MICROSTRUCTURE AND PROPERTIES OF MAO COMPOSITE COATINGS CONTAINING NANORUTILE TiO₂ PARTICLES

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Microarc oxidation (MAO) composite coatings containing rutile TiO₂ were produced on 2024 aluminum alloy in an electrolyte with nanorutile TiO₂ particles. The microstructure and properties of the composite coatings were analyzed by SEM, EDS, laser confocal microscope, XRD, Vickers hardness tester, scratch test and friction test, respectively. The results showed that the composite coatings consisted of γ -Al₂O₃, α -Al₂O₃, mullite and rutile TiO₂. With increasing concentration of rutile TiO₂ particles in the electrolyte, the compactness of the composite coatings was improved significantly. The abrasion performance of the microarc oxidation composite coatings containing rutile TiO₂ was better than that of MAO coatings without rutile TiO₂.

Keywords: 2024 Aluminum alloy; microarc oxidation; nanorutile TiO₂ particles; composite coatings; adhesion strength; abrasion performance.

1. Introduction

Light metals and their alloys are important structural materials and are extensively applied in aerospace and transportation systems.^{1,2} Aluminum alloys with excellent performance have received much attention.³ However, the applications of aluminum alloys are seriously restricted by their low surface hardness and high wear rate.⁴⁻⁷ To date, many aluminum alloy surface treatment methods have been developed and employed to improve the hardness and friction performance of aluminum alloy. However, most of these technologies require high temperature and are complex. In particular, they are not environmentally

friendly.^{6,8-11} Microarc oxidation (MAO)¹²⁻¹⁴ has emerged as a novel technique with broad application prospects. MAO can be used for the preparation of ceramic-like oxide coatings on some light metals based on anodic oxidation, thermochemistry, electrochemistry and plasma chemical mechanisms. The coatings prepared by MAO have high hardness, good adhesion to substrate, good abrasion resistance, etc.¹⁵⁻²¹

However, MAO coatings show high and unstable friction coefficient because of the ceramic properties, and MAO coatings contain many micropores, which are formed via continuous localized spark discharge events during the MAO process. These micropores in

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Table 1. The electrolyte compositions.

Labels	Na ₂ SiO ₃ (g/L)	KOH (g/L)	Rutile TiO ₂ (g/L)	The pH of electrolyte	The conductivity of electrolyte (mS/cm)
a	11	1.5	0	12	7.21
b	11	1.5	0.7	12	7.00
c	11	1.5	1.4	12	6.84
d	11	1.5	2.1	12	6.93
e	11	1.5	2.8	12	6.89
f	11	1.5	3.5	12	6.97

the MAO coatings, however, provide an opportunity to deposit nanoparticles with high hardness or low friction coefficient into the MAO coatings. Recently, the superior performance of MAO composite coatings formed by adding particle additives in the electrolyte has led to extensive attention. For example, using ZrO₂ particles as additives, Hu prepared Al₂O₃/ZrO₂ composite coatings via MAO.⁷ Self-lubricating TiO₂/graphite composite coatings and TiO₂/MoS₂ composite coatings were formed via MAO in an electrolyte containing graphite particles and in an electrolyte containing MoS₂ particles, respectively. TiO₂/ZrO₂ composite coatings were produced via MAO in an electrolyte containing ZrO₂ particles.^{22–30}

Rutile TiO₂ with high hardness, good oxidative stability and a high melting point is used as wear-resistant materials. Moreover, nanorutile TiO₂ particles can be used as a solid lubricant during wear testing. There is little work on using nanorutile TiO₂ particles as additives in MAO composite coatings for improving the abrasion resistance of aluminum alloys. In this paper, 2024 aluminum alloy is processed via microarc oxidation in a silicate system electrolyte with different concentrations of nanorutile TiO₂ particles. The microstructure and abrasion resistance of the Al₂O₃/TiO₂ composite ceramic coatings are analyzed. The adhesion force between the coating and substrate is investigated.

2. Experimental

2.1. Coatings preparation

A 2024 aluminum alloy was used as the experimental material. The main alloy elements (mass fraction, wt.%) of the 2024 aluminum alloy are 3.8–4.9% Cu, 0.5% Si, 0.5% Fe, 0.3–0.9% Mn, 1.2–1.8% Mg, 0.25% Zn, 0.10% Cr and 0.15% Ti, and the remaining with Al.

The sample size of the 2024 aluminum alloy was 30 mm × 15 mm × 2 mm. The samples were polished using abrasive papers from 600# to 2000# and degreased by alcohol. An AC pulse microarc oxidation unit was used in this experiment. The electrolytic tank was used as the cathode and the sample was used as the anode. The silicate electrolyte was prepared in deionized water. The electrolyte compositions are given in Table 1. The additives were rutile TiO₂ nanoparticles, and the average size of the rutile TiO₂ particles was approximately 35 nm. The concentration of rutile TiO₂ particles varied from 0 g/L to 3.5 g/L in the electrolyte. A bipolar constant current power supply was used in this experiment. The current density, MAO processing time, duty ratio and the frequency were +27.8 A/dm²/–9.3 A/dm², 30 min, 43% and 100 Hz, respectively. To improve the suspension performance of rutile TiO₂ particles, the mixing pump was opened, and the electrolyte was stirred continuously during the MAO treatment. The cycle cooling system was opened to ensure that the electrolyte temperature was less than 40°C.

2.2. Testing and characterization

The surface morphologies, cross-section morphologies and thickness of the MAO coatings and composite coatings formed in the electrolyte containing rutile TiO₂ nanoparticles were analyzed by FEI Sirion scanning electron microscopy (SEM). The surface roughness of MAO coatings and composite coatings was measured using an OLS3000 laser confocal microscope, and the distribution of the main components of the MAO coatings and the composite coatings along the cross-section was analyzed by EDS. The phase structure of the MAO coatings and the composite coatings was analyzed via X'Pert PRO X-ray diffraction (XRD).

The adhesion force between coatings and substrate was investigated by a scratch test. A normal load through a diamond indenter was applied to the MAO coatings and composite coatings. The growth rate of the normal load was $35 \text{ N} \cdot \text{min}^{-1}$ and the normal load was linearly increased from 0 N to 35 N. The scratch length was 0.5 cm. The critical load values (L_c) were determined by supplementary data graphics containing acoustic emission, friction force and friction coefficient.

The hardness and abrasion resistance of the microarc oxidation coatings and the microarc oxidation composite coatings were analyzed using a Vickers hardness tester and CETR-UMT-2 ball-on-disk wear tester, respectively. WC balls with a surface roughness lower than $0.05 \mu\text{m}$ and a diameter of 5 mm were chosen as the counterface materials. In the process of the wear tests, the applied load was 5 N. The rotating diameter and rotating sliding speed of the wear tester were 6 mm and 100 r/min, respectively. The test time of each sample measured on the wear tester was 40 min. The volumes of wear tracks for the microarc oxidation coatings and microarc oxidation composite coatings were measured by an OLS3000 laser confocal microscope. The wear rates of the microarc oxidation coatings and the microarc oxidation composite coatings were determined by the volume of the wear tracks, applied load and sliding distance. The computation formula of the wear rate is as follows²²:

$$Q = \frac{V}{FL}. \quad (1)$$

In the above equation, Q is the wear rate, V is the wear volume (mm^3), F is the applied load (N) and L is the sliding distance (m).

3. Results and Discussion

3.1. Coating microstructure

Figure 1 shows the variation curves of voltage. The voltage increased due to the growth of MAO coatings during MAO. The surface morphologies of the microarc oxidation coatings and the composite coatings are exhibited in Fig. 2. The MAO coatings prepared in an electrolyte without nanorutile TiO₂ particles contained many crater-like micropores and a few microcracks. These pores were discharge channels

Fig. 1. (Color online) Variation curves of voltage during preparation of microarc oxidation coatings in an electrolyte containing nanorutile TiO₂ particles: (a) 0 g/L, (b) 0.7 g/L, (c) 1.4 g/L, (d) 2.1 g/L, (e) 2.8 g/L and (f) 3.5 g/L.

formed by spark discharge. In the process of MAO, molten “oxide magma” was formed in the discharge channels due to the localized high temperature and high pressure (approximately $2 \times 10^4 \text{ K}$ and 10^2 MPa).^{31,32} The molten “oxide magma” was cooled, solidified and stacked instantaneously to form the MAO coatings. The rapid cooling of the molten “oxide magma,” however, also produced thermal stress, which caused the microcracks. Figure 2 presents that the porosity of the composite coatings decreased remarkably as the content of rutile TiO₂ particles in the electrolyte changed from 0 g/L to 3.5 g/L because part of the nanorutile TiO₂ particles are captured by the micropores on the composite coatings and the micropores are filled during MAO. As shown in Figs. 2(d)–2(f), the number of microcracks increased remarkably as the content of nanorutile TiO₂ particles in the electrolyte changed from 2.1 g/L to 3.5 g/L. More microcracks were produced by the increase and uneven distribution of the thermal stress, which was promoted by some of the nanorutile TiO₂ particles filling the micropores on the composite ceramic coatings and other rutile TiO₂ particles agglomerating and forming large bulges on the composite coatings.

Figure 3 exhibits the surface roughnesses of the microarc oxidation composite coatings. The surface roughness of the microarc oxidation composite coatings decreased with increasing content of nanorutile TiO₂ particles in the electrolyte from 0 g/L to 0.7 g/L.

Fig. 2. Surface morphologies of the microarc oxidation composite coatings prepared in an electrolyte containing nanorutile TiO_2 particles: (a) 0 g/L, (b) 0.7 g/L, (c) 1.4 g/L, (d) 2.1 g/L, (e) 2.8 g/L and (f) 3.5 g/L.

The surface roughness of the microarc oxidation composite coatings, however, increased remarkably with increasing content of nanorutile TiO_2 particles in the electrolyte from 0.7 g/L to 3.5 g/L. The surface roughness of the microarc oxidation composite coatings prepared in the electrolyte with 0.7 g/L nanorutile TiO_2 particles was the smallest because the surface pores of microarc oxidation composite ceramic coatings were filled with nanorutile TiO_2 particles. However, the surface roughness of the microarc oxidation composite coatings prepared in the electrolyte with 3.5 g/L nanorutile TiO_2 particles was the largest because the surface pores of composite coatings were filled by only a part of nanorutile TiO_2 particles, whereas the other part of nanorutile TiO_2 particles

agglomerated on the surface of the microarc oxidation composite coatings to form large bulges.

The cross-section morphologies and thicknesses of the MAO coatings prepared in an electrolyte without nanorutile TiO_2 particles and the composite coatings prepared in an electrolyte containing nanorutile TiO_2 particles are shown in Figs. 4 and 5, respectively. The MAO coatings and the composite coatings exhibited an obvious double layer. The compactness of the inner layer was higher than the compactness of the outer layer. In the composite coatings, with increasing content of nanorutile TiO_2 particles in the electrolyte, the thickness of the dense layer increased and the porous layer became thinner. The compactness of the composite coatings was remarkably improved due

Fig. 3. (Color online) Surface roughness values of the microarc oxidation composite coatings prepared in an electrolyte containing nanorutile TiO_2 particles: (a) 0 g/L, (b) 0.7 g/L, (c) 1.4 g/L, (d) 2.1 g/L, (e) 2.8 g/L and (f) 3.5 g/L.

to many micropores on the composite coatings being filled with rutile TiO_2 particles.

The cross-section element distributions of the MAO coatings prepared in an electrolyte without nanorutile TiO_2 particles and the composite coatings prepared in an electrolyte containing nanorutile TiO_2 particles are shown in Fig. 6. Figure 6 shows that Ti was detected in the dense layer and the porous layer of the composite coatings, inferring that nanorutile TiO_2 particles were mixed into the composite coatings.

3.2. XRD patterns

As shown in Fig. 7, XRD analysis results revealed that the MAO coatings prepared in an electrolyte without nanorutile TiO_2 particles were mainly

Fig. 4. The cross-section morphologies of the microarc oxidation composite coatings prepared in an electrolyte containing nanorutile TiO_2 particles: (a) 0 g/L, (b) 0.7 g/L, (c) 1.4 g/L, (d) 2.1 g/L, (e) 2.8 g/L and (f) 3.5 g/L.

Fig. 5. (Color online) The thicknesses of the microarc oxidation composite coatings prepared in an electrolyte containing nanorutile TiO_2 particles: (a) 0 g/L, (b) 0.7 g/L, (c) 1.4 g/L, (d) 2.1 g/L, (e) 2.8 g/L and (f) 3.5 g/L.

composed of $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$ and mullite. The composite coatings prepared in an electrolyte with nanorutile TiO_2 particles contained $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-Al}_2\text{O}_3$, mullite and rutile TiO_2 . Rutile TiO_2 was detected in the microarc oxidation composite ceramic coatings, which indicated that rutile TiO_2 particles directly diffused and adsorbed on to the composite coatings. Moreover, with increasing nanorutile TiO_2 particles in the electrolyte, the rutile TiO_2 in the composite coatings increased significantly.

3.3. Adhesive strength of coatings

The supplementary data graphics of the scratch are shown in Fig. 8. The critical loads at which the acoustic emission and friction coefficient increased rapidly are indicated on the graphs. Table 2 exhibits

Fig. 6. (Color online) The cross-section element distributions of the microarc oxidation composite coatings prepared in an electrolyte containing nanorutile TiO_2 particles: (a) 0 g/L, (b) 0.7 g/L, (c) 1.4 g/L, (d) 2.1 g/L, (e) 2.8 g/L and (f) 3.5 g/L.

Fig. 6. (Continued)

the critical load values of the microarc oxidation composite coatings. It can be found that with increasing content of nanorutile TiO_2 particles in the electrolyte, the corresponding critical load values on the composite coatings decreased significantly because more nanorutile TiO_2 particles were mixed into the composite coatings, which decreased the adhesive strength between the coatings and substrate.

3.4. Microhardness and wear resistance of coatings

Figure 9 shows the hardness values of the composite coatings prepared in an electrolyte with different

concentrations of nanorutile TiO_2 particles. The hardness of the composite coatings increased significantly as the concentration of rutile TiO_2 particles in the electrolyte increased from 0 g/L to 2.1 g/L because the surface pores of the composite coating were filled by rutile TiO_2 particles and the density of the ceramic coatings was improved. However, the hardness of the microarc oxidation composite coatings decreased rapidly as the rutile TiO_2 particles in the electrolyte increased from 2.1 g/L to 3.5 g/L because more rutile TiO_2 particles were mixed into the composite coatings and the hardness of Al_2O_3 is higher than the hardness of rutile TiO_2 .

Figure 10 shows the friction coefficients of the wear tracks for the microarc oxidation composite coatings prepared in an electrolyte containing nanorutile TiO_2 particles against WC balls at room temperature during wear testing. Wave peaks existed on the microarc oxidation composite coatings and WC balls, and the friction coefficient increased rapidly in the initial stages of the friction test. After 1000 s, the wave peaks were smoothed flat and the friction coefficient became stable. Moreover, compared to the microarc oxidation coatings, the microarc oxidation composite coatings exhibited a lower friction coefficient, and the fluctuation range of the friction coefficient of the microarc oxidation coatings was narrower.

Figure 11 exhibits the morphologies of the wear tracks for the microarc oxidation composite coatings prepared in an electrolyte containing nanorutile TiO_2 particles against WC balls at room

Fig. 7. (Color online) XRD patterns of the microarc oxidation composite coatings: (a) 0 g/L, (b) 0.7 g/L, (c) 1.4 g/L, (d) 2.1 g/L, (e) 2.8 g/L and (f) 3.5 g/L.

Fig. 8. (Color online) Supplementary data graphics of the scratch for the microarc oxidation composite coatings prepared in an electrolyte containing nanorutile TiO_2 particles: (a) 0 g/L, (b) 0.7 g/L, (c) 1.4 g/L, (d) 2.1 g/L, (e) 2.8 g/L and (f) 3.5 g/L.

Table 2. Critical load values of the MAO coatings.

Coatings	L_c (N)
A [Fig. 8(a)]	17.9
B [Fig. 8(b)]	17.3
C [Fig. 8(c)]	16.9
D [Fig. 8(d)]	16.0
E [Fig. 8(e)]	14.5
F [Fig. 8(f)]	13.8

Fig. 9. (Color online) The hardness values of the microarc oxidation composite coatings prepared in an electrolyte containing nanorutile TiO_2 particles: (a) 0 g/L, (b) 0.7 g/L, (c) 1.4 g/L, (d) 2.1 g/L, (e) 2.8 g/L and (f) 3.5 g/L.

Fig. 10. (Color online) Friction coefficient curves during wear testing: (a) 0 g/L, (b) 0.7 g/L, (c) 1.4 g/L, (d) 2.1 g/L, (e) 2.8 g/L and (f) 3.5 g/L.

temperature after wear testing. The morphologies of the wear tracks for the microarc oxidation coatings exhibited serious furrows. The morphologies of the wear tracks for the microarc oxidation composite coatings prepared in the electrolyte with 3.5 g/L rutile TiO_2 particles showed a wide range of exfoliation. The morphologies of the wear tracks for the microarc oxidation composite coatings prepared in the electrolyte with 2.1 g/L rutile TiO_2 particles showed mild furrows and exfoliation, which showed that the main wear mechanism was abrasive wear and fatigue wear.

Table 3 shows the wear rates of the wear tracks for the microarc oxidation composite coatings prepared in an electrolyte containing nanorutile TiO_2 particles against WC balls at room temperature after wear testing. It can be found that the wear rates of the microarc oxidation composite coatings decreased remarkably because rutile TiO_2 particles were added to the electrolyte. In the electrolyte, when the content of nanorutile TiO_2 particles was more than 2.1 g/L, however, the wear rates of the microarc oxidation composite coatings increased. The wear rate of the microarc oxidation composite coatings formed in the electrolyte with 2.1 g/L rutile TiO_2 particles was the lowest, and the wear rate was only 31.5% that of the MAO coatings.

It is well known that the friction coefficient of ceramic materials is high, and the high porosity of the microarc oxidation coating prompted an unstable friction coefficient. During wear testing, the microbulges on the WC balls easily penetrated into the surface of MAO coatings, which caused serious abrasive wear of the MAO coatings. In contrast, the micropores on the surface of the composite coatings were filled with rutile TiO_2 particles. The density of the composite coatings was higher than the density of the MAO coatings, causing a stable friction coefficient. Meanwhile, during wear testing, because the rutile TiO_2 particles in the micropores could be used as a solid lubricant, the friction coefficient of the composite coatings was decreased remarkably. The wear rates of the composite coatings with high density and microlubricating performance were reduced significantly. However, when the concentration of rutile TiO_2 particles in the electrolyte exceeded a certain value, many microcracks appeared on the composite coatings [Figs. 2(e) and 2(f)]. During wear testing, these microcracks easily expanded and

Fig. 11. The morphologies of the wear tracks for the microarc oxidation composite coatings produced in an electrolyte containing nanorutile TiO_2 particles: (a) 0 g/L, (b) 0.7 g/L, (c) 1.4 g/L, (d) 2.1 g/L, (e) 2.8 g/L and (f) 3.5 g/L.

formed exfoliation [Figs. 11(e) and 11(f)]. Exfoliation could play a microcutting role and could plough the friction surface, increasing the wear rates of the composite coatings.

3.5. Wear mechanism of coatings

Based on the friction behavior of the microarc oxidation composite coatings, the wear mechanism of the composite coating is as follows.

Table 3. Wear rates of the coatings.

Coatings	Wear time (s)	Wear track width (μm)	Wear track depth (μm)	Wear rate ($\text{mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$)
A [Fig. 11(a)]	2400	615.38	4.67	0.038×10^{-4}
B [Fig. 11(b)]	2400	538.46	3.34	0.024×10^{-4}
C [Fig. 11(c)]	2400	461.54	2.67	0.016×10^{-4}
D [Fig. 11(d)]	2400	415.38	2.18	0.012×10^{-4}
E [Fig. 11(e)]	2400	446.15	2.58	0.015×10^{-4}
F [Fig. 11(f)]	2400	492.31	3.05	0.021×10^{-4}

- (a) The micropores and microcracks on the composite ceramic coatings were filled with rutile TiO₂ particles in the process of MAO, and the density of the composite coatings was improved significantly, which made the penetration of the microbulges on the WC balls into the surface of composite coatings more difficult and reduced the wear depth of the composite coatings. Meanwhile, during wear testing, the friction coefficient of the composite coatings was decreased remarkably because the rutile TiO₂ particles in the micropores could be used as a solid lubricant.
- (b) When the content of the rutile TiO₂ particles in the electrolyte exceeded a certain value, many microcracks were found on the surface of the microarc oxidation composite coatings. During wear testing, these microcracks easily expanded and formed exfoliation. Some of the exfoliation was squeezed into the composite coatings under the action of the normal loads and can seriously plough the friction surface, which increased the wear rates of the composite coatings.
- (c) When the contents of the rutile TiO₂ particles in the electrolyte exceeded a certain value, many rutile TiO₂ particles easily agglomerated and formed big bumps on the surface of the composite coatings. During wear testing, these large bulges can easily fall off. Some of the exfoliation was squeezed into the composite coatings due to the action of the normal loads and can seriously plough the friction surface, which increased the wear volume of the microarc oxidation composite coatings.

4. Conclusions

A 2024 aluminum alloy was treated by MAO in a silicate system electrolyte with different concentrations of nanorutile TiO₂ particles, and microarc oxidation composite coatings were prepared. The microarc oxidation coatings formed in the electrolyte without rutile TiO₂ particles contained many crater-like micropores of various sizes. These holes on the surface of microarc oxidation composite ceramic coatings decreased significantly.

The microarc oxidation composite coatings mainly consisted of γ -Al₂O₃, α -Al₂O₃, mullite and rutile TiO₂. With increasing nanorutile TiO₂ particles in

the electrolyte, rutile TiO₂ in the composite coatings increased significantly.

Compared to the microarc oxidation coatings, the microarc oxidation composite coatings produced in the electrolyte containing 2.1 g/L rutile TiO₂ particles exhibited the lowest wear rate, which was only 31.5% that of the microarc oxidation coatings, and the microarc oxidation composite coatings exhibited better wear resistance.

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