Synthesis and mechanism of (101)-preferred orientation rutile titania via anodic spark oxidation

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ABSTRACT

This work is aimed to investigate the mechanism and factors that affect (101) orientation of rutile titania layers by anodic spark oxidation (ASO) treatment. The formation of (101)-preferred orientation of the rutile layer is ascribed to the internal high thermal stress generated by the thermal effect of spark discharges. Under high thermal stress, (101) planes will change their orientations parallel to the layer surface to endure the thermal stress, the residual stresses of samples with different (101)-orientation degree have been calculated using a $\sin^2\psi$ technique of X-ray diffraction (XRD) method. The results indicate that only the arc type discharges can effectively favor (101) orientation because they can generate the thermal stress large enough to cause (101) crystalline planes rotation while both the micro arc and luminescent spark cannot. The anodic mode and electrochemical parameters influence the energy, frequency, and duration time of the arc discharge stage, which lead to different orientation degree. The results also show that high applied voltage, optimal applied current density and H_2SO_4 electrolyte with medium concentration might be beneficial to obtain rutile layers with high (101) orientation.

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1. Introduction

Titanium and its alloys have important applications as bioimplants attributed to their corrosion resistance, good mechanical properties, and biocompatibility [1]. However, titanium metal is bio-inert, which means it cannot form biochemical bond with natural bone [2]. Various strategies have been developed to treat the titanium and its alloys with the ability (bioactivity) to bond directly and reliably to living bone in a short period [3,4]. One of them is to coat the substrate with a bioactive titania layer by means of surface modification techniques, such as solgel deposition [5], chemical modification [6], plasma spray [7], and anodic spark oxidation [8]. Anodic spark oxidation (ASO) is an advanced coating process for forming oxide coating structures on to valve metal surfaces [9]. Recently, anodic spark oxidation (ASO) has become an attractive method to obtain porous crystalline titania layer on titanium substrate for improving its bioactivity.

Crystal structure or texture of the titania layer is of crucial importance to its *in vitro* bioactivity [10], which is often evaluated by examining the apatite-forming ability in Kokubo's simulated body fluid (SBF) [11]. Uchida et al. [12] found that titania gel with amorphous structure did not induce apatite formation in SBF, whereas gels with an anatase or rutile structure induced apatite formation on their surfaces. They considered that the crystalline planar arrangement in crystal structures would facilitate epitaxy of the apatite crystal. Lindberg et al. [13] compared the apatite precipitation on three single-crystal rutile substrates, (100), (110), and (001), and a polycrystalline rutile substrate in phosphate-buffered saline (PBS) solutions. The results showed that hydroxylapatite grew with different speeds and different preferred crystalline directions on different faces of rutile. Yang et al. [14] and Cui et al. [15] both reported that the apatite deposited on the rutile layer with (101)-preferred orientation showed (0002)-preferred orientation, which was ascribed to improved epitaxial growth resulting from the close superposition of oxygen atoms arrangement in the rutile (101) plane with hydroxyl groups in apatite (0002) plane.

On the other hand, the texture of titania film is of crucial importance to their performance in acoustic, optical, and optoelectronic applications [16]. In general, the crystal plane with the lowest surface free energy favors a subsequent preferential growth. Thus, the (110) plane of rutile titania exhibits strongest diffraction peak in standard XRD patterns because (110) plane is the most close-packed plane in all planes of rutile structure [17]. The preferential crystal growth is also strongly dominated by the synthesis parameters or lattice mismatch between film materials and substrates. By using ion beam

assisted deposition techniques [18,19], rutile titania films can grow preferentially with (100), (002) and (101) orientation, depending on the impact angle and arrival ratio of ions to deposited atoms. Goh et al. [20] obtained *c*-axis-oriented rutile titania films on silica glass substrates by TiCl₄ solution deposition, which was due to a combination of preferential growth of the primary crystallites and a geometrical constraint imposed on agglomerating crystallites. It was also reported by Yang et al. [21] that the rutile phase in plasma-sprayed titania coatings presented a preferential orientation along (101) plane, which was ascribed to crystal planes rotation under high thermal stress in the splats during cooling process.

Since rutile titania layer with (101) orientation prepared by anodic spark oxidation (ASO) was supposed to show better *in vitro* bioactivity than that with a random orientation, it is important to more fully understand the mechanism and influence factors so as to prepare rutile titania layers with high (101) orientation. However, to our knowledge, there are few published literatures on it. In our recent paper [22], it was considered that during ASO in H₂SO₄ electrolyte, the formation of (101)-preferred orientation of rutile film was due to high thermal stress in the titania layer resulted from spark discharges. Residual stresses occurred near the interface of the titania layer and the titanium substrate when the titania layer cooled down after the spark discharge due to the mismatch of thermal expansion coefficients of titania layer and substrate.

In the present study, ASO treatments were carried out in H₂SO₄ or CH₃COONa electrolytes under various anodic conditions so as to investigate the effects of various preparing conditions on the (101) texture of anodic rutile layer. In addition, the thermal effect of the spark discharge was theoretically evaluated and the property of spark discharge on the orientation was discussed. To evaluate the residual stress of samples with different (101) orientation degree, the $\sin^2\psi$ technique of X-ray diffraction (XRD) method was used. Finally, the Materials Visualizer module of Materials Studio software 5.0 was applied to model the rutile unit cell and the origin of (101) crystalline planes rotation related to preferred orientation in rutile film was proposed.

2. Materials and methods

Industry pure titanium (TA2 [23]) substrates with size of 7.8 × 7.8 × 1 mm³ were polished carefully with No. 600, No. 400, and No. 800 metallographic abrasive paper and then washed in ultrasonic cleaner with pure acetone, ethanol, and distilled water for 5 min, respectively. ASO treatments were carried out in H₂SO₄ and CH₃COONa electrolytes with a direct current power supply system (Querli DC Power Supply WYJ-500 V 1 A, China). The anodic oxidation system was described in detail elsewhere [24]. Titanium substrates were treated according to a series of anodic conditions. The sample names (AOS100, AOS120, AOS0.25, etc.), anodizing conditions, and description of spark discharges were given in detail in Table 1.

After anodization, all the samples were ultrasonically cleaned in distilled water and finally dried in oven overnight. Then, the surface morphologies of the samples were analyzed by scanning electron microscopy (SEM, Hitachi, S4800). X-ray diffraction (XRD, Philips, X'Pert MPD 3 kW) was used to analyze the crystal structure and crystal orientation of the anodic layers on titanium samples. The scan range was 20°–60°, and the scanning rate was 3.6°/min. In this paper, the degree of (101)-preferred orientation was evaluated by the ratio of relative diffraction intensities of the (101) to (110) peaks (denoted as γ). The γ value calculated from the XRD diffraction patterns of standard rutile powder is 0.5, according to the JCPDS file (no. 21-1276) [25]. Using the well-established $\sin^2\psi$ technique, the residual stresses of the samples with different (101) orientation degree were measured on Rigaku Smartlab high-resolution X-ray diffractometer (Rigaku Corporation, Japan) with Cu Kα source. The stresses were treated as positive when tensile, negative when compressive.

3. Results and discussion

3.1. Spark discharge evolution during the ASO process

As shown in Table 1 and Fig. 1, three typical types of spark discharges can be distinguished during the AOS process. First, intense

Table 1
Sample names, anodizing conditions, and description of spark discharges.

Sample name	Electrolyte composition	Preset voltage (V)	Preset current (A)	Current density (A/cm²)	Anodizing time (min)[a]	Final voltage (V)	Description of spark discharge[b]		
							S	L	M
AOS100	H₂SO₄, 1 M	100	1	1.64	2; 60	–	+	− − −	− − −
AOS120		120	1	1.64	15; 60	–	+	− − −	− − −
AOS150		150	1	1.64	25; 60	–	+	+	+
AOS180		180	1	1.64	53; 60	–	+	+ +	+
AOS200		200	1	1.64	96; 60	–	+	+ + +	+
AOS250		250	1	1.64	377; 60	–	+	+ + + +	+
AOS0.25		–	0.25	0.41	120	160	+	+	− − −
AOS0.4		–	0.4	0.66	120	173	+	+	+
AOS0.55		–	0.55	0.9	120	186	+	+ + +	+
AOS0.7		–	0.7	1.15	120	198	+	+ +	+
AOS0.85		–	0.85	1.4	120	207	+	+ + + +	+
AOS1.0		–	1	1.64	120	212	+	+ + +	+
AOS0.1M	H₂SO₄, 0.1 M	180	1	1.64	5; 60	–	+	− − −	− − −
AOS0.5M	H₂SO₄, 0.5 M	180	1	1.64	23; 60	–	+	+	− − −
AOS2M	H₂SO₄, 2 M	180	1	1.64	73; 60	–	+	+	+
AOS3M	H₂SO₄, 3 M	180	1	1.64	170; 60	–	+	+	+ +
AOS4M	H₂SO₄, 4 M	180	1	1.64	147; 60	–	+	+	+ + +
AOS5M	H₂SO₄, 5 M	180	1	1.64	180; 60	–	+	+	+ + + +
AON100	CH₃COONa, 1 M	100	1	1.64	2; 60	–	+	− − −	− − −
AON120		120	1	1.64	7; 60	–	+	− − −	− − −
AON150		150	1	1.64	10; 60	–	+	− − −	− − −
AON180		180	1	1.64	35; 60	–	+	+	+
AON200		200	1	1.64	74; 60	–	+	+ +	+
AON250		250	1	1.64	480; 60	–	+	+ + + +	+

[a] The two parts in the anodizing time column include the following: the former is time to reach the preset voltage, the latter is duration time at the preset voltage.

[b] S, L, and M represent luminescent sparks, arc discharges, and micro-discharges during anodization process, respectively; "+, + +, + + +, + + + +" represent the semi-quantitative description of duration time of luminescent sparks, arc discharges, and micro-discharges during the anodization process, respectively. For example, + + does not mean exactly two times as +, it just means the duration time is longer than that of + and shorter than that of + + +. "− − −" indicates without such type of spark discharge generated during the process.