Preparation, characterization and mechanical properties of microarc oxidation coating formed on titanium in Al(OH)$_3$ colloidal solution

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A ceramic coating with a thickness of 20–70 μm was grown on titanium plate in Al(OH)$_3$ colloidal solution by microarc oxidation (MAO) in constant current mode. It is found that the as-grown coating consists of rutile TiO$_2$ phase together with a thin layer of Al$_2$TiO$_5$ phase near the surface of the coating. After removing the Al$_2$TiO$_5$ layer by polishing, a single phase of rutile TiO$_2$ coating is achieved, which is different from results reported previously, where the coating is usually composed of two phases of rutile and anatase TiO$_2$. It is suggested that the formation of the coating with single phase of rutile TiO$_2$ is related to the existence of Al(OH)$_3$ in the solution. The growth rate of the coating increases with increasing current density in the range of 17–23 A/dm$^2$, but it increases little in the range of 23–30 A/dm$^2$. The rutile TiO$_2$ coating looks compactness and solidity in the coating grown in the density range of 17–23 A/dm$^2$ but looseness and insubstantiality in the range of 23–30 A/dm$^2$. The hardness and elastic modulus of the rutile TiO$_2$ decreases with the density increasing. The mechanism of formation of the coating is discussed in the present work.

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1. Introduction
Unparalleled advantage of titanium and its alloys has been developed increasingly in aerospace, medicine and other fields. As an important method of surface modification on titanium and its alloys, microarc oxidation (MAO) has been drawn much attention in recent years. Although MAO process has been developed over the past decades, the study of MAO is not stagnant but more systematic and classified. Characterization methods on MAO coating are enriched, making MAO process parameters improve greatly. Performances required for aerospace materials such as mechanical and corrosion resistance of the coating are being promoted.

Wang and Sun et al. [1,2] studied the growth characteristics of the MAO titania coating and its alloys at variety of process parameters, and evaluated the tribological properties of the coatings in sliding and fretting contact conditions, in order to obtain a good antifriction one. Tang et al. [3] studied the effect of cathode pulse on MAO coating characteristics. Chu et al. [4] studied the thermal stability of MAO titania coating. In the recent years, the study of MAO is not just confined in mechanical properties and corrosion resistance which are demanded by structural materials field, but also developed to the medical field [5], such as biocompatibility and drug deposition-release. Sul et al. [6] studied the bone response of oxidized bioactive and non-bioactive titanium implants. Zhou et al. [5,7] found that hydrophilic MAO coating with good deposited sustaining-release ability can be produced by using electrolyte with certain organics added.

In general, the coating is composed by two phases of anatase and rutile TiO$_2$ [3–8]. However, the mechanical properties of the coating composed by the two phases may get worse at high temperatures, due to that anatase TiO$_2$ is metastable and transforms into rutile TiO$_2$ at the temperature range of 550–1000 °C. Compared with the metastable anatase TiO$_2$, rutile TiO$_2$ has a more symmetrical and stable crystal structure, better corrosion resistance and higher hardness, therefore, the coating of single rutile phase may exhibit much better protective properties than that composed by the two phases [1]. Recently, our group fabricated a single rutile TiO$_2$ MAO coating on the Ti substrate in Al(OH)$_3$ colloid solution in the constant voltage mode, and discovered that the coating has stable and reversible electrochromic behavior [9,10]. However, the mechanical properties of the coating are not studied, and MAO current is varied in the constant voltage mode. At the beginning period of the MAO process, a very high current leads to a high coating growth rate, making the new generated coating uneven, while at the ending phase of the MAO process, the existing coating reduces the current, making the growth rate decreasing greatly [11].
It is well known that the coating has constant and relatively high growth rate in constant current mode. Therefore, the MAO coating was produced using Al(OH)₃ colloid solution and constant current mode in this work, phase composition, microstructure, element distribution, hardness and elastic modulus of the coating were investigated, and the growing mechanism is also discussed. The coating prepared in this work has comparative better corrosion resistance and hardness, and high elastic modules. These properties make the coating to show a stronger protective effect in impact and friction, and protect the substrate in some corrosion circumstance. So the MAO technology used in this work provides a better surface protection on titanium, making titanium to be used more widely in aerospace, offshore engineering and biomaterial fields such as aircraft engines, structure material, bioactive implant etc.

2. Experimental details

A layer of titanium oxide was coated on surface of commercial pure titanium plate (40 mm × 10 mm × 1 mm) by using MAO technique in constant current mode, the titanium plate was used as anode and stainless steel bath was used as both cathodes and electrolyte container. The plates were polished with #1000 abrasive paper, washed with acetone and distilled water, and dried at 40 °C. Component of electrolyte was Na₃PO₄ (0.01 mol/L), Al(OH)₃ colloid (0.15 mol/L) and some additives. The temperature of the electrolyte was kept below 50 °C by cooling system. The applied current, frequency, duty cycle and oxidizing time were 17–30 A/dm², 1000 Hz, 10% and 10 min, respectively.

After processing, the samples were cleaned in distilled water, and then dried by hot air. The coating thickness was measured by an eddy current thickness gauge (T240, Time Group Co. America); ten measurements were carried out evenly on both sides of the samples. The microstructure of the coating was analyzed by X-ray diffraction (XRD D8-DISCOVER, Bruker, Germany) using a Cu Kα radiation (λ = 0.15405 nm) with a scanning step of 0.02°. The surface morphology of the coating was characterized by a scanning electron microscopy (SEM, JEOL Co, Japan). The compositional analysis of interfacial coating between substrate and coating was measured with energy-dispersive X-ray detector (EDX). The hardness and elastic modulus were measured with a nanoindentation testing system (Nanoindentor XP, MTS, USA).

3. Experimental results and discussion

XRD results indicates that the coating grown in the current density between 17 and 26 A/dm² has similar XRD pattern to Fig. 1(a), which is a typical XRD pattern of the coating grown at the current density of 23 A/dm², implying that the coating consists of rutile TiO₂ phase and a small amount of Al₂TiO₅ phase. After polishing the surface of the coating, it is found that only diffraction peaks of rutile TiO₂ are observed in the XRD pattern, as shown in Fig. 1(b), implying that the Al₂TiO₅ exists on the surface of the coating and can be removed complete by polishing, and a coating consisting of a single phase of rutile TiO₂ can be obtained by polishing the surface of the coating grown in the current density of 17–26 A/dm². However, when the current density increase to 30 A/dm² only the peaks of Al₂TiO₅ are observed in Fig. 1(c). After taking into account that X-ray has limited penetration depth and the thickness of the coating is larger than the depth, we polished the surface of the coating, and observed the diffraction peaks of rutile TiO₂ phase besides the peaks of Al₂TiO₅ phase in the XRD pattern of the polished coating, as shown in Fig. 1(d). The results of Fig. 1(c) and (d) indicate that the coating grown at 30 A/dm² is dominantly composed of Al₂TiO₅ phase; it is difficult to obtain a coating consisting of a single phase of rutile TiO₂ by polishing the coating grown at 30 A/dm². According to analysis mentioned above, it is concluded that a single rutile TiO₂ phase coating can be obtained by polishing the coating grown in the current density between 17 and 26 A/dm², which is different from the previously reported literature, where the coating is usually composed by rutile and anatase TiO₂.

Based on the XRD data of unpolished coatings, we estimate qualitatively the content ratio of the Al₂TiO₅ to the rutile TiO₂ phases in the coating by calculation of area ratio of the XRD peak of the Al₂TiO₅ at 2θ = 26.5° and the peak of the rutile TiO₂ at 2θ = 27.4°, and found that the content ratio in the coating prepared at the current density of 17, 20, 23 and 26 A/dm² are 0.145, 0.119, 0.116 and 0.294, respectively. It is obvious that the content of the Al₂TiO₅ phase is small and similar in the coating prepared at the current density below 23 A/dm², but increases sharply for the coating prepared at 26 A/dm². Therefore, in the surface of the coating, the content of Al₂TiO₅ increases with the current density increasing, and it is easier to produce thick coating with a single rutile TiO₂ phase in the current density of 17–23 A/dm².

Fig. 2 shows the cross sectional morphology of the coating prepared at different current densities. It can be seen that the coating and Ti substrate contact tightly and irregularly, which makes the binding between coating and the substrate securely. Fig. 2(a)–(c) shows the cross section of the coating prepared at current densities not larger than 26 A/dm², revealing concordant contrast. Combining with result of Fig. 1(a), we conclude that the four coatings
Fig. 2. SEM micrographs of the cross section of the coating prepared at current density of (a) 17 A/dm², (b) 23 A/dm², (c) 26 A/dm², and (d) 30 A/dm² (I: Ti substrate; II: coating; III: looseness coating).

Fig. 3. SEM image (upper) and EDS profiles (lower) of the compositional (Ti, Al, and O) distribution along cross section for the coating prepared at current density of (a) 17 and (b) 26 A/dm² (I: substrate; II: coating).
consist of the rutile TiO₂ and a small amount of Al₂TiO₅ phases. However, the coating prepared at 30 A/dm² is composed by two kinds of layers, as shown in Fig. 2(d). Combing with results of Figs. 1(c) and (d) and 2(a)–(c), it is concluded that the upper white layer (marked by III) consists of Al₂TiO₅ phase and the lower deep gray layer (marked by II) consists of rutile TiO₂ phase or may contain amount of Al₂TiO₅ phase. The upper layer of the Al₂TiO₅ peels from lower layer, and is shed off easily when the coating is rubbed slightly. It is also found that the thickness of the coating increases sharply with increasing the current density in the range of 17–23 A/dm², but very slowly in the range of 23–30 A/dm². Moreover, the coating looks compacted and solidified when it is prepared in the density range of 17–23 A/dm² but loosened as it is fabricated in the density range of 23–30 A/dm². According to above discussion, it is concluded that there is a critical current density of 23 A/dm² for the coating preparation in the present work, below which the coating has good compactness and solidity and higher growth rate and compactability decrease little with the increasing current density, and, above which the growth rate almost does not change, and the coating compactability decreases seriously.

Fig. 1(a) and (b) has proved that the coating prepared at the current density of 17–26 A/dm² are composed by rutile TiO₂ and a small amount of Al₂TiO₅ at the surface and single rutile TiO₂ in the interior. In order to further understand the distribution of the rutile TiO₂ and Al₂TiO₅ in the coating, the distribution of the composition (Ti, Al and O) is measured by EDS line scanning the cross sections of the coating. We hope to find out the distribution of the two phases in the coating by analyzing the element distribution. Part II of the EDS profiles in Fig. 3(a) and (b) give distribution of Ti, Al and O elements in the coating prepared at the current density of 17 and 26 A/dm², respectively. It can be seen from the figures that the relative content of O has keep constant over the range of coating, while the relative content of Al is almost zero in most range of the coating, but increases sharply in the small range near the surface of the coating (about 5 µm away from the surface). Correspondingly, the relative content of Ti keeps constant in the range, where the content of Al is zero, and decreases near the surface of the coating, where the content of Al increases sharply. According to above analysis, it concluded that the Al₂TiO₅ phase only exists in a very small range near the surface. The coating consists of single phase of rutile TiO₂ in the most of range but two phases of rutile TiO₂ and Al₂TiO₅ only in small range near the surface.

Fig. 4 shows the surface morphology of the coating prepared at different current densities. It can be seen that the surface is porous for the coating prepared at a lower current density of 17–23 A/dm². The microarc holes are micron scale in diameter, and some condensation products heap disorderly around the holes, forming the microcosmic rough surface. With increasing the current density to 26 A/dm², density of the microarc holes on the surface decreases, and the condensation products heap in a form of irregular balls with diameter in micro scale around the hole, as shown in Fig. 4(b). However, when the current density reaches 30 A/dm², the surface morphology of the coating is completely different from that shown in Fig. 4(a) and (b). There is no microarc hole on coating surface, but it chops seriously and is easily shed off. From Figs. 1 and 3, it is concluded that the surface consists of Al₂TiO₅ phase. It can be inferred from previous discussions, with the MAO current density increases, the coating surface becomes more rough and choppy. In this condition, although the microarc hole density decreases, coating compactability decreases seriously. So, excessive MAO current density is not conducive to the protection of the substrate.

By using Scherrer formula and XRD diffraction data of the coating, the grain size of the TiO₂ in the coating prepared at the current density of 17, 20, 23, 26 A/dm² are estimated to be 34.1, 34.6, 36.4 and 28.9 nm respectively. Obviously, the grain size increases slightly as the current density increases from 17 to 23 A/dm², but decreases sharply at 26 A/dm² due to formation of more Al₂TiO₅ in the coating, for the appearance of second phase would hinder growing of TiO₂ grain. To study the mechanical properties of the coating prepared at different current density, a nanoindentation testing system is used to measure the hardness and elastic modulus of the coating. In order to understand mechanical properties of the coating composed by rutile TiO₂, the surface of all the samples is polish to remove the layer containing Al₂TiO₅. Fig. 5 shows a group of typical loading–displacement curves in an identical indentation depth of 2000 nm, indicating that both loading and unloading curves are nonlinear. The maximum displacement achieved by the nanoindentation is originated from the elastic and plastic deformation during the unloading process. It can be seen from Fig. 5 that the elastic recovery ratios of the coating prepared at the current density of 17, 20, 23 and 26 A/dm² are 16.8%, 18.1%, 15.8% and 15.5%, respectively, which are far higher than 7.7% of titanium. That is because the residual displacement mainly depends on the plastic deformation, while the ceramics basically exhibited low plastic...
deformation compared to metals, resulting in less residual displacement. By using measurement results of Fig. 5, the hardness and elastic modulus of the coating prepared at various current densities are evaluated, as shown in Fig. 6. Fig. 6 shows that both the hardness and elastic modulus of the coating rise as the current density increases from 17 to 20 A/dm², and then decrease with increasing the current density. Combining with the result of Fig. 2, it can be deduced that the hardness and elastic modulus of the coating may be related to its compactness.

To study the mechanical properties of the coating at different thicknesses, we polished the coating into different thickness and then measured its hardness and elastic modulus. Fig. 7 plotted the hardness and elastic modulus vs the thickness of the coating prepared at 20 A/dm². It can be seen from Fig. 7 that the hardness and elastic modulus increases with increasing the thickness in the thickness ranging from 0 (substrate) to 10 μm and then keeps an uniform values approximative in the thicknesses of 10–30 μm, but decreases at the unpolished coating surface. The decrease at the surface of the coating is due to that the surface is microporous and/or contains a small amount of Al₂TiO₅.

In many reported literatures, it is noted that the MAO coating is usually composed by several phase structure. For instance, in phosphate or silicate solution system, MAO coating is usually composed by rutile and anatase TiO₂ phases [4]. And in aluminate solution system, MAO coating is usually composed by Al₂TiO₅ and some impurity phase [2]. As the coating-forming agent, Na₃PO₄ ensures the generation of the coating. PO₄³⁻ in the solution directly determines the growth of titania oxide and makes the coating generated compactness and solidity. However, we make the coating contain only one kind of TiO₂ with rutile structure by adding Al(OH)₃ colloid in phosphate solution in the present work. We find that the TiO₂ phase tends to form rutile TiO₂ rather than anatase TiO₂ when Al(OH)₃ colloid is added in the solution, which is attributed to that Al(OH)₃ is micelle in the solution. The existence of Al(OH)₃ reduces the mobility of ions in the solution, preventing other ions (like PO₄³⁻) from entering the microarc area and involving in reactions during MAO processing. So at the beginning of MAO process, there is no Al₂TiO₅. Through the theory of series resistance [12], the whole current circuit of MAO (including power supply, electrolyte, sample and electrode) can be treated as a series resistance circuit. Obviously, based on Joule’s law, the power of microarc area is directly proportional to its relative resistance in this circuit. Since addition of Al(OH)₃ colloid decreases mobility of ions in the solution, ion concentration in microarc area decreases which leads to increment of resistance of this area, therefore increases of the power of MAO. Due to existence of Al(OH)₃ colloid, microarc process get more intense and produce higher temperature at microarc moment, resulting in the transformation of TiO₂ to high temperature rutile phase rather than low temperature anatase phase. That is the reason why no anatase phase is found in the coating.

The coating consists of Al₂TiO₅ in small range near the surface. That is because constant current mode is used in the MAO process. In this mode, with the coating thickness rising, MAO voltage rises gradually. At the last phase of the MAO process, the voltage reaches its peak. High voltage makes process temperature very high. The following reactions will occur:

\[ 2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \]

\[ \text{TiO}_2(\text{surfeit}) + \text{Al}_2\text{O}_3 \rightarrow \text{Al}_2\text{TiO}_5 + \text{TiO}_2 \]

Al₂TiO₅ is generated at the last phase of the MAO process. So it can explain why Al₂TiO₅ exists only near the surface of the coating.

4. Conclusion

In Al(OH)₃ colloidal solution, a ceramic coating was grown on titanium substrate by MAO. The coating is composed by dominant rutile TiO₂ and a small amount of Al₂TiO₅ near the surface. The formation of the coating with a single phase of rutile TiO₂ rather than the two phases of rutile and anatase TiO₂ is attributed to
addition of the Al(OH)_3 in the solution, which makes the MAO reaction occur at high temperature, leading to formation of high temperature phase of rutile TiO_2. By polishing the surface, single rutile phase TiO_2 coating is achieved.

The growth rate of the coating increases with current density increasing in the range of 17–23 A/dm^2, but increases little in the range of 23–30 A/dm^2. With the current density rising, the coating compactability decreases, so the hardness and elastic modulus of the coating decrease too. The highest hardness and modulus are 5.1 and 145 GPa, respectively. The elastic modulus of the coating is larger than the values of the coating composed by rutile and anatase TiO_2 reported previously. The most suitable current density for growing the coating is 17–23 A/dm^2 in the present work.

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