Effects of Different Electrolytes on Microstructure and Antibacterial Properties of Microarc Oxidized Coatings of CP-Ti

L. C. Tsao

Abstract—Titania-based coatings on commercially pure titanium (CP-Ti) were formed by micro-arc oxidation in different electrolyte solutions containing anions such as phosphate (PO₄³⁻) and silicate (SiO₄³⁻). The surface topography, phases, and elemental compositions of the P-TiO₂ and Si-TiO₂ coatings were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDS), and X-ray diffraction (XRD), respectively. Staphylococcus aureus (S. aureus) was used to evaluate the antibacterial properties of the MAO coatings. The experimental results demonstrate that the P-TiO₂ coated sample had amorphous phase, main anatase-TiO₂, and a small amount of P₂O₅. However, the Si-TiO₂ coated samples were composed of SiO₂, anatase-TiO₂, and amorphous phase. After 24 h of incubation, the antibacterial activities against S. aureus were 96.4% for the P-TiO₂ coated sample and 98.6% for the Si-TiO₂ coated sample.

Index Terms—Commercially pure titanium, micro arc oxidation, corrosion, antibacterial property.

I. INTRODUCTION

Ti and Ti-based alloys are extensively used in many applications, from aerospace to the biomedical sciences. They have excellent properties, such as high specific strength, good formability, corrosion resistance, non-toxicity, and excellent biocompatibility [1], [2]. New titanium alloys for biomaterials such as Ti-Nb [3], Ti-Cu [4], Ti-Cu-Sn [5] have been developed.

The good biocompatibility and corrosion resistance of these materials are attributed to a thin oxide layer (TiO₂ in case of titanium) that forms naturally on the surface of titanium. Typically, the thin oxide layers that form on these metals have an amorphous structure, film thickness of about 3-10 nm, and stoichiometric problems [6]. It is known that the stability of the oxide depends strongly on the composition structure and thickness of the film [7]. Therefore, they are usually used with protective coatings [8].

Various surface modification technologies have been studied for use with Ti and its alloys, examples being anodizing [9], physical vapor deposition (PVD) [10], plasma and laser nitriding [11], and ion implantation surface treatment [12]. In recent years, micro-arc oxidation (MAO) has proven to be a promising surface coating technology for forming thick oxide coatings on aluminum (Al), titanium (Ti), and magnesium (Mg) components [13], [14] and [15]. These thick oxide coatings have a hard ceramic property, good wear resistance, high corrosion resistance, and especially good adhesion between metal and coating in comparison with the conventional anodizing. Chang et al. [16] reported that microstructure characterization of the oxidized TiO₂ layer can be greatly affected by the discharge voltage on CP-Ti alloy during MAO treatment. Generally, current density is one of the most important parameters affecting the microstructure and properties of the MAO coating. However, little research has focused on the effects of different electrolytes on oxide coatings on CP-Ti alloys.

In the present study, the effects of different electrolyte systems on the formation of micro arc oxidation ceramic coatings of CP-Ti alloy were analyzed. The morphology, microstructure, phase constituents, corrosion resistance, and antibacterial activity of the MAO coatings were analyzed. The corrosion behavior was also evaluated by potentiodynamic polarization in 3.5 wt.% NaCl solution.

II. MATERIALS AND METHODS

A. Preparation of Samples

The nominal composition of commercially pure titanium (CP-Ti) is shown in Table I. The specimens were cut into squares 20.0 × 20.0 × 1.0 mm, which were polished with different grades of emery papers up to 800 grits and then degreased in pure ethanol alcohol under ultrasonic conditions. The micro-arc oxidation treatment device, illustrated in Fig. 1a [17], consisted of a DC power supply unit, a 316 stainless steel container that also served as the counter electrode and a stirring and cooling system; the samples served as the anode.

| TABLE I: CHEMICAL COMPOSITION OF CP-Ti (WT.%). |
|-------|-------|-------|-------|-------|-------|
| Fe    | N     | H     | O     | Si    | Ti    |
| 0.08  | 0.02  | 0.012 | 0.10  | <0.04 | Bal.  |

The constant current density, applied DC voltage, and duration time were fixed at 33A/dm², 350V and 30 min, respectively. The electrolyte temperature was maintained within 20 ± 2 ºC. To investigate the influence of electrolyte in the MAO process, the experiment was performed in two
different solutions. For P-TiO₂ coating samples, the CP-Ti plates were treated by MAO in 10 g/L H₂PO₄ solution. The Si-TiO₂ coating samples were treated by MAO in 10 g/L NaH₂PO₄ and 20 g/L Na₂SiO₃ solution. After the MAO processes, samples were cleaned with distilled water and then dried in hot air.

![Image](image_url)

Fig. 1. Device for MAO treatment [17].

B. Microstructure Analysis

The surface morphology and composition of the treated samples were observed by scanning electron microscopy (SEM) (SEM, Hitachi S-4700, Japan) and energy-dispersive X-ray spectroscopy (EDS, XFlash detector 4010, Bruker, Germany). The crystal phase of the MAO coating sample was analyzed by X-ray diffractometry (XRD, Dmax III-A type, Rigaku Co., Japan) using Cu Kα radiation (λ= 1.5406 Å), a tube voltage of 40 kV, a current of 40 mA, and the 2θ range of 20-80º.

C. Corrosion Behavior

Corrosion behavior of the coatings in electrochemical polarization experiments was initiated using a typical three-electrode cell, no stirring, and degassing of the solution at room temperature by an EG & G M273A potentiostat. The reference potential was a saturated calomel electrode (SCE) at a noble direction to an anodic 2 V at a scanning rate of 1 mV/s.

D. Antibacterial Activity Tests

The photocatalytic activities of P-TiO₂ and Si-TiO₂ matrices were evaluated against S. aureus under visible light at room temperature (25 ± 2°C) by % viability (% survival) of bacteria. The MAO coating samples were sterilized by autoclave at 120°C for 30 min. The antimicrobial effect was evaluated with the Japanese Industrial Standard (JIS) Z2801:2000 method. This standard is commonly used to estimate the antimicrobial abilities of antimicrobial products [18], [19]. The MAO sample sizes were 5.0 × 5.0 cm. After culture medium containing bacteria (about 0.4 ml) was dripped onto the MAO samples, the samples were covered with film (4.0 × 4.0 cm).

The cell culture medium was a nutrient broth with distilled water diluted 500-fold. The nutrient broth was prepared by diluting beef extract (3.0 g), peptone (10.0 g), and sodium chloride (5.0 g) in purified water (1000 g), with the pH adjusted to 7.0 ± 0.2 using sodium hydroxide or hydrochloric acid.

The bacterial solution with a concentration of 1.8 × 10⁵ CFUs/mL was dripped onto the surface of MAO samples at a density of 0.05 mL/cm². After the bacteria were cultured for 24 h at 35± 1°C, the bacteria CFUs were counted in the whole culture. The antibacterial activity was calculated using the following formula [20]:

$$R = \frac{(N_{control} - N_{sample})}{N_{control}} \times 100\%$$  

where $N_{control}$ is the average number of the bacterial colony on the control sample at 24 h, and $N_{sample}$ is the average number of the bacterial colony on the MAO sample at 24 h.

| Samples       | Composition (wt.%) | Phase identification |
|---------------|--------------------|----------------------|
| P-TiO₂        | Ti 18.96 O 75.27 P 5.78 | TiO₂ + P₂O₅          |
| Si-TiO₂       | Ti 8.76 O 76.69 P 1.41 Si 13.13 | TiO₂ + SiO₂         |

III. RESULTS AND DISCUSSION

A. Microstructures

Fig. 2 shows the surface morphologies of the coatings prepared in different electrolytes. It can be clearly observed that the coatings exhibited quite different surface morphologies in the different electrolytes. The surfaces of the P-TiO₂ coating samples displayed rough topographies, and the surfaces contained numerous micropores or crater structures, separately and homogeneously distributed over the coatings (Fig. 2a). In our previous study [21], the same phenomenon was also observed. However, the surfaces of the Si-TiO₂ coating samples displayed smooth topographies and few micropores. The density of the micropores on the P-TiO₂ coating sample was higher than that on the Si-TiO₂ coating sample. The cross section and thickness of the coatings prepared in different electrolytes are shown in Figs. 3 and 4, respectively. The thicknesses were approximately 3.25 ± 0.61 μm for the Si-TiO₂ coating sample, respectively. Jiang et al. reported that the adsorption degree of ceramic coatings is in the order of SiO₂⁺ > PO₄³⁻ > VO₄³⁻ > MoO₄²⁻ > B₂O₅³⁻ > CrO₄²⁻ [22].

Fig. 5 summarizes the elemental compositions of the P-TiO₂ coating and Si-TiO₂ coating samples determined on their surfaces by energy dispersive spectroscopy (EDS). The results are summarized in Table 2. Only Ti (18.96 wt.%), O (75.27 wt.%) and P (5.78 wt.%) were detected in the P-TiO₂ coating samples. These results suggest that the coating film contained TiO₂ and P₂O₅ phase [21]. In previous work, the TiO₂ films were formed on CP-Ti by MAO process by the following steps [23], [24]:
Ti/Ti: Ti ↔ Ti$^{2+}$ + 2e$^-$  

$2\text{H}_2\text{O} ↔ 2\text{O}^{2-} + 4\text{H}^+$  

$2\text{H}_2\text{O} → \text{O}_2 \text{(gas)} + 4\text{H}^+ + 4\text{e}^-$  

Ti$^{2+}$ + 2O$^{2-} → \text{TiO}_2 + 2\text{e}^-$  

Thus, TiO$_2$ is major phase in the MAO coating process. Furthermore, it has been reported that both P$_2$O$_5$ and titanium pyrophosphate (TiP$_2$O$_7$) have been deposited on a sample surface [21]. In Si-TiO$_2$ coating samples, the elemental composition was Ti (8.76 wt.%), O (75.27 wt.%), Si (13.13 wt.%) and traces of P (1.41 wt.%). This composition suggests that the Si-TiO$_2$ coating samples had TiO$_2$ and SiO$_2$ phases.

B. Corrosion Behavior

The potentiodynamic polarization curves of CP-Ti coated samples are shown in Fig. 7. The corrosion current density...
(\(I_{\text{corr}}\)), corrosion potential (\(E_{\text{corr}}\)), critical current density (\(I_{\text{crit}}\)) and polarization resistance (\(R_p\)), obtained by fitting the polarization curves, are listed in Table III. Polarization resistance (\(R_p\)) has been used for the kinetics of electrode reactions that can be calculated from the equilibrium potential [26]. It corresponds to the endurable degree of corrosion process [27]. \(R_p\) is defined as [28]:

\[
R_p = \frac{dE}{dl} \left|_{E_{\text{corr}}-0} \right.
\]

(5)

According to the Stern–Geary equation [29], the analysis of the \(R_p\) of MAO coating samples was based on the \(E_{\text{corr}}\), \(I_{\text{corr}}\) and the anodic/cathodic Tafel slopes (\(\beta_a\) and \(\beta_c\)), which were obtained from the measured polarization curves. The corrosion resistance (\(R_p\)) value was determined from the relationship [26], [29]:

\[
R_p = \left( \frac{1}{2.303I_{\text{corr}}} \right) \left( \frac{\beta_c}{\beta_a + \beta_c} \right)
\]

(6)

For P-TiO\(_2\) coating samples, \(E_{\text{corr}} = -170.8\) mV\(\text{SCE}\), \(I_{\text{corr}} = 1.75\) \(\mu\text{A/cm}^2\), \(I_{\text{crit}} = 6.09\) \(\mu\text{A/cm}^2\) were measured. However, the Si-TiO\(_2\) coating samples exhibited an obvious shift in \(E_{\text{corr}}\) toward the noble direction (-140.7 mV\(\text{SCE}\)). and a significant one-order decrease in both \(I_{\text{corr}}\) (0.37\(\mu\text{A/cm}^2\)) and \(I_{\text{crit}}\) (6.09\(\mu\text{A/cm}^2\)). These data corroborated their \(R_p\) values. The corrosion resistance of Si-TiO\(_2\) coating samples was higher than that of P-TiO\(_2\) coating samples. The MAO coating developed in the electrolyte solution containing NaSiO\(_3\) had the highest corrosion resistance of SiO\(_2\) phase as compared to the P\(_2\)O\(_5\) phase in the P-TiO\(_2\) coating samples. In addition, the corrosion behavior of MAO coated samples had better corrosion resistance than CP-Ti alloy untreated substrate (Table III). Hence, it is clear that the corrosion resistance of CP-Ti was significantly enhanced by the MAO coating process.

**TABLE III: THE RESULTS OF POTENTIAL-DYNAMIC CORROSION TESTS IN A 3.5 WT. % NACl SOLUTIONS**

| Samples | \(E_{\text{corr}}\)(mV\(\text{SCE}\)) | \(I_{\text{corr}}\)(\(\mu\text{A/cm}^2\)) | \(I_{\text{crit}}\)(\(\mu\text{A/cm}^2\)) | \(\beta_a\)(mV/decade) | \(\beta_c\)(mV/decade) | \(R_p\)(Ohms/cm\(^2\)) |
|---------|---------------------------------|------------------|------------------|----------------|----------------|----------------|
| P-TiO\(_2\) | -170.8 | 1.75 | 6.09 | 1019.2 | -833.1 | 1132.1 |
| Si-TiO\(_2\) | -140.7 | 0.37 | 0.48 | 1031.1 | -718 | 2774.9 |

**TABLE IV: COLONY NUMBERS AND THE ANTIBACTERIAL ACTIVITY FOR DIFFERENT SAMPLES AGAINST S. AUREUS BACTERIA.**

| Sample | Negative sample(CFU/ml ) | No. of bacteria on the coated samples after 24 h ( CFU/ml ) | Antibacterial activity(%) |
|--------|--------------------------|-----------------------------------------------------------|--------------------------|
| P-TiO\(_2\) | 1.8x10 | 6.4x10 | 96.4 |
| Si-TiO\(_2\) | 1.8x10 | 2.5x10 | 98.6 |

### C. Antibacterial Property

Before the antibacterial behavior of MAO coating samples was examined, a bacterial growth curve for *S. aureus* was developed. Fig. 8 shows the photos of colony forming units of viable *S. aureus* after contact with the MOA samples. When exposed to *S. aureus*, MAO coating samples showed good antibacterial properties, with a kill rate of 96.4 %. Compared to the P-TiO\(_2\) coating samples (96.4 %), Si-TiO\(_2\) coating samples (98.6 %) exhibited a stronger antibacterial action due to the higher concentration of Si in the MAO coated surfaces (Table IV). There are many factors that may reduce bacterial counts on MAO coated samples, such as the morphology, the surface free energy, and the material modified (Ag, Cu, SiO\(_2\)). The coating surface is critical to its antibacterial effects. Both Ag and Cu are widely known to be antibacterial agents [30], [31]. Zhang et al. reported that a Ag-modified TiO\(_2\) coating showed excellent antibacterial activity against *Escherichia coli* (*E. coli*) within 24 h and that the antibacterial rate gradually rose with increasing contact time [30]. Zhu et al. reported that Cu-incorporated TiO\(_2\) coatings were highly effective at inhibiting the adhesion of *S. aureus* and exhibited excellent biological activity in promoting osteoblastic adhesion, early
proliferation, and late differentiation [31]. Furthermore, silica nanoparticles have high thermal and chemical stability, high surface area, and good biocompatibility, making them a good option for delivering drugs such as antibiotics [32], [33] and [34]. It is demonstrated that MAO layers incorporating Si can enhance antimicrobial properties.

IV. CONCLUSIONS

In summary, the MAO technique has successfully been used in this study to grow TiO$_2$ on CP-Ti alloy in different electrolytes. After the MAO process, the P-TiO$_2$ sample surface was rough and porous, with largely micro-sized pores. The P-TiO$_2$ film had amorphous phase, main anatase-TiO$_2$, and a small amount of P$_2$O$_5$. However, the Si-TiO$_2$ sample surface was smooth and had few nano-sized pores. The Si-TiO$_2$ films were composed of SiO$_2$, anatase-TiO$_2$, and amorphous phase. It was found that MAO coatings significantly improved the corrosion behavior of the CP-Ti substrate. The corrosion protection of the Si-TiO$_2$ coated sample was better than that of the P-TiO$_2$ coated sample. The antibacterial activities against S. aureus at 24 h were 96.4% for the P-TiO$_2$ coated sample and 98.6% for the Si-TiO$_2$ coated sample.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Tsoa author carry out all works.

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