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Characterization of micro-arc oxidation coatings on Ti6Al4V with addition of SiC particle

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Abstract

In the present work, particles of SiC were applied to the micro-arc oxidation (MAO) treatment of Ti6Al4V, characterization of MAO coatings with different SiC particle concentration were evaluated. X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) results show that the structure and morphology of MAO ceramic coatings could change with different amounts of SiC in the electrolyte. Both of the number and size of the pores on the ceramic coating surface were decreased, while the layer thickness increased with the increase in SiC particles in the electrolyte. A dense double-layer structure coating composed of a Ti-based layer and a SiC-based layer with a thickness of about 40 \( \mu \)m was prepared. It was shown that the addition of SiC particles participated in the process of micro-arc oxidation and changed the microstructure of MAO coating.

1. Introduction

Titanium and its alloys are widely used because of their high strength/weight ratio, low density, good biocompatibility, and high corrosion resistance [1, 2]. The corrosion resistance of titanium-based materials arises from the native oxide layer (TiO\textsubscript{2}) formed at the surface [3]. However, this native oxide layer provides insufficient protection against wear and fretting as well as corrosion in aggressive environments. Therefore, various surface modification techniques have been proposed to improve the surface properties of titanium alloys, such as conventional anodization, physical vapor deposition (PVD) [4], chemical vapor deposition (CVD) [5], gas nitriding, and micro-arc oxidation (MAO) [6]. The native oxide layer generates on titanium-based materials makes it difficult to form a layer that can firmly stick to the substrate. Among the different techniques, the MAO process is an attractive technique that generates a hard, thick, and relatively dense ceramic surface on valve metals with good adhesion within a short time. The ceramic surface can enhance the base with increased hardness, better corrosion resistance, and wear resistance [7–9]. Moreover, MAO has advantages over other techniques because of relatively low requirements in experimental conditions and eco-friendly procedures [10].

Low friction and low wear loss rate are desirable to reduce the wear between sliding pairs. Research work shows that coatings applied by microarc oxidation from phosphate baths reduce the friction coefficient [11, 12], while the wear resistance of the rutile/anatase films are still not good enough due to the poor load support property. Generally, there are two ways to improve the tribological behaviors of MAO coatings: incorporation of anionic components into the electrolytic solution and formation of composite coatings during MAO process by the addition of nano or micro size particles. Research work reported that beside substrates oxides, ZrO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} were introduced in the MAO coatings by adding K\textsubscript{2}ZrF\textsubscript{6} [13] and NaAlO\textsubscript{2} [14, 15] into electrolytes, respectively. The formation of ZrO\textsubscript{2} or Al\textsubscript{2}O\textsubscript{3}, reduces the coatings defects and hence, improves the wear resistance of such coatings. Composite coatings also can be prepared by adding nano or micro size particles into
the electrolytes during the MAO treatment of metals. Particles of ZrO$_2$ [16], and Al$_2$O$_3$ [17] applied to the MAO treatment proved that the coatings have shown more efficient protection after the incorporation of such nanoparticles. Silicon carbide (SiC) is known for its outstanding hardness, good wear resistance, and high-temperature stability, indicating that SiC can withstand high temperature during the MAO process and be a good supporter on MAO surfaces. While it is rarely reported to using SiC as an additive to the MAO treatment though it has been used for coating in other techniques [18–21].

In the present study, particles of SiC were applied to the MAO treatment of Ti6Al4V, characterization of MAO coatings with different SiC particle concentration were evaluated. The result demonstrated that SiC could change the morphology of the ceramic coating surface, and there was a critical change in the thickness of layers when a certain amount of SiC particles was added.

2. Specimen preparation and experimental setup

The MAO coatings were accomplished on commercial Ti6Al4V using a set of homemade micro-arc oxidation equipment. The device consists of a potential adjustable AC pulse power supply up to 500 V, a container, a stirring and cooling system. Ti6Al4V specimen and the wall of the container were used as two electrodes, respectively. Ti6Al4V specimens with size of 20 mm $\times$ 20 mm $\times$ 3 mm were ground with SiC abrasive paper up to 1200#, cleaned in alcohol and distilled water, and successively dried in air. Na$_3$PO$_4$ (0.3 mol l$^{-1}$) was added to distilled water as the base composition of the electrolyte, and glacial acetic acid was added to adjust the pH value to 10. Micro-sized SiC particles of purity 97% supplied by Aladdin Industrial Corporation, Shanghai, China, were added to the base electrolyte. The SiC powder particle sizes were measured by a laser diffraction particle size analyzer (LMS-30). Figure 1 shows the particle size distribution of SiC particles which had an average diameter of about 3 $\mu$m and range in size between 0.3 and 3.6 $\mu$m. The added SiC particles (3 gl$^{-1}$, 6 gl$^{-1}$, 9 gl$^{-1}$, and 12 gl$^{-1}$, respectively) were dispersed by a magnetic stirring apparatus located at the bottom of the container.

A segmented pattern of voltage was provided during processing. First, the voltage was raised from 0 V to 320 V in 2 s. Then, the voltage was raised from 320 V to 450 V in 130 s. Finally, the voltage was kept at 450 V for 600 s. The frequency was 500 Hz, and the duty ratio was 60%. Samples processed with different electrolytes were named TMP3, TMP6, TMP9 or TMP12 (T for Ti6Al4V, M for MAO, and P for particle; marked numbers indicate the amount of SiC particles added in the electrolyte). For comparison, samples micro-arc-oxidized in base electrolyte without SiC particles were also prepared, which were marked as TM.

The phase component of the ceramic coating surface was analyzed by Cu Kα radiation with a wavelength of 0.154 056 nm using a diffractometer from Rigaku Japan (DMAX-2500RB) in step scan mode with a step size of 0.02° and a scanning rate of 2° per min. The surface morphology and cross-section of samples were observed by scanning electron microscopy (SEM; FEI Quanta250 Environmental Scanning Electron Microscope). A contour graph (Dektak 150; Bruker Corporation) was used to test the roughness of each surface.

![Figure 1. The size distribution of SiC powder particles.](image-url)
3. Results

The XRD patterns of the samples indicated that the composition of the coating varied with the amount of added SiC in the electrolyte, as shown in figure 2. The peaks in the XRD patterns of TMP9 and TMP12 demonstrated that SiC was successfully incorporated on the surface through MAO, and SiC was dominant in the layer of the TMP12 sample. The absence of SiC peaks in the XRD patterns of TMP3 and TMP6 may be attributed to amounts of SiC that were too low to be detected. Peaks of titanium dioxide, anatase TiO2, and rutile TiO2 were reduced with an increase in the amount of added SiC particles. Titanium could be detected in the base due to the penetration of x-rays and porosity of the MAO layer [22]. The reduction of titanium peaks and disappearance of titanium oxide phases in the TMP12 sample may be caused by the formation of a thick SiC-dominated ceramic coating layer.

Figure 3 shows the surface morphologies of ceramic coatings prepared with different electrolytes. The surface of the coating formed in the electrolyte without SiC particles exhibited characteristics of the MAO process, as shown in figure 3(a); it contained many grains with various sizes. Micro-pores with a size of 1 \( \sim \) 2 \( \mu m \) were found on the edge of some large grains. The number and size of the pores on the coating surface were both decreased with an increase in the amount of SiC particles in the electrolyte. The surface morphology of the coating formed in the electrolytes with 3 g l\(^{-1}\) and 6 g l\(^{-1}\) SiC particles was almost similar to the morphology of the TM sample. Small particles, which belong to SiC as energy dispersive spectrum analysis results shown in figure 4, were found to be distributed homogeneously among the MAO coating. The morphology of the surface was noticeably different when the amount of SiC particles was increased to 9 g l\(^{-1}\) in the electrolyte. The loose porous morphology gradually became denser and rough.

Figure 5 shows the average coating thickness and surface roughness of different ceramic coatings prepared with different electrolytes. The coating thickness of TM varied in the range of 34 – 37 \( \mu m \). Lower amounts of SiC (TMP3 and TMP6) did not significantly change the thickness of oxide coating. However, the incorporation of higher amounts of SiC (TMP9 and TMP12) increased coating thickness by more than 20% compared with the thickness of the TM sample. Mean surface roughness results revealed that the surface roughness of TM, TMP3, and TMP6 was around 0.5 \( \mu m \), as shown in figure 5(b). The roughness of TMP9 and TMP12 was markedly increased.

The greater roughness of TMP9 was attributed to its unique morphology, as shown in figures 6(a) and (b), with bulges on the surface. The part of the surface of TMP9 without bulges was similar to that of TMP6 (figure 3(c)) with smaller and fewer pores, while the morphology of the bulge was similar to the morphology of TMP12 (figure 3(e)). Energy dispersive spectrum (EDS) results show that the bulge (figure 6(d)) was mainly composed of SiC, similar to the composition of the surface of TMP12; on the other hand, the residue part of the surface (figure 6(c)) had a similar composition to that of TMP6. It is reasonable to speculate that some SiC could begin to accumulate on the surface when the amount of added SiC particles was 9 g l\(^{-1}\). In addition, morphological changes were consistent with the appearance of SiC peaks on XRD patterns. Figure 6(e) shows a
Figure 3. Morphology of ceramic coatings. (a) TM, (b) TMP3, (c) TMP6, (d) TMP9, and (e) TMP12.

Figure 4. Energy dispersive spectrum analysis result of TMP3 coating. (a) Surface morphology of TMP3 coating, (b) energy dispersive spectrum of ‘1’ marked in (a), (c) energy dispersive spectrum of ‘2’ marked in (a).

Figure 5. Variation in (a) coating thickness and (b) mean surface roughness.
cross-section line scanning of the TMP12 sample, demonstrating that a double-layer structure composed of a Ti-based layer and a SiC-based layer was formed.

4. Discussion

Based on the results, the formation mechanism of the MAO process in electrolytes with different amounts of SiC can be elucidated, as illustrated in figure 7. As shown in figure 7(a), in the electrolyte without SiC particles, there was a large amount of small gas bubbles (i.e., O₂ and H₂O) on the sample surface initially, and a thin oxide film with dopants and defects was formed in the conventional oxidation stage [22]. As the reaction proceeded, a bubble layer was formed due to the increasing number of gas bubbles. The bubble layer was subsequently broken down; micro-arc discharges initially occurred at the weakest dielectric point, where the dopants and defects exist. These micro-arc discharges continued to occur at the weakest place and gradually increased until the whole surface was covered.

TMP3 and TMP6 had a small quantity of SiC particles in the electrolyte. As shown in figure 7(b), during the MAO process, melted SiC particles absorbed part of the thermal energy, and the melted liquid can compensate...
for ejected metals that decrease the size of pores and number of cracks. A decrease in the thickness of the MAO layer due to additives has also been reported by researchers [23, 24]. According to the theory of electron avalanche, the reproduction of electrons is critical for intriguing plasma. Although SiC is dielectric at room temperature, it will become a good conductor at high temperatures. Hence it can absorb electrons and extinguish sparks during MAO. Therefore, sparks would be limited, and a denser and thinner Ti-based ceramic layer can form.

As shown in figure 6(a), the bulges of TMP9 revealed that increasing SiC particles could accumulate on ceramic coatings. Thermal energy was well transmitted and absorbed by the large amount of SiC particles, and the residue part of SiC particles was sintered on the Ti-based layer as a bulge, which was positioned at the location of the spark, as shown in figure 7(c). Figure 6(b) revealed that fewer spark channels were observed on the cross-section of the non-bulge area, and the interface of the ceramic coating and substrate at the bulge locations had more fluctuations. This finding suggests that these locations had been broken down several times. The morphological changes indicated that breakdown happened on the bulge instead of the residue part during MAO. SiC particles incorporated into the coating layer could limit the growth of TiO2, and the stack of SiC particles can leave some small cracks or channels for the electrolyte to pass through, which may cause the bulge area to become the weak point in the TMP9 coating. With repeated breakdown on the bulge, nearby areas were heated and reached the breakdown voltage more easily. Finally, several groups of bulges were scattered on the coating.

When the amount of SiC particles added in electrolytes was increased to 12 g l\(^{-1}\), the density of SiC particles was increased, and the cracks in bulges were fewer, as shown in figure 7(d). As the reaction proceeded, breakdown would cover the entire surface of the substrate and create a sintered SiC layer.

5. Conclusion

Following results are concluded from current research work:

(1) By increasing the amount of added SiC particles, the number and size of the pores on the ceramic coating surface were both decreased. The thickness of layers was increased with an increase in SiC particles in the electrolyte. The thickness of MAO coatings with addition of SiC (9 g l\(^{-1}\), 12 g l\(^{-1}\)) increased coating thickness by more than 20%.

(2) The morphology of the layers indicated that there was a critical change in the thickness of layers when a certain amount of SiC particles (9 g l\(^{-1}\)) was added.

(3) A dense and thick SiC-dominated outer layer and titanium dioxide inner layer composite MAO coatings were prepared by adding 12 g l\(^{-1}\) SiC into the electrolyte.
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References

[1] Yazıcı S K, Muhaflı F and Baydogan M 2014 Effect of incorporating carbon nanotubes into electrolyte on surface morphology of microarc oxidized Cp–Ti Appl. Surf. Sci. 318 10–14
[2] Li Y et al 2012 Preparation, characterization and mechanical properties of microarc oxidation coating formed on titanium in Al(OH)3 colloidal solution Appl. Surf. Sci. 258 2538–43
[3] Chen J et al 2006 Preparation and properties of hydroxyapatite–containing titania coating by micro-arc oxidation Mater. Lett. 60 2538–43
[4] Ceschini L et al 2008 Comparison of dry sliding friction and wear of Ti6Al4V alloy treated by plasma electrolytic oxidation and PVD coating Wear 264 86–95
[5] Zhu Y et al 2012 Deposition of TiC film on titanium for abrasion resistant implant material by ion-enhanced triode plasma CVD Appl. Surf. Sci. 262 156–68
[6] Yan X et al 2019 Improvement of tribological performance by micro-arc oxidation treatment on selective laser melting Ti6Al4V alloy Mater. Res. Express 6 096509
[7] Vangolu Y et al 2010 Optimization of the coating parameters for micro-arc oxidation of Cp–Ti Surf Coat Tech. 205 1764–73
[8] Wang Y M et al 2004 Growth, microstructure and mechanical properties of microarc oxidation coatings on titanium alloy in phosphate–containing solution Appl. Surf. Sci. 233 258–67
[9] Curran J A and Clyne T W 2005 Thermo-physical properties of plasma electrolytic oxide coatings on aluminium Surf Coat Tech 199 168–76
[10] Wang Y Q, Wu K and Zheng M Y 2006 Effects of reinforcement phases in magnesium matrix composites on microarc discharge behavior and characteristics of microarc oxidation coatings Surf Coat Tech 201 353–60
[11] Gnedenkov S V et al 2001 Chemical composition of antifriction micro-arc oxide coatings on titanium alloy BT16 Prot. Met. 37 168–72
[12] Wang Y M et al 2006 Microarc oxidation coatings formed on Ti6Al4V in Na2SiO3 system solution: microstructure, mechanical and tribological properties Surf Coat 201 82–9
[13] Liu F et al 2011 Corrosion behavior of the composite ceramic coating containing zirconium oxides on AM30 magnesium alloy by plasma electrolytic oxidation Corros. Sci. 53 3845–52
[14] Yan Y et al 2010 Effect of NaAlO2 concentrations on microstructure and corrosion resistance of Al2O3/ZrO2 coatings formed on zirconium by microarc oxidation Appl. Surf. Sci. 256 6359–66
[15] Yerokhin A L, Leyland A and Matthews A 2002 Kinetic aspect of aluminum titanium formation on titanium alloys by plasma electrolytic oxidation Appl. Surf. Sci. 200 172–84
[16] Zhong Y et al 2014 Characterization and thermal shock behavior of composite ceramic coating doped with ZrO2 particles on TC4 by micro-arc oxidation Surf. Coat Tech. 311 158–63
[17] Zhang D, Gou Y, Liu Y and Guo X 2013 A composite anodizing coating containing superfine Al2O3 particles on AZ31 magnesium alloy Surf Coat Tech 256 52–5
[18] Hei H et al 2015 Growth of beta-Sic interlayers on WC-Co substrates with varying hydrogen/tetramethylsilane flow ratio for adhesion enhancement of diamond coatings Surf Coat Tech 272 278–84
[19] Liu Y et al 2015 Oxidation behavior of 2D C/SiC composites coated with multi-layer SiC/Si-B-C/SiC coatings under wet oxygen atmosphere Appl. Surf. Sci. 353 214–23
[20] Paul B, Prakash J and Sarkar P S 2015 Formation and characterization of uniform SiC coating on 3D graphite substrate using halide activated pack cementation method Surf Coat Tech 282 61–7
[21] Wang P et al 2015 Thermal cycling and oxidation resistance of B modified ZrB2–SiC coatings on SiC coated graphite Surf Coat Tech 280 330–7
[22] Wang L et al 2010 Optical emission spectroscopy studies of discharge mechanism and plasma characteristics during plasma electrolytic oxidation of magnesium in different electrolytes Surf Coat Tech 205 1651–6
[23] Zhong Y et al 2010 Characteristic of microarc oxidized coatings on titanium alloy formed in electrolytes containing aluminate and ZrO2 particles Advanced Materials Research 105-106 502–4
[24] Mu M et al 2012 Preparation and tribological properties of self-lubricating TiO2/graphite composite coating on Ti6Al4V alloy Appl. Surf. Sci. 258 8570–6