

# The Effect of Treating Frequency on Characteristics of Pure Titanium MAO Coating

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**Abstract:** Using a multifunctional pulse power supply, porous titania coatings were prepared on pure titanium substrates in a  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SiO}_3$  electrolytic solution by microarc oxidation (MAO) under constant voltage. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed to characterize the coating phase composition and microstructure, respectively. The effects of the treating frequency (500-8000Hz) on the coating thickness, phase composition and surface morphology were studied. The experimental results show: (1) the coating consists of dominant rutile and anatase phases, which are invariable with the treating frequency, and a little  $\text{Ti}_6\text{O}_{11}$  phase; and (2) the coating thickness, surface morphology, and  $\text{Ti}_6\text{O}_{11}$  phase depend strongly on the treating frequency. With the increasing of treating frequency, the coating thickness decreases swiftly,  $\text{Ti}_6\text{O}_{11}$  phase disappears gradually, and the size of micropores existing on the coating surface decreases by degrees, while the pore number increases little by little.

**Keywords:** Titanium coating; Microarc oxidation; Treatment frequency; Phase composition; Surface morphology

## 1. Introduction

Due to the excellent combination of properties: high strength to weight ratio, high melting point, high corrosion resistance and good biocompatibility, titanium and its alloys can be used in many fields. However, the poor wear resistance without protective coatings on the surface seriously limits their extensive applications, especially as moving components or mechanical conjunctions. The microarc oxidation (MAO) is gaining increased attention as a relatively novel technique for fabricating the coatings on titanium and its alloys surfaces. By means of the technique, the coatings with high microhardness, high adhesion, wear resistance, and corrosive resistance, can be synthesized [1-3].

MAO is a multifactor-controlled process. The MAO coating quality can be controlled by technical parameters, such as the composition and temperature of electrolyte, alloy composition, treating voltage or current density, and treatment time, etc [4-7]. High quality coatings can be formed by suitable selection of deposition parameters. Although significant progress has been made on the preparation of MAO coatings in the past decades, there is little research on the effect of the treating frequency on characteristics of the MAO coating. Here we present our investigation results of the treatment frequency effects on the growth features of MAO coatings at the constant pulse voltage and duty cycle.

## 2. Experimental details

The pure titanium, with the nominal composition (wt %) (0.3Fe, 0.5Si, Ti balanced), was used as substrate in pre-

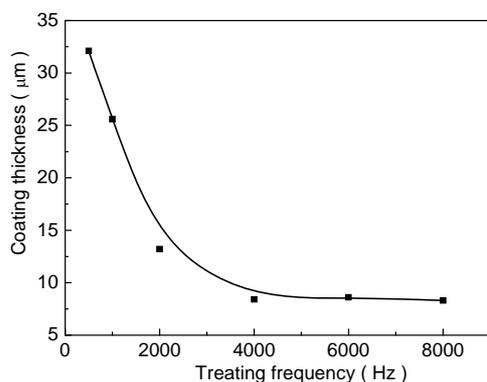
sent study. The rectangular samples, with the dimensions of  $10 \times 10 \text{ mm}^2$  and the thickness of 1 mm, were fabricated. The surface of samples was ground with 1000# abrasive papers and cleaned with acetone, ethanol and distilled water prior to MAO treatment. As an anode, the samples were dipped into the aqueous electrolyte, which consists mainly of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ . The electrolyte cell of stainless steel was used as a cathode. The coatings were accomplished with a homemade microarc oxidation system. The unit consists of a unipolar pulse power supply, an electrolyte cell, a stirring system, and a cooling system. The pulse parameters (i.e. frequency, duty cycle, the voltage and current amplitudes etc.) of the power supply can be adjusted independently.

MAO process was carried out under the following conditions: 1) the treating frequency was in the range of 500-8000Hz; 2) the pulse voltage and duty cycle were 400 V and 10%, respectively; 3) depositing time was 10 min; 4) the electrolyte cell bath was water-cooled, and its temperature was maintained below  $25^\circ\text{C}$ . The treated samples were washed with distilled water, and dried at room temperature for microstructure and phase composition testing. The coating thickness was measured by an optical microscopy with a CCD camera. The coating surface morphology was observed by scanning electron microscopy (SEM; SSX-550, SHIMADZU, Japan). The phase compositions of the coatings were analyzed by X-ray diffraction (XRD; D8 DISCOVER, Bruker, Germany) using  $\text{Cu K}\alpha$  radiation at a scanning speed of  $5^\circ/\text{min}$ .

## 3. Results and Discussions

### 3.1 Coating thickness

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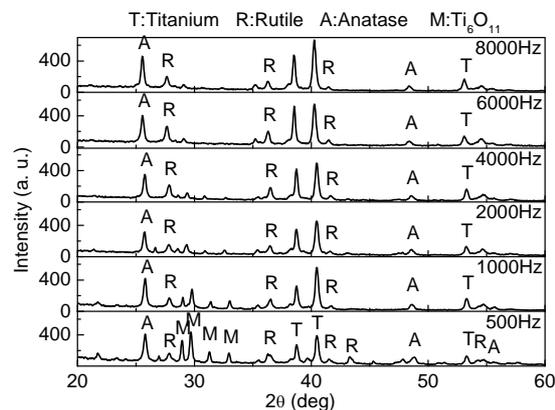
**Figure 1. Influence of treating frequency on coating thickness**

Fig.1 illustrates the influence of MAO treating frequency on the coating thickness. From Fig.1 we can see that the coating thickness decreases swiftly against the increasing treating frequency in the range of 500 Hz - 2000 Hz. While the frequency is between 2000 and 4000Hz, the coating thickness decreases slowly as the frequency increases; whereafter, it keeps almost invariable with the increasing treatment frequency (4000-8000Hz).

Microarc oxidation is an anodizing accompanied by sparking microdischarge due to dielectric breakdown, which is also regarded as the intrinsic feature differing from conventional anodizing. The applied voltage exceeding the critical value for dielectric breakdown is the prerequisite for microarc oxidation to be able to proceed in consideration of electrical aspect, while the unipolar pulse energy during MAO process of the constant treatment time and duty cycle decreases with the increasing treatment frequency and the pulse energy define the coating growth rate. Therefore, the coating thickness decreases gradually with the increasing treatment frequency. At the lower frequency (500-2000Hz), the pulse energy changes swiftly with the frequency variation; while it changes smoothly and slowly at the higher frequency (4000-8000Hz). Therefore, the result in Fig.1 is obtained.

### 3.2 Phase composition

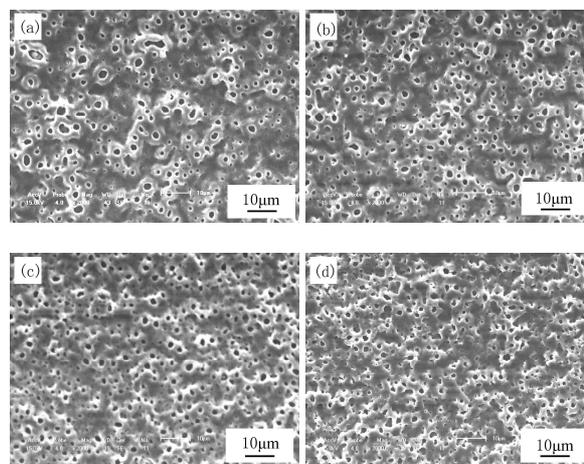
Fig.2 illustrates the effect of the treating frequency on XRD patterns of the coatings. This figure shows that these coatings consist of dominant anatase and rutile phases, and a small amount of  $Ti_6O_{11}$ . No other phase was detected except Ti substrate. With the increasing of the treating frequency, the content of anatase and rutile phase keeps invariable, and  $Ti_6O_{11}$  phase disappears gradually. It shows that the frequency influence on the content of rutile and anatase phase in coatings is unobvious.

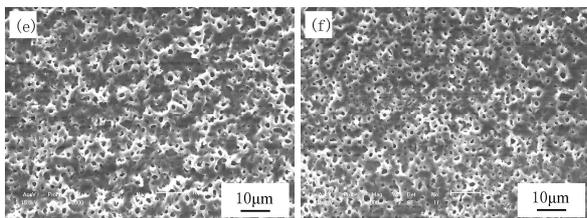


**Figure 2. XRD patterns of the MAO coating fabricated at different treatment frequencies**

The  $Ti_6O_{11}$  ( $TiO_{1.83}$ ) phase is one of the  $TiO_{2-x}$  Magneli phase, which can be considered as  $TiO_2$  phase with oxygen deficiency [8]. As some researchers described [9-11], while the voltage goes up and over a critical value, the dielectric breakdown takes place in the insulating oxide coating on the surface of titanium anode, and spark or microarc discharges appear. Many visible sparks or microarcs move rapidly on the titanium alloy surface in the aqueous solution. The plasma atmosphere is formed in those small discharge zones (channels) where the instantaneous temperature and pressure can reach  $10^3$ - $10^4$  K and  $10^2$ - $10^3$  MPa, respectively [3]. Thus,  $Ti^{4+}$  ions from the substrate and  $O^{2-}$  ions from the aqueous solution would rapidly combine to form  $TiO_2$  compound in the discharge channels [12]. From Fig.1 we can see that the coating thickness fabricated at lower frequency is thicker than those obtained at higher frequency. Therefore, it is speculated that  $TiO_2$  phase with oxygen deficiency is most likely formed in the coatings fabricated at lower frequency because the shift inboard rate of  $O^{2-}$  ions possibly slows down in the thicker coatings. However, further investigation is required to confirm this hypothesis.

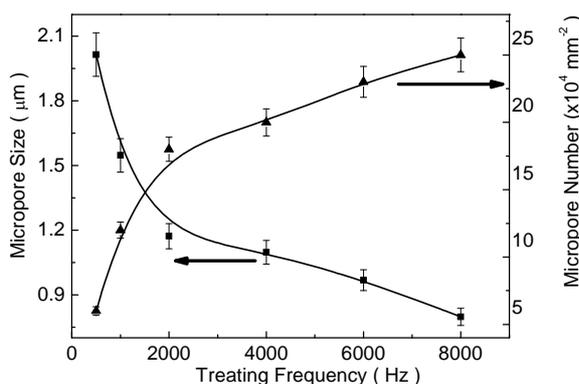
### 3.3 Surface morphology





**Figure 3. The surface morphology of MAO coatings at 1000× magnification processed for (a) 500; (b) 1000; (c) 2000; (d) 4000; (e) 6000; and (f) 8000 Hz.**

Fig.3 illustrates the surface features of the coated samples that were MAO treated for different pulse frequencies at a magnification of 1000×. The micrographs clearly indicate the presence of discharge channels appearing as dark elliptical or circular spots distributed all over the surface of the coatings. The micropore size of the sample surface fabricated at 500 Hz, in which channels disperse irregularly and asymmetrically, are more than 1.5 µm. It is also apparent: 1) the number of such channels is gradually increasing with the increasing treatment frequency; 2) the shape of micropore (or the channel) changes by degrees from elliptical to circular as the treating frequency increases; and 3) the surface roughness reduces little by little with the increasing treatment frequency.



**Figure 4. Influence of the treating frequency on the micropore size and number**

For measuring the size of the discharge channels, the micrographs obtained at 2000× magnification were utilized. In particular, the size of ten largest channels was measured after magnifying the areas of the selected channels individually. The average value of ten such channel sizes for each sample corresponding to a particular treatment frequency was calculated and this average value represents the channel size of the sample. The number of discharge channels was measured by analyzing the SEM micrographs obtained at 1000× magnification using Adobe Photo Deluxe software. Each channel was then marked and the total number of channels was

counted using the software. The density of the discharge channels i.e. the average number of channels per square millimeter area was then calculated. Variations in size and number of micropores are presented in Fig.4. It can be clearly seen that: 1) when the treating frequency is less than 2000Hz, the micropore number increases rapidly, and the micropore size decreases clearly with the treating frequency increase; and 2) when the treating frequency is over 2000 Hz, the pore number increases slightly, and the pore size decreases mildly. This regular corresponds to the phenomenon of microarc discharges during the MAO process.

Because the duration and intensity of the sparking discharge depend on the pulse width and energy, respectively, a change in the pulse cycle can regulate the surface discharge characteristics, which are responsible for the growth, microstructure and phase composition of the coatings [12]. The pulse energy  $E_p$  is defined as:

$$E_p = \int_0^t U_p I_p dt \quad (1)$$

Where  $U_p$  is the pulse voltage,  $I_p$  is the pulse current and  $t_p$  is the pulse width. In this case, a constant voltage (400 V) is applied, which implies that the energy of a single pulse depends on the pulse width. Because the pulse width at a constant duty cycle decreases with the increasing treatment frequency, the increasing of the treatment frequency leads to the decreasing of pulse energy and the weakening of microdischarge. As a result of the decreasing sparking discharge duration and discharge intensity, the accumulated production mass of oxide induces a gradually decreasing pore size, which was caused by decreasing pulse width. Therefore, at a frequency over 2000Hz, fine pores are obtained, and the distribution of the pores becomes more homogeneous. However, below a frequency of 2000Hz, the long-term discharge duration and the very strong discharge intensity cause the coating production to splash out into the electrolyte, which leads to a decreasing growth rate of the coating (Fig.1). Moreover, the quality of the coatings becomes coarser when bigger pores and protuberances are formed as shown in Fig.3 (a).

#### 4. Conclusions

Based on the experiments mentioned above, it is clear that the treatment frequency ( $f$ ) has an intense effect on the MAO coating thickness, phase composition, and surface morphology. The coating thickness decreases swiftly against the increasing  $f$  ( $500 \text{ Hz} \leq f \leq 2000 \text{ Hz}$ ), and when  $2000 \text{ Hz} \leq f \leq 4000 \text{ Hz}$ , the thickness decreases slowly with the increase of  $f$ , whereafter it keeps almost invariable with the increasing  $f$ . The coating consists of dominant rutile and anatase phases, a small amount of  $\text{Ti}_6\text{O}_{11}$  phase. With the increasing  $f$  in  $500 \text{ Hz} \leq f \leq 8000 \text{ Hz}$ ,  $\text{Ti}_6\text{O}_{11}$  phase disappears gradually, while the content of rutile and anatase phases keeps al-

most invariable. The coating surface has a large number of micropores (discharge channels), and the pore size decreases gradually, while the number of micropores increases by degrees with the increasing  $f$ .

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