Vol 14 No 12, December 2005
1009-1963/2005/14(12)/2598-04
Chinese Physics
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and IOP Publishing Ltd

Characteristics of grain growth of microarc oxidation coatings on pure titanium

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(Received 17 May 2005; revised manuscript received 29 August 2005)

Grainy titania coatings are prepared by microarc oxidation on pure titanium (TA2) substrates in a Na_2SiO_3–NaF electrolytic solution. The coating thickness is measured by an optical microscope with a CCD camera. Scanning electron microscope (SEM) and x-ray diffraction (XRD) are employed to characterize the microstructure and phase composition of coatings. The results show that the coating thickness increases linearly as the treatment time increases. The coatings are mainly composed of anatase and rutile (TiO_2). With the increase of treatment time, the predominant phase composition varies from anatase to rutile, which indicates that phase transformation of anatase into rutile occurs in the oxidizing process. Meanwhile, the size of grains existing on the coating surface increases and thus the surface becomes much coarser.

Keywords: microarc oxidation, grain growth, microstructure, phase composition
PACC: 8115L, 6150C

1. Introduction

As a novel surface modifying technique, microarc oxidation (MAO) is increasingly arousing people's interest in fabricating oxidation coatings on titanium and its alloys, with the purpose of corrosion- and wear-resistance or various functional properties.[1−6] The reliability of the various functions of coated titanium and its alloys mentioned above depends on the thickness, composition, and microstructure of coatings. Early work paid more attention to selecting and optimizing the composition and concentration of electrolytes, aiming at obtaining a desirable microstructure for improving properties.[5−11] However, little work about the grain growth of MAO coatings were reported in the past. Because the grainy structure can influence the functions of coatings, the multi-grains titania coatings are prepared, and the grain growth on MAO coatings is investigated and correlated with evolutions of microstructure, and phase composition of coatings are also determined in this study.

2. Experiment

TA2 plates with a size of 10mm×10mm×1mm were used as substrates for MAO treatment. The plate surfaces were polished with 600# abrasive papers and cleaned sequentially with acetone, ethanol and distilled water prior to treatment. A pulsed microarc oxidation device was used to prepare ceramic coatings on the TA2 surfaces, and its parameters of voltage, current, frequency, and duty cycle each can be adjusted independently by using their respective electronic amplifiers. In this study, the current density, pulse frequency and duty cycle were fixed at $5A/dm^2$, 5000Hz and 10%, respectively, but the deposition time could be varied from 3min to 60 min. An aqueous electrolyte was used, which mainly contained $Na_2SiO_3{\cdot}9H_2O$ and NaF. The electrolyte was stirred throughout the reaction period so as to remain uniform. The temperature of the electrolyte was kept below 30°C. The prepared samples were washed with distilled water and dried in air prior to their characterization.

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The coating thickness was measured by an optical microscope with a CCD camera. The morphologies of coating surfaces were observed by scanning electron microscope (SEM; SSX-550, SHIMADZU, Japan). The phase compositions of the coatings were investigated by x-ray diffraction (XRD; D8 DISCOVER, Bruker, Germany) using Cu$K\alpha$ radiation at a scanning speed of 5°/min.

3. Results and discussion

Figure 1 shows the variation of coating thickness with the treatment time at a current density j=5A/dm^2. Clearly, an approximately linear growth of coatings is found in the treatment process. The coating growth rate is 1.3μm/min. The results accord with those given by Wang *et al.*[12]

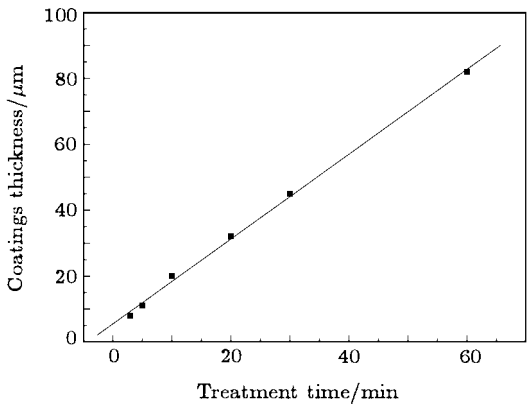


Fig.1. Variation of coating thickness with treatment time during microarc oxidation treatment at a constant current density on TA2.

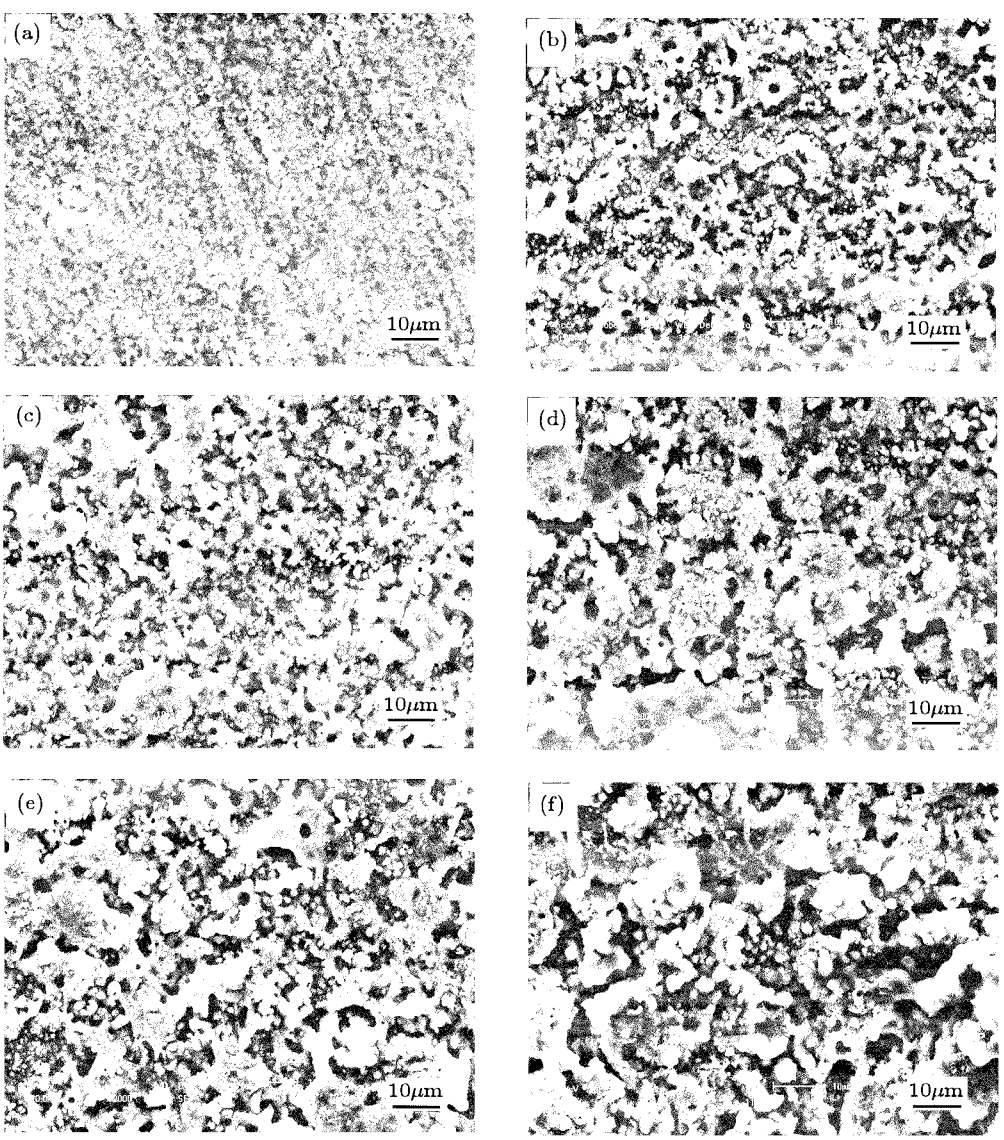


Fig.2. Evolutions of microarc oxidation coatings on TA2 at a constant current density and in different treatment times: (a) 3min; (b) 5min; (c) 10min; (d) 20min; (e) 30min; (f) 60min.

Microarc oxidation is an anodizing accompanied by sparking microdischarge due to dielectric breakdown, which is regarded as its intrinsic feature different from that of 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 current density in the MAO process determines the coating growth rate.[12] Therefore, coating thickness increases at an invariable rate during MAO treatment in the constant current density mode.

Figure 2 illustrates the surface features of the coated samples which were MAO-processed for different treatment times. The micrographs clearly indicate the grains distributed all over the coating surfaces, meanwhile, the coating surfaces are coarse. Obviously, at the initial oxidation stage (3min), fine and uniform grains with sizes less than 2μm distribute randomly on the surface of the coating (Fig.2(a)). As the treatment time increases, it is evident that the sizes of grains increase gradually, and the coating surface becomes much coarser.

The number of grains was measured by analysing the SEM micrograph with the help of Adobe Photo Deluxe software. Each grain was then marked and the total number of grains was counted using a software. The density of the grains i.e. the average number of grains per square micron was then calculated. Variations in size and number of grains are presented in Fig.3 from which we can see clearly: (1) when the treatment time is less than 20min, the grain number decreases rapidly and when the treatment time is over 20min, the number of grains decreases slightly; and (2) the grain size increases linearly with the increase of treatment time.

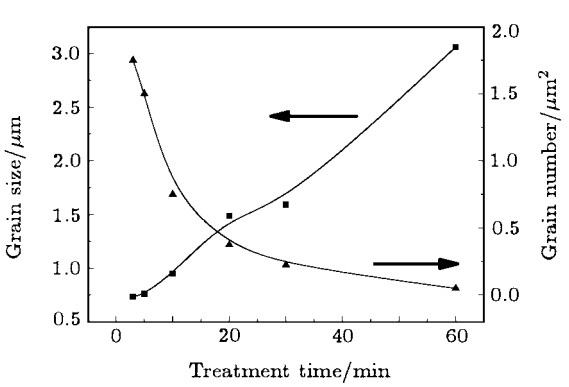


Fig.3. Effect of treatment time on grain size and grain number.

MAO is based on the modification of the growing anodic film by spark/arc micro-discharges, which are initiated at potentials above the breakdown voltage of the growing oxide film and move rapidly across the anode surface.[13,14] Since the microarc rapidly develops and extinguishes (within 10^{-4}–10^{-5}s),[13,14] the discharge heats the metal substrate to less than 100–150°C. At the same time, the local temperature and pressure inside the discharge channels can reach 10^3–10^4K and 10^2–10^3MPa, respectively, which are sufficient to give rise to plasma thermochemical interactions between substrate and electrolyte.[14] These interactions result in the formation of melt-quenched high-temperature oxides (such as titania). It is speculated that the melt-quenched titania crystallizes into grains and converts to anatase, and subsequently to rutile by virtue of local high temperature–pressure sintering in the proceeding microarc discharging. The local high temperature–pressure sintering is the most likely instantaneous process since the microarcs rapidly develop and extinguish, and thereby the grain growth is suppressed.[15] With oxidizing time increasing, the voltage value increases, accompanied with an increase in discharging energy of a single pulse, therefore, the product mass is increased in the duration of each single pulse, which contributes to the augmentation of the grain sizes. However, further investigation is required to confirm this hypothesis.

Figure 4 gives XRD patterns from the surfaces of microarc oxidation coatings formed in different treatment times. The coatings are mainly composed of anatase and rutile phase. The coating contains only anatase phase for the treatment time 3min, and rutile phase appears after a treatment time of 5min. As the treatment time increases, the relative content of anatase in the coatings decreases, while the content

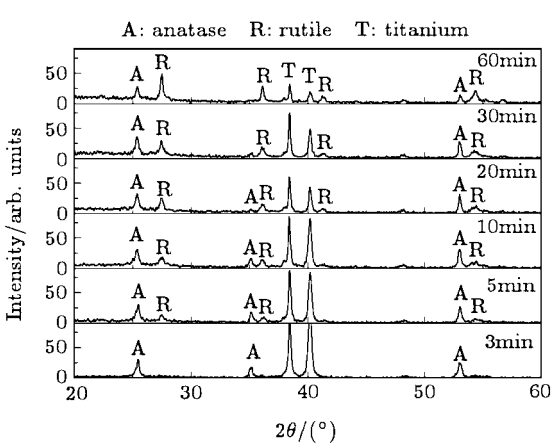


Fig.4. XRD patterns of microarc oxidation coatings in different treatment times at a constant current density on TA2.

of rutile increases, and after a certain period of oxidation, the rutile phase becomes predominant in the coatings. This fact indicates that phase transformation of anatase to rutile occurs in the oxidizing process. There are also the noticeable peaks of Ti which probably reflect the effect of the substrate in these thin films.

During microarc oxidation, the temperature and pressure in the discharge channels can respectively reach about 10^3–10^4K and 10^2–10^3MPa, [14] which promote the conversion of Ti substrate into titanium oxides. As the coating thickness increases, the previously formed products are calcined repeatedly under the repetitively pulsed microdischarges, which facilitates the anatase-to-rutile transformation; meanwhile the thermal conductivity of titanium dioxide causes the underlying layer of the coatings to be heated, which also promotes the further transformation of the initially formed metastable anatase to the stable rutile phase.[16] Thereby, the content of rutile in the coatings increases with the increase of treatment time.

4. Conclusion

Grainy titania coatings have been formed on TA2 alloy in a Na_2SiO_3–NaF electrolytic solution, using the DC pulsating microarc oxidation method. With the frequency (5000Hz), duty cycle (10%) and current density ($5A/dm^2$) fixed throughout the MAO process, the growth rates of coatings and the sizes of grains on the coating surfaces are all dependent on the treatment time. The growth rate of the coatings increases linearly, when the treatment time increases from 3min to 60min. The coatings are mainly composed of anatase and rutile (TiO_2). With the increase of treatment time, the content of anatase decreases, while the content of rutile increases and becomes the predominant phase. Meanwhile, the size of grains existing on the coating surface increases and thus the surface becomes coarse. The fine film with uniform and small size of grains is obtained in a treatment time of 3min as compared with the coatings prepared in other different treatment times.

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