Characterization of Oxide Coatings Deposited on Pure Titanium by Alternating-current Microarc Discharge in Electrolyte

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Microarc oxidation is an advanced coating process to deposit thick, hard ceramic oxide coatings on metal surfaces. In this paper, a ceramic oxide coating of 30 μm was prepared on TA2 pure titanium by alternating-current microarc oxidation in aluminate solution. Its morphology, composition and structure were characterized by scanning electron microscopy, X-ray diffractometry, Raman spectroscopy. The Al, Ti, O concentration profiles across the coating were determined by energy dispersive spectroscopy. The outer layer of the coating is composed of a large amount of TiAl2O5 and a little rutile type TiO2 compounds. But the rutile content in the inner layer is much higher than in the outer layer while the TiAl2O5 content decreases obviously in the inner layer. All of these oxides derive from a rapid solidification of the melt in microarc discharge zone. The Al atoms from the aqueous solution have diffused to the coating/titanium substrate interface, but are enriched in the outer layer. However, the oxygen and aluminum atoms have not diffused into the unoxidized titanium substrate, even near the coating/substrate interface. This facilitates maintaining mechanical properties of pure titanium substrate after microarc oxidation treatment on titanium surface.

KEY WORDS: microarc oxidation; pure titanium; phase structure; ceramic coating.

1. Introduction

Although titanium and its alloys offer many attractive properties, their use is largely restricted to non-tribological applications, owing to high friction and wear and a strong tendency to galling. On the other hand, there has been increasing interest in titanium alloys in many fields, in which wear resistance, antiscuffing, loadbearing capacity and biocompatibility are frequently of major concern.1 In recent years, some attempts have been made to overcome the problem by means of many surface engineering techniques such as anodic oxidation,2–3) ion implantation4) and thermal oxidation.5) However, anodic oxidation film on titanium is usually less than one micron; ion implantation on titanium still has a depth limitation (<0.5 μm) though it can produce significant surface hardening. So the application of these two techniques on titanium and its alloys is largely limited. In addition, thermal oxidation can produce a 15–30 μm thick oxide layer of the rutile-type TiO2 phase. Unfortunately, due to the long-term high temperature action, thermal diffusion processes lead to the formation of an oxygen solid solution in titanium substrate, and development of phase segregation and coalescence, which may cause substrate embrittlement and worsened mechanical and corrosion performance.

Microarc oxidation (MAO) is an unconventional plasma-chemical–electrochemical method of forming ceramic oxide coatings on valve metals such as Al, Mg, which devolves from anodic oxidation.5–11) Microarc discharge device for aluminum alloys has two modes: a direct-current (DC) mode and an alternating-current (AC) mode.10–12) It is believed that the AC mode is more effective to deposit the MAO coatings on aluminum alloys than the DC mode. In recent years, some researchers13,14) have tried to study microarc oxidation or anodic spark deposition on titanium using a DC power supply in order to deposit corrosion-resistant or functional oxide coatings. Nevertheless, it is difficult to obtain a dense and thick coating. Recently, we have tried to deposit ceramic coatings on Ti–6Al–4V alloy using an asymmetric AC power supply in silicate solution.15) The results show that it is more promising to deposit MAO coatings on titanium alloys using an AC power supply.

In this work, dense ceramic oxide coatings were first deposited on pure titanium by AC microarc oxidation in aluminate solution. Their microstructure and composition were studied by scanning electron microscopy (SEM), Raman spectroscopy and X-ray diffraction (XRD). In addition, the formation mechanism of oxides in the coatings was also discussed.

2. Experimental Procedure

TA2 pure titanium (0.30% Fe, 0.15% Si, 0.10% C, 0.05% N, 0.015% H, 0.20% O) plates in size of 25 mm×25 mm×1 mm were used as the substrate materials. Oxidation was carried out using a home-made 30 kW AC microarc oxidation system. As shown in Fig. 1, the device is mainly composed of a potential adjustable AC power source up to 1 000 V, a 80 L stainless steel container, a stirring and cooling system. The optimal electrolyte is a 10 g/l NaAlO2 solution prepared with analytical grade NaAlO2 and distilled water. The oxidation time is 3 h. The current density is
about 20 A/dm². The anode potential is in a range of 400 to 550 V, which is much higher than conventional anodizing voltage on metals. Under such high voltage, the dielectric breakdown of oxide film on titanium will take place and lead to spark or microarc discharge. However, electrolytic discharge phenomenon for titanium is similar to for aluminum. During the oxidation, the solution was stirred and cooled to prevent heating over 45°C. After the MAO treatment, the coated specimens were cleaned in running water and dried in warm air.

Some as-coated plates were sectioned and metallographic specimens were prepared. Microstructure and composition in a cross-sectional specimen were analyzed by SEM (OPTON CSM 950 with EDS attachment). The distributions of titanium, aluminum and oxygen elements across the coatings were determined using point and line analyses of EDS.

On the other hand, the outer layer of the coatings was ground with SiC paper, and then a dense layer was left. Phase components of the polished and unpolished specimens were determined using a DMAX-3A diffractometer and a Nicolet NEXUS 670 Infrared-Raman spectroscope.

3. Experimental Results

3.1. Microstructure and Composition of the MAO Coatings on Pure Titanium

Figure 2(a) reveals the surface morphology of microarc oxidation coatings on pure titanium, which is similar to MAO coatings on aluminum. It is found that the coating surface contains many grains with various sizes. Microarc discharge over many times at the same position of specimen would result in one large grain due to the deposition of erupted melt from the discharge channel. One crater-like pore of several microns is remained at the center of grain as shown in Fig. 2(b). Specifically, the trace of rapid solidification of oxide melt can be clearly observed on this large grain surface around the center of the discharge pore. It can be predicted that the instantaneous temperature in the microarc discharge zone reaches several thousand degrees Centigrade and the coating is locally molten. Furthermore, several small cracks can also be observed on the coating surface. They result from the thermal stress in the process of rapid solidification of erupted melt.

Figure 3 indicates the microstructure and composition of a cross-section of the MAO coating deposited on TA2 pure titanium in aluminate solution. The average thickness of the coating is about 30 μm, which is almost consistent with the result determined nondestructively by eddy current thickness. Generally, the coating is dense though there are also some micropores without contact each other. The coating/titanium interface is irregular, which is helpful for improving the adhesive strength of coating. As shown in Fig. 3(a), Ti element EDS scanning line across the coating and substrate has two steps. That suggests the oxide coating actually contains two layers, an outer layer and an inner layer. The titanium concentration in the outer layer is lower than in the inner layer; on the contrary, the oxygen concentration in the outer layer is higher. On the other hand, the coating morphology also illustrates a double-layer structure of the coating. The inner layer is about 15 μm thick; but the coating surface is rather rough and the thickness of the outer layer changes in a range of 10–25 μm.

Analogous to Ti element analysis, Al element EDS scanning line (see Fig. 3(b)) clearly displays the so-called double-layer structure in the MAO coating. The Al concentration in the outer layer is much higher than in the inner layer. All of these aluminum atoms come from the electrolytic solution. It demonstrates that AlO₂⁻ ions in the solution have intensely involved in the physical and chemical reactions taking place in the microarc discharge zone and has incorporated into the whole coating. However, these ions in solution are much easier to enrich in the outer layer.

EDS point analyses show the outer layer of the coating possesses a high aluminum content (Fig. 3(c)); on the contrary, Ti content in the inner layer (Fig. 3(d)) is higher than in the outer layer. That is in agreement with Ti and Al elements line analyses above. High Al content and Al gradient distribution in the coating suggest that the composition and phase component of the coating on titanium and its alloys can be modified by changing the electrolytic constituent...
Figure 4 indicates the coating/titanium interface of the specimen. Because a SEM backscattered electron image can reflect the average value of atomic number at the test point on the specimen, the higher the average value the brighter the image at this point will be. As shown in Fig. 4, the contrast at two sides of the coating/substrate interface is rather high, and the interface is very clear; no obvious transition layer between the oxide coating and titanium substrate can be observed. The microarc discharge hardly influences on the microstructure of unoxidized substrate, and no thermal effect zone in the titanium substrate near the interface is observed. During the oxidation, the temperature in the substrate must be much lower than the titanium melting point of 1943 K.

Ti element scanning line across the coating/titanium interface (see Fig. 4(a)) has one step where the Ti concentration dropped rapidly. This scanning line in the Ti substrate or coating is almost flat. On the other hand, Al element scanning line (see Fig. 4(b)) indicates that Al atoms from the solution have incorporated into the interior of the oxide coating and arrived at the interface. However, it is specially interesting that the Al atoms have not diffused into the rest titanium substrate.

Ti–O binary phase diagram\(^{16}\) shows that oxygen has a large solubility (over 30 at%) in low-temperature titanium.
So titanium is easy to absorb oxygen atoms. Nevertheless, if titanium absorbs a large quantity of oxygen atoms, its mechanical performance such as tensile strength would be lowered. Fortunately, Fig. 4(a) displays that oxygen atoms, as well as aluminum atoms, have not diffused into the unoxidized titanium substrate even near the interface. That is much favorable to maintain the mechanical performance of the pure titanium substrate. Hence, after the TA2 pure titanium is subjected to the microarc oxidation treatment, its surface properties such as hardness, wear resistance and corrosion resistance may be significantly improved; meanwhile, the mechanical performance of the substrate can be maintained as possible. That shows one unique feature of microarc oxidation technique.

3.2. XRD and Raman Analyses for the MAO Coatings on TA2 Pure Titanium

XRD patterns for the MAO coatings are given in Fig. 5. The outer layer consists of a large amount of TiAl₂O₅ phase and a little rutile type TiO₂. Nevertheless, TiAl₂O₅ content of only bands at 438 and 612 cm⁻¹ in the outer layer of the coating is in good agreement with Al and Ti composition profiles as shown in Fig. 2. In addition, the presence of the TiAl₂O₅ and TiO₂ rutile compounds with higher melting points suggests the temperature in microarc discharge channel is certainly very high.

Titanium has several oxides, e.g. Ti₂O, Ti₃O₅, TiO₂, TiO₂. Under different experimental conditions, anodic oxidation film on titanium may contain one or several titanium oxides though it is very thin. However, in this work, only titanium dioxide phase in the microarc oxidation coatings on titanium is found.

In nature, TiO₂ has two crystallographic forms: anatase and rutile. Rutile with tetragonal lattice structure, is a stable phase at all temperatures and pressures. However, anatase is a metastable phase, and it may be transformed into rutile by heating. Raman frequencies of TiO₂ rutile phase have 142, 244, 440, 610, 825 cm⁻¹, among which the bands at 440 and 610 cm⁻¹ are usually much strong. As for anatase phase, its frequencies have 143, 394, 512, 630 cm⁻¹. Although the band at 142 cm⁻¹ may be present in the Raman spectra of both anatase and rutile phases, it is weak in rutile and very intense in anatase. Therefore, as well as XRD patterns, Raman spectra can clearly verify rutile and anatase. Figure 6 depicts the Raman spectra of the microarc oxidation coating on pure titanium. The presence of only bands at 438 and 612 cm⁻¹ in figure confirms this coating contains rutile rather than anatase. In addition, the Raman signals at 438 and 612 cm⁻¹ in the outer layer of the coating are very weak (see Fig. 6(a)), but the two corresponding bands are very strong in the inner layer (see Fig. 6(b)). That suggests that the rutile fraction is rather high in the inner layer, but very low in the outer layer of the coating. These results are in accordance with XRD analyses above.

4. Discussion

In the initial stage of oxidation, the voltage between the titanium specimen and stainless steel electrode increases gradually, and a thin anodic film on titanium is formed in aqueous solution. That is actually an anodizing stage. When the voltage is over a critical value of about 100 V, the dielectric breakdown in the oxide film takes place, and then spark or microarc discharges appear on the surface of titanium anode. If this higher voltage is held, many visible sparks or microarcs cover the whole surface and move rapidly. Klapkiv suggests that the instantaneous temperature in these discharge channels can be over 7,000 K, where the plasma atmosphere is generated. Under such a high temperature, the oxide coating on TA2 pure titanium may by locally and temporarily molten, as shown in Fig. 2. When the spark or microarc quenches, the Ti–Al–O melt in the microplasma discharge zone rapidly solidifies due to the aqueous solution cooling. Thus both the coating thickness and insulation property are enhanced in these previous discharge spots. Then the micorarcs move to other spots because the dielectric breakdown always occurs at a relative thin part of the coating. With increase of oxidation time, the coating thickness increases and the breakdown becomes
more and more difficult, so the quantity of sparks or microarcs decreases gradually. While the coating grows to a certain thickness, it will not be broken down. In this stage, microarcs disappear completely and the oxidation ends.

The melt in the discharge channel solidifies rapidly to form TiO$_2$ and TiAl$_2$O$_5$ crystal phases. However, the high cooling rate also suppresses the eutectoidal reaction of TiAl$_2$O$_5$→TiO$_2$+Al$_2$O$_3$ occurred in 1280°C. $^{16}$ thus TiAl$_2$O$_5$ phase will be not decomposed into TiO$_2$ and Al$_2$O$_3$. So the diffraction peaks of alumina are not observed in Fig. 5. On the other hand, the critical cooling rate of sparking or microarc, its diameter is small in a range of 0.1–10μm; additionally, the tube-like discharge channel has extended to the coating/metal interface from the coating surface. The lifetime of each microarc is less than 1 ms, so the melting-solidification process occurred in the channel is very short. When the microarc quenches, the oxide melt in the discharge channel has a very high cooling rate at the surface layer of coating. In the meantime, its cooling rate near the coating/titanium substrate interface is also much higher than the interior of the coating due to titanium substrate cooling. Hence, the instantaneous high temperature and high pressure in the microarc zone would hardly have influence on the microstructure of titanium substrate. Meanwhile, the aluminum and oxygen atoms from the solution could not diffuse into the unoxidized titanium substrate, even near the coating/substrate interface. Of course, that facilitates remaining the mechanical properties of TA2 pure titanium substrate after the MAO treatment.

5. conclusions

From the experimental results mentioned above, some conclusions are drawn as follows:

(1) A ceramic oxide coating of 30μm is deposited on TA2 pure titanium by alternating-current microarc oxidation in aluminate solution. The Al and Ti composition profiles show that the coating contains an outer layer and an inner layer. The outer layer is composed of a large amount of TiAl$_2$O$_5$ and a little rutile type TiO$_2$ phases. But in the inner layer, TiAl$_2$O$_5$ and rutile contents are rather high. In addition, the TiAl$_2$O$_5$ content in the inner layer is much lower than in the outer layer, while the rutile content obviously increases in the inner layer. However, a metastable anatase type TiO$_2$ and other titanium oxides except TiO$_2$ could not be found in this coating.

(2) In the process of microarc oxidation, electrolyte ions in solution have involved in physical and chemical reactions occurred in the discharge channels. The Al atoms from solution have incorporated into the whole coating, even reached to the coating/titanium interface. From the coating surface to the interface, aluminum concentration gradually decreases while titanium concentration oppositely changes. However, oxygen and aluminum atoms from solution have not diffused into the unoxidized titanium substrate, even near the coating/titanium substrate.

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REFERENCES

1) H. Dong, A. Bloyce and T. Bell: Surf. Eng., 14 (1998), No. 6, 505