Effect of $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ Addition in Electrolyte on the Microstructure and Tribological Behavior of Micro-Arc Oxidation Coatings on Aluminum Alloy

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Abstract Micro-arc oxidation (MAO) coatings with different concentrations of $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ in the sodium silicate base electrolyte were prepared on 6061 aluminum alloy with the aim of promoting a better understanding of the formation mechanisms and tribological behaviors of the coatings. Scanning electron microscopy (SEM) assisted with energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and friction test were employed to characterize the MAO processes and microstructure of the resultant coatings. Results showed that the composition and microstructure of the coatings were significantly affected by the addition of $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$. A sealing microstructure of MAO coating was obtained with the addition of $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$. Ti element from $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ was only absorbed into the defects of micropores under surface energy in the early stage, while in the later stage, Ti element was predominant in the micropores and distributed on the coatings under plasma discharge to form TiO_2 . It was demonstrated that Ti and Si elements from the electrolyte could interact with each other during the MAO process and the interaction mechanism was systematically analyzed. Wear resistance of the MAO coatings with $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition was significantly improved compared with that of the MAO coatings without $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition.

KEY WORDS: Aluminum alloy; Micro-arc oxidation; $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$; Coating formation mechanism; Tribological behavior

1 Introduction

6061 aluminum alloy exhibits great application potentials as brake pad material due to its convenient processing characteristic, excellent mechanical and thermal properties [1, 2]. However, its application is restricted because of the poor wear resistance, which cannot satisfy the working condition requirements of brake pad.

Micro-arc oxidation (MAO), also called plasma electrolytic oxidation (PEO), has been well utilized to improve the properties of metallic materials because it is a simple and environmental-friendly process, and the resultant coatings exhibit superior properties like ceramics and are metallurgically bonded with the substrates [3–9]. As a result, the corrosion resistance and wear resistance of aluminum alloys can be significantly improved [10, 11]. However, detailed investigations found that there are a large number of micropores on the MAO coating surface due to the high energy of the breakdown discharge, which would result in materials failure under harsh friction and wear conditions [12]. More importantly, the theoretical value of thermal conductivity of in situ alumina ceramic coating could reach up to $31.5 \text{ W m}^{-1} \text{ K}^{-1}$, and thermal conductivity value might be decreased for its porous microstructure because of air in the micro-holes of

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MAO coating (thermal conductivity value of air: $0.023 \text{ W m}^{-1} \text{ K}^{-1}$) [13, 14]. Thus, a dense MAO coating microstructure will be beneficial for brake pads since it would enhance the thermal conductivity and wear resistance, and meanwhile reduce the friction coefficient. It has been reported that the characteristics of the MAO oxide coatings are influenced by chemical composition of electrolyte, electric parameters, such as duty cycle, frequency and current mode [3, 15–19]. Particularly, the composition and microstructure of the MAO coatings can be significantly altered by chemical composition of electrolyte [18, 19]. Wang *et al.* [20] attempted to add NaAlO_2 into electrolyte for preparing MAO ceramic coatings on aluminum. The results demonstrated that the number of the discharge channel diameter increased and the corrosion rates of MAO coatings decreased at first and then increased with increasing NaAlO_2 concentration. Cui *et al.* [21] found that a self-sealing MAO coating could be obtained in K_2ZrF_6 -containing solution. Dong *et al.* [22, 23] reported a self-sealing pore MAO coating formed on magnesium alloy in fluorotitanate electrolyte system. Our previous work also demonstrated a sealing phenomenon of MAO coating on magnesium alloy in K_2TiF_6 -containing solution [24]. Recently, incorporations of solid particles have been intensively reported to improve the properties of MAO coatings. Incorporation of MoO_2 and ZrO_2 particles into the MAO oxide coating with small size of the micropores on 7075 Al alloy was developed by Kaseem *et al.* [25] to enhance corrosion resistance. Shokouhfar and Allahkaram [26] added SiC and SiO_2 nanoparticles to aluminate-based electrolytes and found a decrease in roughness and porosity in the MAO coatings due to the deposition of nanoparticles within their micropores. MAO self-lubricating composite coatings with low friction coefficient and superior wear resistance were prepared by Ma *et al.* [27] through a micro-arc plasma oxidation with graphite added in electrolyte solution.

It is interesting that the ceramic anodizing coatings formed through adding the rare metal, such as cobalt, titanium, zirconium and other salts, and the rare salt hydrolysis can be deposited on the pores of the coating [28, 29]. Consequently, the anodic oxide coating possesses a compact microstructure, high hardness, good wear resistance and corrosion resistance [30]. $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ is usually added into the above base solution to obtain ceramic anodizing coating with excellent comprehensive properties. However, chromic acid or oxalic acid is usually used as the electrolyte of ceramic anodizing technology, which is easy to cause environmental pollution [29]. It is well known that MAO technique is developed from anodic oxidation, which can be used as reference for the preparation of MAO coatings with high performance. Base on the above consideration,

in the present work, preparation of dense Ti-containing MAO coatings on 6061 aluminum alloy was attempted by adding potassium titanium oxalate ($\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$) as Ti source into the base electrolyte. Effect of $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ concentration on microstructure and wear resistance was studied.

2 Experimental

6061 aluminum alloy disks (the nominal composition in weight percent: 0.4%–0.8% Si, 0.70% Fe, 0.15%–0.4% Cu, 0.15% Mn, 0.8%–1.2% Mg, 0.04%–0.35% Cr, 0.25% Zn, 0.15% Ti and Al remainder) with a diameter of 25 mm and thickness of 5 mm were used as substrates. Before MAO treatment, the specimens were gradually grounded from 400 # to 1500 # SiC paper, rinsed in distilled water and dried in a stream of warm air. A direct current power supply (MAO65-II, made by Xi'an University of Technology, China) was used to prepare MAO coatings on aluminum alloy surface. The 6061 aluminum alloy samples were used as anode with the wall of the stainless steel container as the cathode. Constant voltage mode was selected for MAO treatment with a predefined constant voltage of 400 V at a frequency of 400 Hz and a duty ratio of 10% for 10 min. Electrolytes for the MAO treatment were composed of 25 g/L Na_2SiO_3 aqueous solutions with $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ concentrations varying from 0, 3, 6 to 10 g/L. The solution temperature was kept below 35 °C during MAO process.

Thickness of MAO coatings was measured using a TT230 eddy current thickness meter. The thickness of the MAO coatings was approximately 8–10 μm . A field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan) with an energy-dispersive spectroscope (EDS) was used for morphological characterization of the MAO coatings. An AXIS UTLTRADLD X-ray photoelectron spectroscopy (XPS) with Al (mono) $K\alpha$ irradiation at pass energy of 160 eV was utilized to characterize the chemical bonds of the coatings. The binding energies were referenced to the $\text{C}1s$ line at 285.0 eV. The analysis was carried out right on the pristine surface after 180 s Ar^+ etching to decrease the effect of surface contamination or adsorption. Sliding friction and wear behavior were evaluated in the ball-on-plate sliding tests against GCr15 (diameter of 6 mm) on a ball disk wear tester (M-2000, China) at room temperature with a relative humidity of 50%–60% under the dry sliding conditions. The sliding mode was performed with sliding velocity at 0.1 m/s for 300 s. The diameter of the wear track was 7 mm, and the applied normal load was 6 N.

3 Results and Discussion

3.1 Characterization of the Microstructure

Figure 1 shows the surface morphologies of the MAO coatings formed in electrolyte with different $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ concentrations. A non-uniform porous layer, with an average pore size ranging from 0.1 to 3 μm , can be observed on the surface of MAO coating. These volcano-like micropores are characteristic of the MAO coatings due to the gas bubble emission [31]. With increasing concentration of $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$, there are still some discharge holes distributing on the coating surface. However, compared with the MAO without any addition of $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$, the number of micropores with pore size of 2 μm in average gradually decreases and the coating surface

becomes smoother apparently (as shown in Fig. 1b–d). The surface roughness (average Ra values) of the four MAO coatings is shown in Fig. 2. It is noted that with increasing addition of $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$, the Ra value of the coatings decreases, which indicates that the coating surface becomes smoother. Compared with the MAO coating prepared in the solution with Na_2SiO_3 addition (about 3600 nm, with pulsed frequency of 500 Hz) [8], the surface roughness Ra values of the coatings formed in the solution with $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition remarkable decreased. So, the addition of $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ into the base electrolytes can cause a decrease in the number and diameter of the micropores, and therefore the surface porosity of the coatings.

Elemental analysis of MAO coatings formed at different $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ concentrations was conducted by EDS, and the results are listed in Table 1. It is noted that all the four

Fig. 1 Surface microstructure of MAO coatings prepared in electrolytes with different $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition: **a** 0 g/L, **b** 3 g/L, **c** 6 g/L, **d** 10 g/L

Fig. 2 Ra values of MAO coatings prepared in electrolytes with different amount of $K_2TiO(C_2O_4)_2$ addition

MAO coatings are mainly composed of Al, O and Si elements, which is consistent with the elemental composition of MAO coatings on 6063 aluminum alloy [32] and 6061 aluminum alloy [33] in sodium silicate aqueous solution. Furthermore, it was demonstrated that the solute ion Si was strongly involved during the MAO coating formation process. For the $K_2TiO(C_2O_4)_2$ additive sample, the Ti content gradually increased with the increment of $K_2TiO(C_2O_4)_2$ concentration. It was interesting that the Si contents of the MAO coatings slightly decreased with the increase in Ti contents of the coatings. It can be speculated that different solute ions added into the electrolyte will interact with each other during the MAO process. This result will be further discussed by XPS analysis. It is worth noting that the filling phenomenon takes place during the MAO process because some rare salt hydrolysis deposits on the pores of the coating and results in excellent properties of the ceramic anodizing coatings. So, the MAO formation mechanism is revealed through analyzing the different formation stages of MAO coating with $K_2TiO(C_2O_4)_2$ addition.

Figure 3 shows the surface morphologies of MAO coatings with 10 g/L $K_2TiO(C_2O_4)_2$ addition during the growth at different oxidation time. As shown in Fig. 3a, the surface morphology of aluminum alloy is inhomogeneous

at the arc starting moment, and some discharge holes presented on the surface. The distribution of solute ions at two different typical regions (with or without micropores) on the coating surface is analyzed by EDS, and the results are listed in Table 2. A small quantity of Ti element is detected in region I, but there is no Ti element found in region II. It is indicated that $TiO(C_2O_4)_2^{2-}$ ions in solution participate in reactions during MAO process in region I, which results in the presence of Ti on the coating surface. It is known that porous active surface possesses abundant surface energy, which results in preferential adsorption of $TiO(C_2O_4)_2^{2-}$ ion in solution on these surfaces in order to reduce surface energy of the coatings [34]. However, Si element from the solution exists in both regions I and II of the coating, attributing to form the film with high impedance [35]. In addition, the atomic percent content of Si element in region I is higher than that in region II due to the different surface energy in these two regions. Moreover, region I had higher O content than region II. There are a large number of micropores with a size up to 0.5 μm in diameter presented in the MAO coating for 120 s as shown in Fig. 3b. Different from the coating at the arc starting moment, the contents of Ti and O in coating surface increase as listed in Table 2. In addition, Ti element not only fills and covers the micropores (region III), but also disperses throughout this coating surfaces (region IV). The coarse porous is formed in the MAO coating for 600 s (Fig. 3c). Some large volcano-like pores are formed with a size up to 3 μm in diameter. Compared with the coatings formed for 85 and 120 s, the contents of Ti and Si in ceramic layer present an increasing tendency, but the content of Al decreases obviously.

Typical $Si2p$ and $Ti2p$ high-resolution XPS spectra of the MAO coatings with or without addition of $K_2TiO(C_2O_4)_2$ after Ar sputtering are shown in Fig. 4. The $Si2p$ peak can be deconvoluted into two peaks of 102.77 eV and 104.70 eV, indicating the existence of $Al_2Si_2O_7 \cdot H_2O$ and SiO_2 in the MAO coating without $K_2TiO(C_2O_4)_2$, as shown in Fig. 4a. However, the $Si2p$ peak of 102.67 eV corresponding to $Al_2Si_2O_7 \cdot H_2O$ is formed in the MAO coating with the addition of $K_2TiO(C_2O_4)_2$, as shown in Fig. 4b. The $Ti2p$ peak could be deconvoluted into two peaks of the $Ti2p_{3/2}$ peak and $Ti2p_{1/2}$ peak. The $Ti2p_{3/2}$ peak of 455.48 eV and the $Ti2p_{1/2}$ peak of 463.46 eV in the MAO coating with $K_2TiO(C_2O_4)_2$ addition all indicate the existence of TiO_2 , as shown in Fig. 4c. So, it could be speculated that the effect of the $K_2TiO(C_2O_4)_2$ addition on the formation of MAO coating has twofold effects. On the one hand, compared with the MAO coating with K_2TiF_6 addition without the formation of TiO_2 , $K_2TiO(C_2O_4)_2$ participates in the formation of MAO coating and TiO_2 are formed in the coating. From the analysis of Fig. 3, it has been known that Ti not only mainly fills into the

Table 1 EDS results of MAO coatings prepared in the electrolytes with different amount of $K_2TiO(C_2O_4)_2$ addition

Coatings (g/L)	O (at.%)	Al (at.%)	Si (at.%)	Ti (at.%)
MAO-0	24.84	42.99	24.22	–
MAO-3	25.39	46.25	23.94	0.48
MAO-6	26.08	46.79	23.26	0.83
MAO-10	25.59	46.94	18.22	1.36

Fig. 3 Surface morphologies of MAO coatings with 10 g/L $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition during the growth at different oxidation time: **a** 85 s, **b** 120 s, **c** 600 s

Table 2 EDS results in different regions of the MAO coatings at different preparing time with 10 g/L $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition

Oxide time (s)	Region	O (at.%)	Al (at.%)	Si (at.%)	Ti (at.%)
85	I	17.40	68.38	8.13	0.34
	II	10.23	87.02	1.93	—
120	III	20.55	66.74	8.45	0.38
	IV	31.81	60.00	5.85	0.26
600	V	23.59	56.94	11.27	0.80
	VI	27.48	40.83	7.05	0.56

Fig. 4 Typical $\text{Si}2p$ and $\text{Ti}2p$ high-resolution XPS spectra of **a** without $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition, **b, c** with $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition on Al alloy substrate after Ar sputtering

micropores, but also disperses on the surface of the MAO coating. So, it can be concluded that the MAO coating with TiO_2 possesses a self-sealing characteristic and it might exhibit excellent properties for the characteristics of TiO_2 . This might also be the reason for adding $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ into the solution to form the ceramic anodizing coatings. On the other hand, it is interesting to find that the addition of $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ has an influence on the existing form of Si element from the solution to the MAO coating, which makes some Si atoms have no time to form its oxide. As a result, the Si atom translates into only $\text{Al}_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$ in the

MAO coating with $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition. So, different solute ions could interact with each other during the formation process of MAO coating, which further affects the existent morphology of the solute ions. These results are of significance for guiding the selection of the MAO electrolyte.

3.2 Tribological Behavior

Dry ball-on-disk (alumina ball) sliding wear tests under a constant load of 200 g are applied to the coatings without

and with different $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition against GCr15. Figure 5 shows the friction coefficients of the coated samples vs sliding time. At the beginning, the friction coefficients of all the samples increase rapidly and then rise gradually for the remaining distance. The friction coefficient of the MAO coating without $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition fluctuates during sliding, and the process transits from the running-in stage to the stabilization stage and the friction coefficient reached 0.56. The main characteristic of the MAO coatings is the presence of the micropores on their surfaces, and the volcano-like micropores result in high and unstable friction coefficient. During the early 80 s of period, the friction coefficients of the MAO coating with 3 g/L $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition show a similar variation trend to that of the MAO coating without $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition, exhibiting a lower stabilization friction coefficient (0.48). However, the friction coefficient of this MAO coating fluctuated more significantly during sliding than that of the coating without $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition after 80 s. Adding 6 g/L $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ into the solution, the stabilization friction coefficient of this MAO coating also reaches 0.56 compared with the coating without $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition, but the fluctuations in the friction coefficient becomes smaller. Furthermore, it is found that the stabilization friction coefficient of the MAO coating with 10 g/L $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition is only 0.18, which is much lower but more fluctuated than the coatings prepared in the solution with NaAlO_2 addition (about 0.6) [36]. It is known that the variation of friction coefficient of the coatings could reflect their tribological behavior, and the MAO coating demonstrates an unusual tribological behavior.

The differences in tribological properties of the coated samples with and without $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition are further investigated by comparing the FE-SEM morphologies

Fig. 5 Coefficient of friction (COF) of MAO coatings with 0 g/L, 3 g/L, 6 g/L and 10 g/L $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition as a function of sliding time

of their wear tracks. Approximately wide and rough wear scars can be seen on the worn surface of all composite coatings, as shown in Fig. 6. It is measured that the wear scar width of the coated sample without $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition is about 746 μm , but all the coated samples with different $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ additions show a decreased wear scar width. In particular, the wear scar width of the MAO coating with 10 g/L $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition is only 390 μm , showing an excellent tribological property. This result is in accordance with the variation of friction coefficient. However, the wear scar width of the MAO coating with 6 g/L $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition is 690 μm , which is higher than that of the coating with 3 g/L $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition (555 μm). Considering the abnormal variation of friction coefficient of this coating, it could be speculated that the MAO coating containing uneven distribution TiO_2 results in this abnormal phenomenon and it will be further analyzed in Sect. 3.3.

Figure 7 shows the worn surfaces SEM images of the MAO coatings without and with different $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ additions. The porous microstructure of the MAO coating without $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition leads to seriously rough feature after wear test. It can be observed that some dark regions appeared on the coating surface (marked by white circle in Fig. 7a), which might be due to the formation of transfer layer of GCr15 ball during the friction, indicating a severe form of adhesive wear (abrasion wear). This is also consistent with its high friction coefficient. With the addition of $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ into the base electrolyte, the micropores of the MAO coatings are filled by TiO_2 , which densifies the coatings and reduces their roughness, and consequently results in a decreased friction coefficient. As a result, a large amount of transferring layer of GCr15 ball is formed on the coating surface, illustrating a kind of adhesive wear—general adhesive wear. On the other hand, the formation of a large number of transferring layers causes an uneven surface of the MAO coating, which results in the fluctuations of friction coefficient. It is interesting to note that, adding 10 g/L $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$, the friction coefficient of the MAO coating still fluctuates obviously, but the table value of friction coefficient is the smallest among the four coatings, which indicates that Ti is strongly participated in the formation of the MAO coating and an obviously filling effect of TiO_2 is obtained.

In order to further prove the occurrence of adhesive wear and the formation of transfer layer of GCr15 ball for the MAO coatings during friction test, two different regions of the MAO coating with 6 g/L $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition in Fig. 7c are analyzed by EDS, and the results are listed in Table 3. It is found that region I contains a large number of O, Si and Al elements, and a small amount of Fe and Ti elements. There is no Cr element detected in this region. Compared with the EDS result of this MAO coating

Fig. 6 SEM images of wear scar width on MAO coatings prepared in electrolytes with different $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition: **a** 0 g/L, **b** 3 g/L, **c** 6 g/L, **d** 10 g/L

before wear test, it could be concluded that this complete MAO coating is not damaged during the wear process, suggesting an excellent wear resistance. A large amount of Fe element and a few amount of Cr element are found in region II. Meanwhile, a small amount of O and Si elements is detected, indicating a formation of transferring layer of GCr15 ball. In addition, Al element is not detected on the wear scar, which reveals that the transferring layer has a certain thickness.

3.3 Discussion

A typical phenomenon of anodic oxidation is the large number of gas bubbles rising from the sample surface but no arc during the early stage of MAO process. Schematic

diagram of electric circuit of MAO is shown in Fig. 8. Under the external electric field, the surface of the aluminum substrate on the anode will take the following reaction:

Al^{3+} ion is formed by losing electrons of Al atoms on the anode surface. The electrons migration might conduct in two possible ways: (1) Electrons reach the cathode through an external circuit and (2) enrichment of OH^- ions on the anode surface could receive electron to produce O_2 , as shown in reaction (2).

According to the electrochemistry knowledge, the electron

Fig. 7 SEM local magnification images of wear scar on MAO coatings prepared in electrolytes with different $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition: **a** 0 g/L, **b** 3 g/L, **c** 6 g/L, **d** 10 g/L

Table 3 Chemical composition at wear tracks of MAO coatings with 6 g/L $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition in Fig. 7c

Coating	Region	O (at.%)	Al (at.%)	Si (at.%)	Fe (at.%)	Cr (at.%)	Ti (at.%)
MAO-6 g/L	I	25.51	37.88	15.51	4.56	–	0.67
	II	4.92	–	1.55	83.17	1.39	–

migration must be preferred to pass through the way (1), thus inhibiting the OH^- ion to receive electron. So reaction (3) inevitably occurred preferentially on the anode surface:

The formation of $\text{Al}(\text{OH})_3$ was attached to the surface of the anode. Then the thermal decomposition occurred as the heat accumulation reached 140 °C under the external

electric field, which was an exothermic reaction, generating gasifying water and $\gamma\text{-Al}_2\text{O}_3$.

Exothermic reaction (4) further produces heat accumulation and increases gas pressure. And then reaction (2) could start at high temperature and high pressure to produce oxygen. The previous study found that the generation of

Fig. 8 Schematic diagram of MAO electric circuit

electron current during the process of anodic oxidation resulted in the oxygen precipitation, which was the main reason for the formation of micro-holes [37]. At this moment, there is micro-arc in the local area of micro-holes. It is known that the high surface energy is at the defect division and the reaction is always moving in the direction of low surface energy, playing a role of adsorptive center. In order to reduce surface energy, SiO_3^{2-} and $\text{TiO}(\text{C}_2\text{O}_4)_2^{2-}$ in solution are adsorbed on these surfaces, as shown in Fig. 9a. It has been reported that SiO_3^{2-} is easy for the occurrence of micro-arc due to the formation of high-impedance film by the reaction between SiO_3^{2-} ions and Al, as listed in Table 2. Si atoms are not only in the micro-defect on the surface, but also in other regions without defect. Of course, SiO_3^{2-} ions are mainly concentrated in the micropores. The more important thing is that the arc is a high energy state, which leads to the phase transformation of alumina (the $\gamma\text{-Al}_2\text{O}_3$ could be converted into $\alpha\text{-Al}_2\text{O}_3$ at 1200 °C) [38]. Furthermore, thermal effects generated by arc discharge could further exacerbate the gas release. Then reaction (2) takes place more severely and micro-phenomenon becomes prominent, showing a structure diagram in Fig. 9b. The solute ions were strongly moved into the microporous of the coating under surface energy, and oxygen plasma was formed, whose strength gradually weakened from the interface between the

substrate and the film to the interface between the film and the solution. Then the internal pressure of the electrolyte decreased and the “oxygen plasma” core was expanded rapidly, which could develop into gas bubble and gas cavity. The bubble would collapse with the change in the internal pressure in the electrolyte, forming a great jet stream. The micro-holes were in a high-temperature and high-pressure environment, and some solute ions were carried into the interface between the electrolyte and the coating, promoting the transformation of the solute ions into their oxide due to the quenching effect by solution [34], and then, the molten titanium oxide was solidified immediately and metastable oxide phases formed, shown as reactions (5) and (6). This process is illustrated in Fig. 9b.

TiO_2 existed on the coating surface and in the micropores through the above analysis. So the effects of adding $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ into the electrolyte were reflected in two aspects. On the one hand, the sealing characteristics are shown in Fig. 1. On the other hand, TiO_2 has excellent performance, which is helpful to improve the performance of MAO coating. As a result, adhesive wear is restrained, and abrasion wear of the MAO coating without $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition transfers into general adhesive wear of the coating with $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition. However, it is found that wear resistance of the MAO coating with 6 g/L $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition is deteriorated compared with the MAO coatings with 3 or 10 g/L $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition, which might be due to the amount and distribution of TiO_2 on the coating surface.

Fig. 9 Schematic illustration of the main MAO processes at different stages **a** at the moment of starting arc, **b** severe micro-arc discharge

4 Conclusions

- (1) MAO coatings with different $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ additions were prepared on aluminum alloy surface in the Na_2SiO_3 base solution. The number and diameter of the micropores on the MAO coatings decreased with the increase in the concentration of $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ and the coatings became smoother.
- (2) The addition of $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ participated in the formation of MAO coating and TiO_2 had been formed in this coating. The Ti and Si elements from the electrolyte could interact with each other during the formation process of MAO coating.
- (3) During the MAO process, $\text{TiO}(\text{C}_2\text{O}_4)_2^{2-}$ was adsorbed into the defects in the coating at the first stage. At the second stage, thermal effects generated by arc discharge could exacerbate the gas release, forming a great jet stream to carry some solute ions from the micropores into the interface between the electrolyte and the coating, and promoting the transformation of the solute ions into their oxide due to the quenching effect by solution.
- (4) The wear resistance of the MAO coatings could be improved with $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ additions, and abrasion wear of the MAO coating without $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition changed into general adhesive wear of the coating with $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition. The MAO coating with 10 g/L $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ addition had the lowest wear scar width and friction coefficient, showing the best wear resistance.

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