alloy through the treatment with the mature and widely-used electrical parameters. Nano-zirconia of different concentrations was added into the electrolyte to investigate the variation of microstructure and comprehensive mechanical properties of the micro-arc oxidation film. The influence of nano-zirconia on the film was discussed. Results show that with increasing the nano-zirconia concentration, the film thickness barely changes, but the composition and component concentration of the film differ: the brookite phase appears in the film, and its concentration is increasing. When the nano-zirconia concentration is 2 g/L, the roughness of the film layer is greatly reduced, compared with that without nano-zirconia addition, and the wear resistance of the film layer is optimal. In addition, the micropore diameter on the layer surface is the smallest and uniform, and the corrosion resistance is optimal.

**Key words:** micro-arc oxidation; microstructure; nano-zirconia; wear resistance; corrosion resistance

Due to their excellent corrosion resistance, high specific strength, and good biocompatibility, titanium alloys are widely used in marine, aviation, medicine, and military fields. Among them, TC4 titanium alloy has been extensively researched and used[1]. However, the application of titanium alloys is restricted due to the destruction of passivation film in special environments. Therefore, the comprehensive performance of titanium alloys in special environments has attracted much attention[2]. It is of great significance to improve the comprehensive properties of titanium alloys in special environments by forming a film layer on the surface of titanium alloys. Among various surface technologies, micro-arc oxidation (MAO) has the advantages of fast film formation, strong bonding force between film and substrate, and environmental-friendly economy, thereby becoming a widely used surface treatment technique.

Because MAO film layer is a ceramic layer formed by in-situ reaction on the substrate, it bonds with the substrate through metallurgical bonding, resulting in strong bonding force[3]. The electrolyte composition can significantly affect the film quality and the performance of MAO film by additives. Most electrolytes for MAO process contain alkaline, which may generate pollution to the environment. The wear resistance and corrosion resistance can be improved by changing the electrolyte composition[4].

In this research, the commonly used electrolyte and electrical parameters were used for MAO process, and monoclinic zirconia additive of 50 nm in size was added into the electrolyte to change the microstructure and comprehensive mechanical properties of the film. Nano-zirconia has the characteristics of high hardness, high-temperature resistance, corrosion resistance, and wear resistance[5–6]. When the nano-zirconia participates in the MAO reaction process, it can effectively transfer the load, thereby improving the wear resistance and corrosion resistance of the film[7–9].

## 1 Experiment

TC4 titanium alloy was processed into a circular metal sheet of $\Phi$35 mm with thickness of 3 mm. The specimens were polished by sandpaper and ultrasonically cleaned by

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acetone solution and ethanol solution to remove oil stains and oxide films on the surface. The electrolyte contained 16 g/L $Na_2SiO_3$, 2.0 g/L $Na_2$(ethylenediaminetetra-acetic acid), 10.0 g/L $Na_2HPO_4$, and nano-zirconia with different concentrations, as shown in Table 1. During the experiment, the forward and negative voltages were kept at 420 and 80 V, respectively; the frequency was 100 Hz; the duty cycle was 50%; the oxidation duration was 30 min. When the nano-zirconia concentration was higher than 5 g/L, the surface roughness of the film layer was high, and a strong popping sound occurred during the reaction process. Therefore, the maximum concentration of titanium dioxide was 5 g/L in this research. The specimens were connected to the anode through a wire, and the stainless-steel container was the cathode. The temperature of the treatment solution was controlled below 30 ° C by cooling circulating water, and the electrolyte was stirred during the whole process of MAO. After MAO and the voltage becoming 0 V, the specimens were taken out of the electrolyte. Finally, the electrolyte on the specimen surface was cleaned by deionized water and the specimen was dried.

The thickness of the film layer was measured by OXFORD INSTRUMENTS CMI 233 magnetic induction/eddy current dual-purpose thickness gauge. The cross-section thickness was observed by scanning electron microscope (SEM). The surface roughness was observed by laser confocal microscope (LSM700). The line scanning was conducted along three *X*-axes and three *Y*-axes with equal intervals in the area of 1.3 mm×1.3 mm on the specimen. The average value was used for analysis. The microstructure of the surface and cross-section was observed by SEM. The element content and distribution in the film layer were analyzed by energy dispersive spectrometer (EDS). The phase composition of MAO film was detected by X-ray photoelectron spectroscope (XPS) and X-ray diffractometer (XRD, PW1700, Cu Kα radiation) with scanning angle of 20°–80° and scanning rate of 2°/min. The adhesion between the film layer and the substrate was tested by automatic adhesion scratcher (6 scratches were made on the front and back sides, and the average result was used for analysis). The sudden change of the electrical signal was used to reflect the adhesion force of the film layer when it was scratched. The wear resistance was tested by DZ-322TABER rotary wear tester. The pressure load was 750 g, the speed was 50 r/min, and the mass loss was measured. The corrosion resistance of the film layer was tested by YWS-250 salt spray box (Beijing Zhongke Environmental Testing Instrument Co., Ltd, Beijing, China). The test method was according to the national standard GB-T10587-2006. The NaCl content was 5wt% , and the temperature of the salt spray process was controlled at 35±2 ° C. The entire salt spray process was conducted for 720 h, and the surface was observed.

**Table 1 MAO treatment parameters of different specimens**

| Specimen | Nano-zirconia concentration/g·L$^{-1}$ |
|---|---|
| S0 | 0 |
| S1 | 1 |
| S2 | 2 |
| S3 | 3 |
| S4 | 4 |
| S5 | 5 |

## 2 Results and Discussion

### 2.1 Growth process of MAO film

Fig. 1 shows the effect of different nano-zirconia concentrations on the reaction current of MAO process. It can be seen that the addition of nano-zirconia changes the peak current of MAO process. The current change can be divided into three stages, namely the initial oxide film formation stage, the micro-arc induction stage, and the equilibrium oxidation stage[10]. When the nano-zirconia concentration is 2 g/L, the peak current of the first two stages is the highest. With increasing the concentration of nano-zirconia, the peak current in the third stage is gradually increased, and the time for peak current occurrence is gradually prolonged. This is because in the initial oxide film formation and micro-arc induction stages, the substrate and the primary oxide film are relatively smooth, which increases the instantaneous current[11]. The nano-zirconia additive promotes the nucleation of ceramic film. When the concentration of nano-zirconia is too high, due to the extremely inferior conductivity of nano-zirconia, the current breakdown occurs and the instantaneous peak current decreases. During the equilibrium oxidation stage, an oxide film forms on the surface layer, which is rougher than the substrate. At this time, the nano-zirconia is reattached to the surface, which can hardly induce discharge.

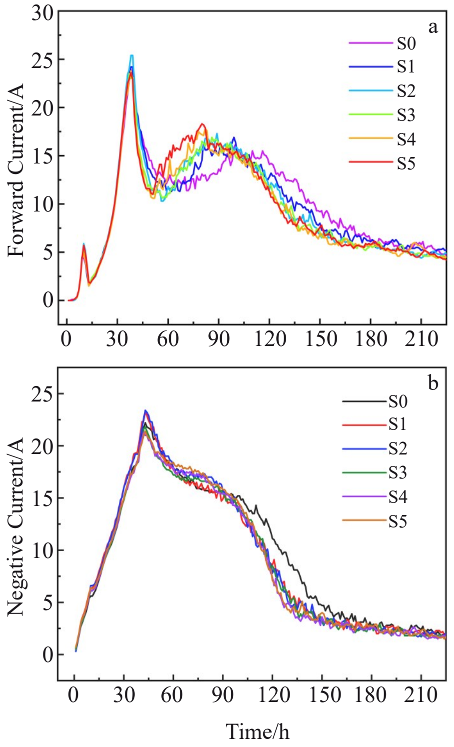


Fig.1 Forward (a) and negative (b) current of different specimens during MAO process

Therefore, in the third stage, the concentration of nano-zirconia becomes an important factor affecting the current. The higher the nano-zirconia concentration, the greater the current, and the longer the time for peak current occurrence. After MAO reaction for 3 min, the growth process only occurs in the weak local position of the film, the current decreases slowly, and the film growth is slow[12]. As a result, the addition of nano-zirconia barely has effect on the current.

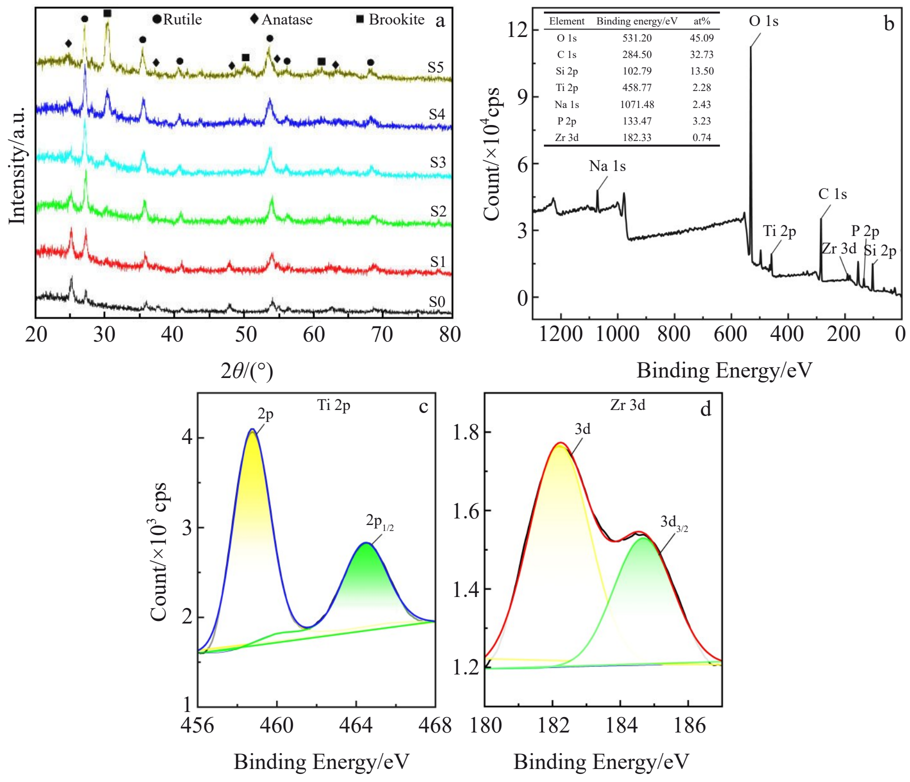
### 2.2 Phase composition

Fig. 2a shows XRD patterns of different films prepared on TC4 titanium alloy with different nano-zirconia concentrations. It can be seen that the crystals form in all films under rapid cooling. Without nano-zirconia addition, there are only two phases in the film, namely rutile and anatase. With increasing the nano-zirconia concentration, the intensity of diffraction peaks of anatase in the film layer is gradually weakened, and the peak intensity of rutile phase is gradually increased, indicating that the anatase content is decreased and the rutile content is gradually increased. The brookite titanium dioxide appears, and its content gradually increases. When the concentration of nano-zirconia is 5 g/L, the brookite content in the film reaches the maximum value. This is because the nano-zirconia addition increases the current of MAO film, resulting in the more intense reaction process. Anatase phase can be converted to rutile phase at high temperature, and the formation conditions of rutile and brookite phases are similar[13]. Therefore, both the rutile and brookite titanium dioxides increase simultaneously. With increasing the nano-zirconia concentration, the peak current is increased and then decreased rapidly, which leads to the instantaneous temperature rise. However, the energy release during the whole process is not significant, presenting long energy release time. This phenomenon can shorten the conversion time from brookite phase to rutile phase, which is conducive to the increase in brookite content. However, the brookite titanium dioxide is extremely unstable and has no practical value. Thus, the increase in brookite concentration is not conducive to the improvement of film performance[14].

Fig. 2b shows the overall XPS spectrum of S2 film. It is worth noting that Na, Si, and P exist in the film, which originate from the electrolyte. According to Fig. 2c, the Ti peaks are at binding energy of 458.7 and 464.3 eV, indicating that Ti mainly exists in the form of titanium dioxide in the film layer, which is consistent with XRD results. The appearance of Zr indicates that the nano-zirconia as the additive successfully enters into the film. The Zr peaks are at binding energy of 182.30 and 184.5 eV. It is shown that nano-zirconia participates in the film formation, but no chemical reaction occurs, indicating that the nano-zirconia only has mechanical bonding with the substrate.

### 2.3 Microstructure

Fig. 3 shows SEM microstructures of oxide films formed under different nano-zirconia concentrations. It can be seen that there are many pores on the film surface. This is because in the MAO process, the micro-arc discharge breaks the primary oxide film and generates high temperature, which causes the melt and ejection of metal materials. The craters form under the rapid cooling of the electrolyte, acting as the discharge channel. Without nano-zirconia addition, the pore size is large and non-uniform. The maximum pore size is



| Element | Binding energy/eV | at% |
|---|---|---|
| O 1s | 531.20 | 45.09 |
| C 1s | 284.50 | 32.73 |
| Si 2p | 102.79 | 13.50 |
| Ti 2p | 458.77 | 2.28 |
| Na 1s | 1071.48 | 2.43 |
| P 2p | 133.47 | 3.23 |
| Zr 3d | 182.33 | 0.74 |

Fig.2 XRD patterns of different MAO films on TC4 titanium alloy (a); XPS spectra of S2 film: (b) overall, (c) Ti 2p, and (d) Zr 3d

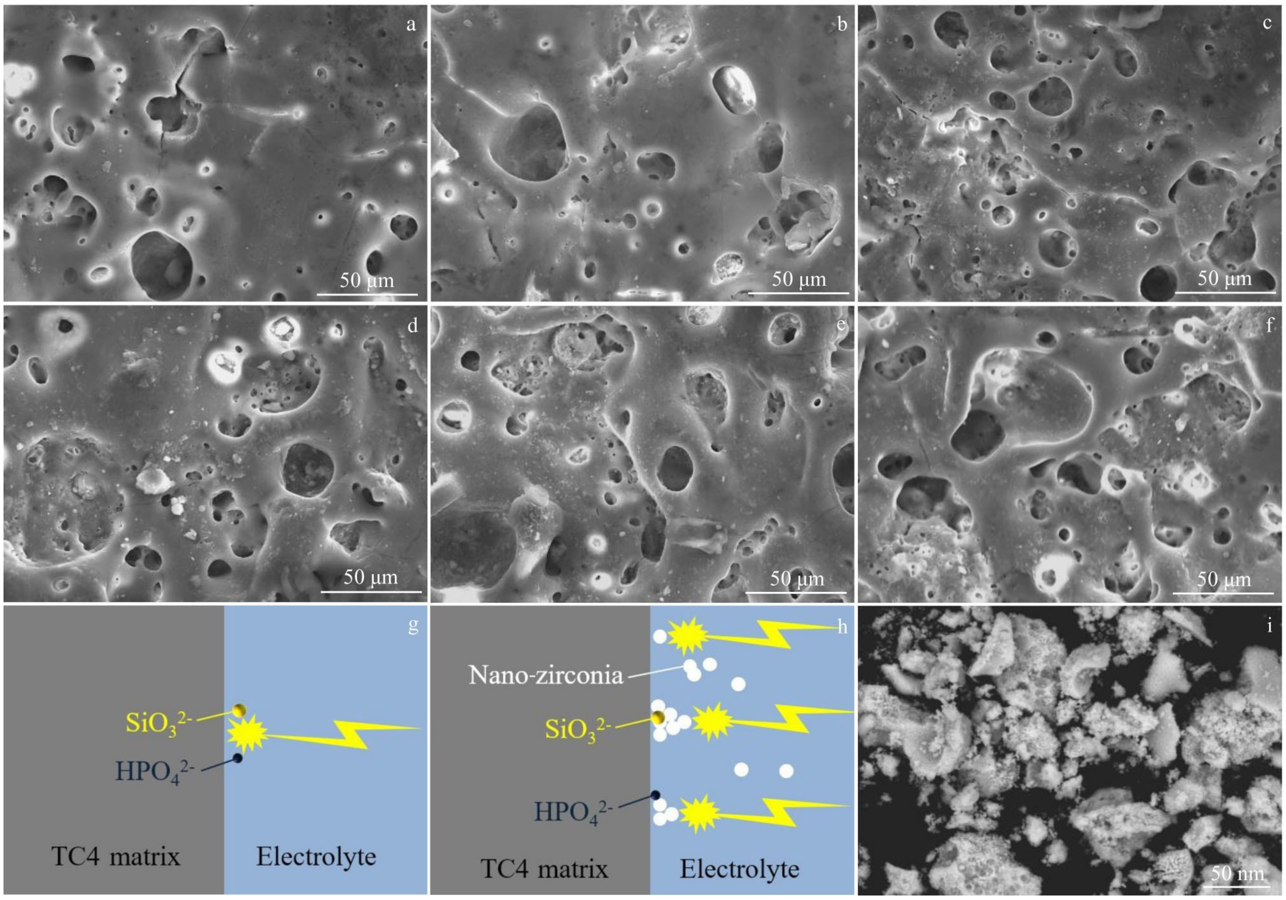


Fig.3 SEM microstructures of S0 (a), S1 (b), S2 (c), S3 (d), S4 (e), S5 (f) MAO films, and nano-zirconia (i); schematic diagrams of MAO process without (g) and with (h) nano-zirconia addition

about 40 μm, and the film layer has large cracks. After the nano-zirconia addition, the pore size tends to decrease. This is because the nano-zirconia addition can increase the micro-arcs and improve the nucleation rate of the film layer, therefore increasing the number of micro-pores and reducing the pore size, as shown in Fig.3g and 3h[15–16]. In addition, the diffusion of nano-zirconia in the electrolyte can release partial heat, accelerate the cooling and solidification processes of the surface melt, and reduce the pore size[17]. After adding nano-zirconia, fillers can be obviously observed in the surface pores. This is because the nanoparticles wrapped by melt can participate in MAO reaction with the electrolyte[18]. With excess addition of nano-zirconia, the nanoparticles accumulate on the outer surface of the film layer, which affects the further reaction. Meanwhile, a large number of nano-zirconia particles may also affect the surface roughness of film. When the nano-zirconia concentration is 2 g/L, the cracks are less and the pore size is the smallest and most uniform, compared with that of the films prepared without nano-zirconia or that under other nano-zirconia concentrations. Fig.3i shows SEM microstructure of nano-zirconia. The average particle size is about 50 nm. The nano-zirconia has irregular shape with sharp corners, which will be wrapped in the melting material sprayed by micro-oxidation. Therefore, the nano-zirconia exists in the film layer and can hardly be observed on the film surface.

Fig. 4 shows the cross-sectional morphologies of different film layers. The left side is the TC4 substrate, the inner film layer is dense, and the outer film layer is loose. The dense and the loose layers are staggered together, presenting good bonding force[19]. Without nano-zirconia addition, the film thickness is about 120 μm. After the addition of nano-zirconia, the film thickness slightly changes. This is because the chemical properties of nano-zirconia are extremely stable, resulting in the difficult entrance into the film layer by chemical reactions. Thus, the current increment is small, leading to the small increase in the thickness of film layer[20]. In addition, when a large number of nano-zirconia particles accumulate on the surface of film layer, they may hinder the further MAO reaction. It can be seen that Zr element appears in the film layer, indicating that the nano-zirconia enters into the film layer and participates in the formation of MAO film layer. The content variation of Zr element in the film layer is similar to that of Si and P elements, indicating that the movement trend of nano-zirconia is consistent with that of the anion. These phenomena all suggest that the nano-zirconia particles scattered in the electrolyte are negatively charged. The Zr content sharply decreases at the surface layer, indicating that the nano-zirconia particles participate in the growth process of film layer. However, the film thickness

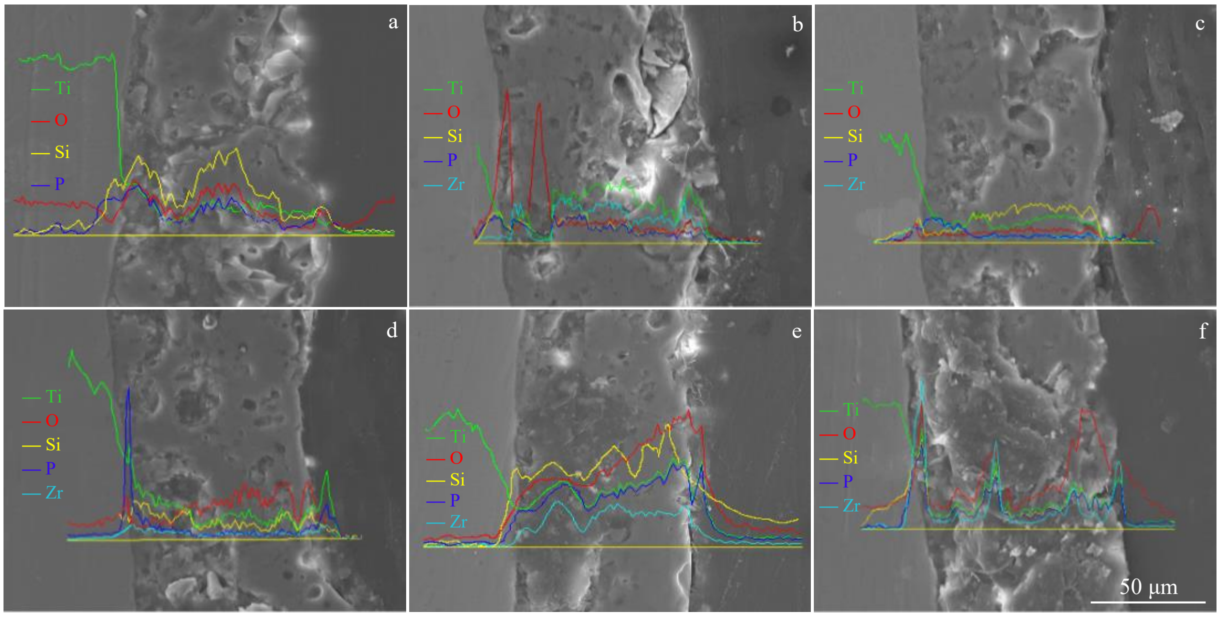


Fig.4 SEM cross-section morphologies and EDS line scanning results of S0 (a), S1 (b), S2 (c), S3 (d), S4 (e), and S5 (f) MAO films

barely changes, indicating that the nano-zirconia is successfully embedded into the film[21]. In addition, the ions in the electrolyte can be combined with the oxide layer[22]. The appearance of Si and P elements is due to the presence of a large amount of $SiO_3^{2-}$ and $HPO_4^{2-}$ in the solution. The specimen acts as the positive electrode, so those ions move to the positive electrode and participate in the formation of film layer under the action of electric field, as shown in Fig. 5[23]. The element distribution in the film layer is not uniform, which is related to the porous structure of the film layer. When the nano-zirconia concentration is 2 g/L, the thickness of the film layer is about 100 μm, and the film layer is relatively dense with uniform element distribution. When the nano-zirconia concentration exceeds 2 g/L, the element distribution of the film layer becomes non-uniform, and serious segregation occurs, which is not conducive to the uniformity and stability of the film layer.

## 2.4 Thickness and roughness

Fig. 6 shows the thickness and roughness of MAO films under different nano-zirconia concentrations. It can be seen that the S0 film thickness is 120 μm. The thickness decreases slightly to 110−120 μm for all MAO films prepared with the nano-zirconia addition. This result indicates that the nano-zirconia has a little effect on the film thickness. This is because the stable chemical properties of nano-zirconia severely hinder the chemical reactions under high pressure[15]. In addition, when a large amount of nano-zirconia accumulates on the film, the further reaction is hindered, the amount of spraying molten metal is reduced, and the continuous film growth is impeded. During MAO process, the nano-zirconia and oxide film are bonded through mechanical bonding, and the molten metal wraps the nano-zirconia particles and fills the film voids. As a result, the nano-zirconia addition has a little effect on the thickness of film layer. When the nano-zirconia concentration is 2 g/L, the surface roughness reaches the lowest of $R_a$=30.579 μm.

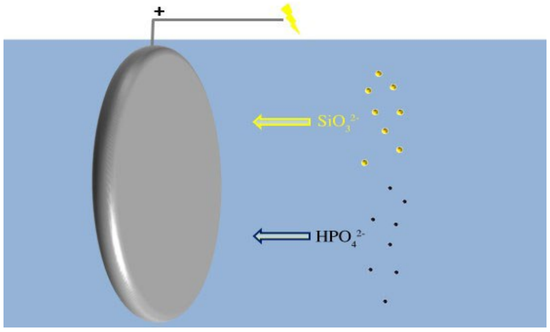


Fig.5 Schematic diagram of ion migration

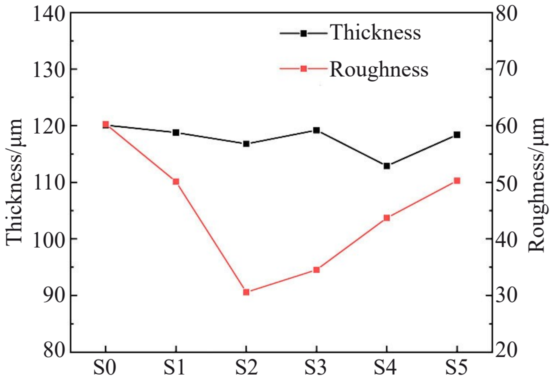


Fig.6 Thickness and roughness of different MAO films

Fig. 7 shows 3D morphologies of different film surfaces. When the nano-zirconia concentration is 5 g/L, the maximum height difference of 800 μm is obtained. When the nano-zirconia concentration is 2 g/L, the lowest roughness with less undulation is obtained. The maximum height difference in this case is 400 μm, suggesting that the S2 film surface is smoother than other films. This is because the appropriate addition of nano-zirconia can fill the surface pores. However, the excess nano-zirconia particles can only accumulate around the surface pores, which increases the height difference of the film layer, resulting in larger roughness[11,24–25].

## 2.5 Adhesion force

Fig. 8 shows the scratch morphologies of different MAO films. It can be seen that the load applied by the diamond scribing needle increases continuously until the scratches appear on the film surface, indicating that the substrate material is exposed. The instantaneous force of the film layer is used to characterize the adhesion force of the film layer to the substrate. This is because the vertical load of the film layer gradually increases until the critical value, resulting in the fact that the shear force increases and finally breaks the adhesion between the film and substrate. This unit area film needs to be removed from the substrate glass. The shear force is equal to the adhesion force[26]. According to Fig. 9, the adhesion force between the film and substrate is relatively high, because MAO film forms the metallurgical bonding with the substrate. When the nano-zirconia concentration is 2 g/L, the maximum adhesion force of the film of 62.075 N is achieved. However, as shown in Fig. 8, peeling phenomena occur around the scratches. The larger the peeling area, the lower the adhesion force of the film layer. The bonding force between the film layer and substrate is less than that between the film layers. When the load reaches a critical value, the film layer peels off. Fig.8c shows that when the nano-zirconia concentration is 2 g/L, no obvious peeling phenomenon occurs around the scratch, indicating that the adhesion force of S2 film layer is large, the film layer is relatively uniform, and the critical load is the highest. When the nano-zirconia concentration is higher than 2 g/L, the film layer of a small area peels off. This is because the composition of the film layer is not uniform, resulting in the easy peeling off of film from the substrate[27].

## 2.6 Wear resistance

Fig. 10 shows the worn surface morphologies of different oxide films. No obvious plastic deformation can be observed on the surface of oxide films after wear tests. The pores are greatly reduced, because the friction generated by MAO process occurs on a hard ceramic layer, and plastic deformation can hardly occur. Therefore, during the wear process, the surface protrusions are fractured under large stress, accumulate in the large pores, and fill the micropores[28]. There is a large diameter difference between

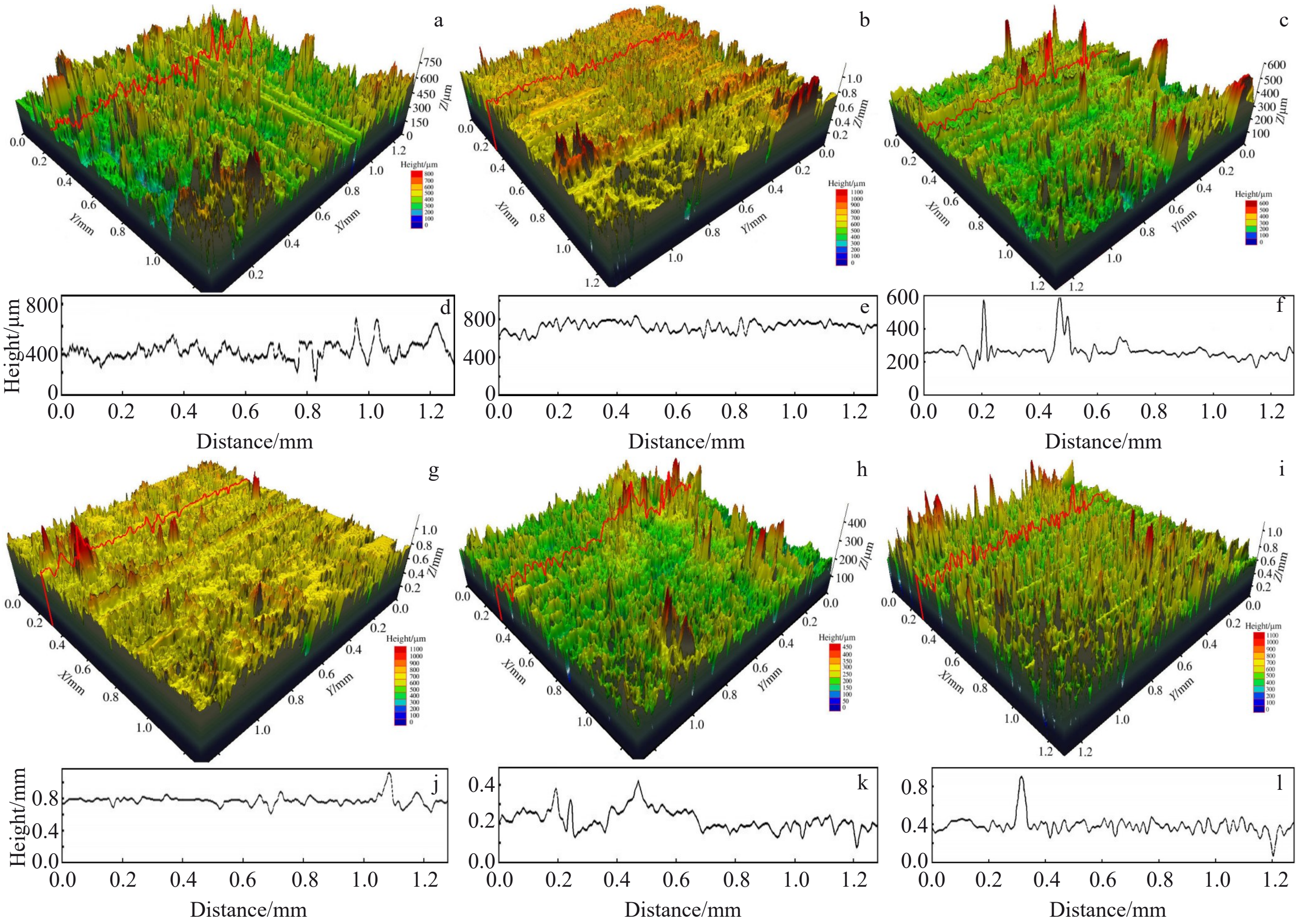


Fig.7 3D morphologies (a–c, g–i) and surface height distributions (d–f, j–l) of S0 (a, d), S1 (b, e), S2 (c, f), S3 (g, j), S4 (h, k), and S5 (i, l) MAO films

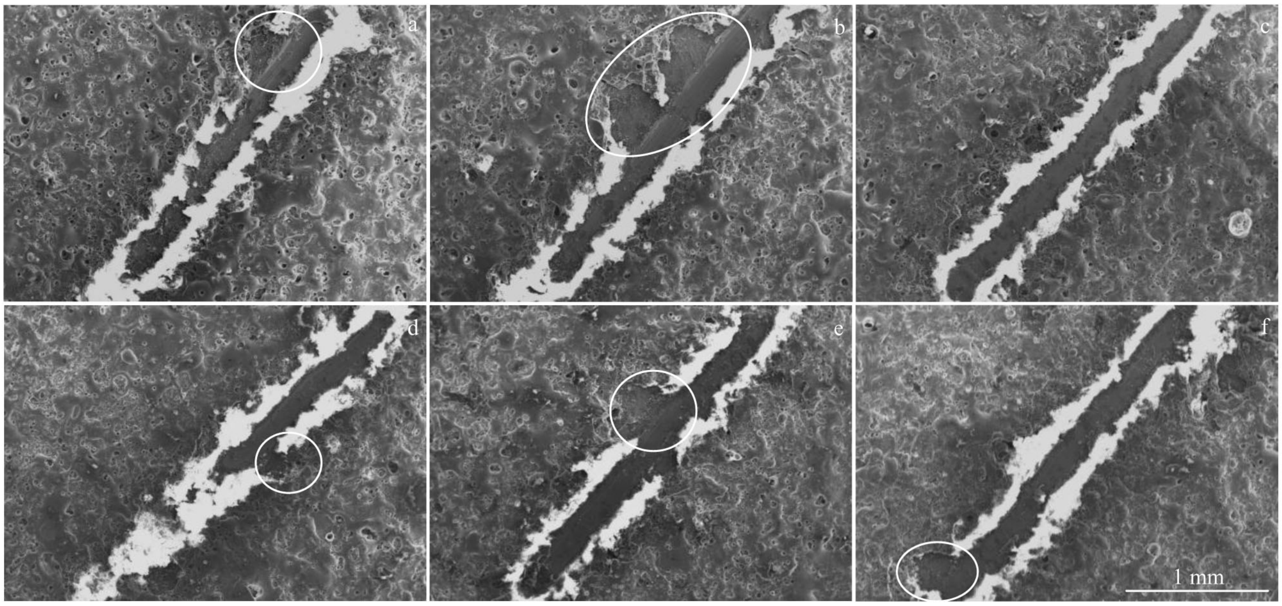


Fig.8 Scratch morphologies of S0 (a), S1 (b), S2 (c), S3 (d), S4 (e), and S5 (f) MAO films

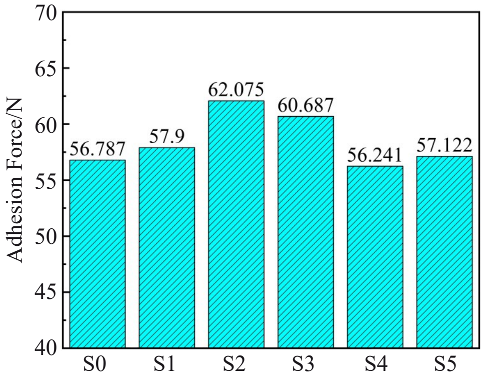


Fig.9 Adhesion force of different MAO films

the wear particles and the pores. As shown in Fig. 10c, the large pores are almost filled and the tiny pores do not have changes, indicating that the pore size in the S2 oxide film layer is the closest to that of the wear particles. Fig. 11 shows the mass loss curves of different oxide films during wear tests. It can be seen that in the early stage of wear test, the mass loss is increased linearly with increasing the number of wear test cycles. Subsequently, the mass loss increases slowly, which is related to the larger density of film layer. The outer film layer is relatively loose with many microcracks, and the worn layer can easily peel off, therefore resulting in mass loss. The inner film layer is dense, leading to less mass loss, compared with that of the outer film layer. In addition, the surface roughness

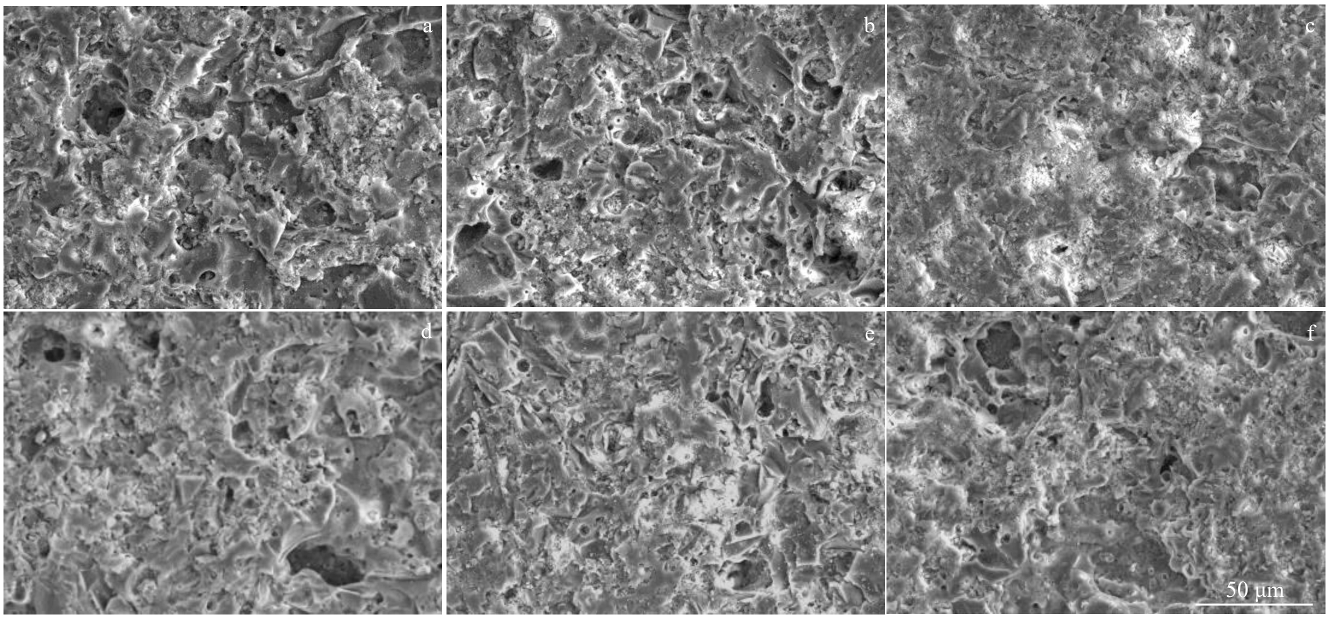


Fig.10 Worn surface morphologies of S0 (a), S1 (b), S2 (c), S3 (d), S4 (e), and S5 (f) MAO films

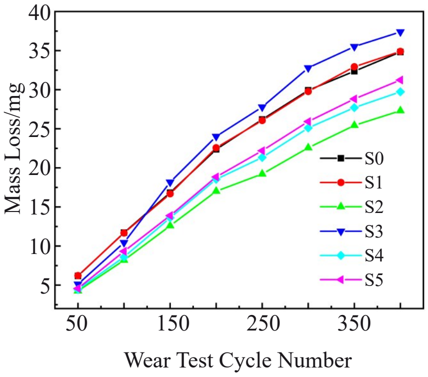


Fig.11 Mass loss of different MAO films

of the film layer directly affects the amount of wear loss. When the surface is rough, the convex parts are subjected to larger stress, resulting in mass loss after wear. The greater the roughness, the greater the initial mass loss[29]. As a result, the surface roughness of S2 film is the lowest, and thus its mass loss is the lowest.

## 2.7 Corrosion resistance

The main component of the oxide film is titanium dioxide, and the corrosion failures mainly occur in special environments. Therefore, the corrosion in marine environment was simulated by salt spray[30] in this research. Fig. 12 shows the surface morphologies of different films after salt spray corrosion for 0, 228, 528, and 720 h. It can be seen that the pitting corrosion occurs after the salt spray process. This is because when the salt spray particles fall on the surface of oxide films, the chloride ions are formed and then enter the inner film layer through the micropores, resulting in the aging or corrosion of the film layer[31]. However, the degree of pitting corrosion differs on different film surfaces, indicating that the addition of nano-zirconia can affect the corrosion resistance of the oxide film. When the nano-zirconia concentration is lower than 2 g/L, the pitting corrosion appears in the later stage, and the number of corrosive pits is less. When the nano-zirconia concentration is higher than 2 g/L, the pitting corrosion occurs earlier and the number of corrosive pits increases, indicating that the corrosion resistance is the optimal when the nano-zirconia concentration is 2 g/L. This result is related to the appropriate pore diameter and surface roughness of S2 film. When the nano-zirconia concentration is 2 g/L, the diameter of the surface micropores is the smallest, which hinders the entry of chloride ions to a certain extent. With excess addition of nano-zirconia, the particle accumulation occurs, resulting in the rough surface which is conducive to the attachment of salt spray particles[32]. In addition, the corrosion resistance of the film is also related to the crystal structure[33]. With increasing the nano-zirconia concentration from 0 g/L to 2 g/L, the anatase phase in the film layer is decreased, whereas the rutile phase is increased.

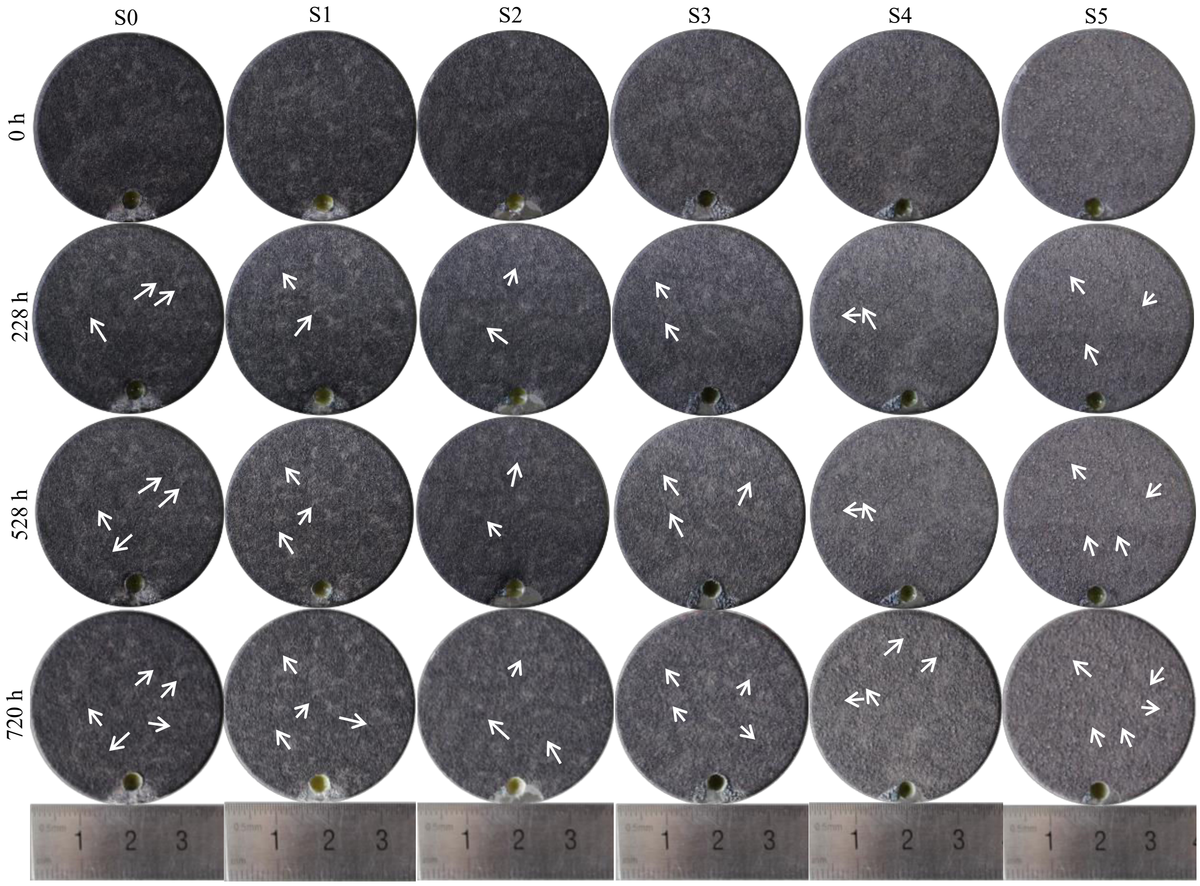


Fig.12 S0, S1, S2, S3, S4, and S5 MAO film surfaces after salt spray corrosion for different durations

Because the chemical properties of rutile phase are more stable than those of anatase phase, the corrosion resistance is improved with increasing the nano-zirconia concentration from 0 g/L to 2 g/L. When the nano-zirconia concentration is higher than 2 g/L, the brookite phase gradually increases. However, the chemical properties of brookite phase are unstable, leading to the degradation of the corrosion resistance.

## 3 Conclusions

1) After the addition of nano-zirconia into the electrolyte, the phase composition of film prepared by micro-arc oxidation (MAO) changes: the anatase phase decreases; the rutile and brookite phases increase. The micropore diameter of the film layer is firstly decreased and then increased with increasing the nano-zirconia concentration. When the nano-zirconia concentration is 2 g/L, the micropore size is the smallest with the most uniform distribution.

2) The addition of nano-zirconia has no obvious effect on the MAO film thickness, but it can reduce the film roughness. When the nano-zirconia concentration is 2 g/L, the film roughness is the lowest and the surface fluctuation is the smallest.

3) With increasing the concentration of nano-zirconia, the wear resistance and corrosion resistance of the film layer are firstly increased and then decreased. When the nano-zirconia concentration is 2 g/L, the wear resistance and corrosion resistance of MAO film are optimal.

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# 纳米二氧化锆对TC4钛合金微弧氧化膜的影响

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**摘　要：**利用多功能微弧氧化电源，采用目前工艺较为成熟和应用最广泛的电参数对TC4钛合金进行微弧氧化，并在电解液中添加不同浓度的纳米二氧化锆，对比微弧氧化膜层的微观形貌和综合力学性能，探究纳米二氧化锆对膜层的影响。实验结果表明，随着纳米二氧化锆浓度的增加，膜层厚度几乎不发生变化，但膜层的成分和含量发生改变：膜层中出现板钛矿相，且含量不断增加。当纳米二氧化锆浓度为2 g/L时，膜层的粗糙度相比未添加纳米二氧化锆时大幅下降，膜层耐磨性能最好，且此时膜层表面微孔直径最小且尺寸均匀，耐腐蚀性能最佳。

**关键词：**微弧氧化；微观形貌；纳米二氧化锆；耐磨性能；耐腐蚀性能

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