

Electrochemical Behavior Analyses of Anodic Oxide Film Obtained on TA2 Pure Titanium in Sulfuric Acid Electrolyte

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Anodic oxide films on pure titanium surface were prepared with potentiostatic method in the 10% sulfuric acid electrolyte. The chrono-amperometric curve, potentiodynamic polarization curve, electrochemical impedance spectroscopy and Mott-Schottky curve of anodic oxide films were obtained using an electrochemical method in 3.5% NaCl solution. The results show that colorful, flat and smooth anodic oxide films are obtained in the experimental processing parameters. Chrono-amperometric curve shows that formation of oxide film is the process of dynamic growth and dissolution. The potentiodynamic polarization curves and electrochemical impedance spectra show that TA2 pure titanium has better corrosion resistance after anodizing, and the higher the anodic oxidation voltage, the better corrosion resistance. Mott-Schottky curves show that anodic oxide film is an n-type semiconductor. The donor concentration decreases with increasing potential, the corrosion resistance increases.

1. Introduction

Titanium and titanium alloys are widely used in aerospace, automotive, military, chemical and other fields with good mechanical properties, low density, high stiffness, low hardness, high temperature resistance and good corrosion resistance. However, there are some inherent defects in titanium and titanium alloys, such as low hardness, poor wear resistance, poor thermal conductivity (Liu et al., 2014). Under normal circumstances titanium and titanium alloy surface to generate a layer of natural oxide film can play a protective role, but the natural oxide film is too thin and vulnerable to damage, and thus the corrosion resistance and wear resistance is limited (Zhu, 1995) titanium and titanium alloy materials are needed.

Anodic oxidation technology is a common surface modification technology of titanium and titanium alloy. A layer of dense oxide film was prepared on the surface of titanium and titanium alloy by anodic oxidation technology, which can improve the corrosion resistance and wear resistance of the oxide film. Compared with other acid anodic oxidation, anodic oxidation in sulfuric acid production at low cost, less electric consumption of electrolysis, the film wear resistance and corrosion resistance and good. During anodic oxidation, anodic oxidation parameters (electrolyte, potential, anode current density, temperature and anodic oxidation time) greatly affect the growth of anodic film and the performance of the film (Wu et al., 2014; Ysn et al., 2015). In recent years, although many scholars have done a lot of research on the influence of potential on corrosion resistance, the research on the growth and properties of anodic film in low potential (<10V) has not been reported.

In this paper, anodic oxide films of TA2 pure titanium in sulfuric acid electrolyte were prepared, and the chrono-amperometric curve, potentiodynamic polarization curve, electrochemical impedance spectroscopy and Mott-Schottky curve of the anodic film formed under the low potential were determined. Formation process and coating corrosion resistance and semiconductor properties of oxide film were studied through these curves, which provide a basis to further application of titanium oxide film.

2. Experiment

2.1 Preparation of anodic oxide film

The experimental material is TA2 commercially pure titanium, and its composition is shown in Table 1. The sample is cut into two kinds of sheets, one of is 100 mm×25 mm×0.2 mm. Another sheet is 10 mm×10 mm×0.2 mm. The latter kind of sheet is used for electrochemical testing, which is made of electrode. The TA2 pure titanium ground from 800 to 2000 grit sic paper and then cleaned ultrasonically with acetone and distilled water separately. Subsequently, the electrochemical polishing to the Ti specimens was conducted in the solution (HF: HNO₃: H₂O volume ratio for 3:6:100) at 25 °C. Ti specimen was set as cathode and graphite sheet as anode. The constant potential of 5 V was loaded for 3 min. Then the Ti specimens were rinsed in distilled water and dried in a drying oven.

The polished Ti specimens were anodized in the electrolyte solution with 1.88 M sulfuric acid containing methyl sulfonic acid at room temperature with a regulated DC power supply. The passive films were formed at different anodization potentials (2~65 V) for 180 s. After the anodic oxidation process, it can be seen from Figure 1 that films were obtained with rich color, uniform and smooth surface. The surface of the sample under different anode voltage is different.

Table 1: chemical compositions of TA2 commercially pure titanium (mass fraction, %)

Element	O	N	C	H	Fe	Si	Ti
Mass fraction	0.15%	0.05%	0.05%	<0.015%	<0.30%	<0.15%	Bal.

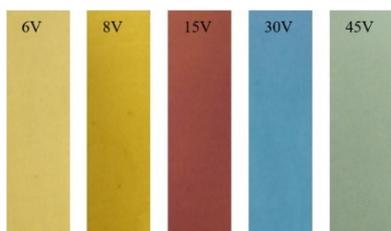


Figure 1: Photos of TA2 pure titanium surface under different anodization potentials

2.2 Electrochemical test

The chrono amperometric curve, potentiodynamic polarization curve, electrochemical impedance spectroscopy and Mott-Schottky curve were measured by CHI760E electrochemical workstation in a three-electrode cell containing 3.5 wt% NaCl solution at room temperature. The specimen with a nominal surface area of 1 cm² was used as the working electrode, with a saturated calomel reference electrode (SCE) and a platinum counter electrode. When the chrono-amperometric curve is tested, the selected operating voltage is the same, and the time is changed from 0 to 60 min. Potentiodynamic polarization curves test was conducted in 3.5 wt% NaCl solution with three electrode cell. The scanning rate was 1mV/S, and the scanning range was from -4V to +4V. Electrochemical impedance spectroscopy measurements was undertaken over the frequency range from 100 kHz to 0.01Hz, and the perturbation amplitude was 5mV. The initial retard of 300 s was set to obtain a stable testing system. Mott Schottky curve frequency is 1kHz. The disturbance sine wave amplitude is 5 mV. The measurement of the potential range is from -2 to 4V from a high potential to low potential move. Test is carried out at room temperature.

3. Results and Discussion

3.1 Anodic oxidation process analysis

Figure 2 was I-t curves of anodic oxide films prepared with constant potential. As can be seen from the Figure 2, curve trend of 8 V and curve of 2, 6 V are different. This is because barrier type anodic oxide film generated under 2 V and 6 V potential. The breakdown voltage is reached when the potential increased to 8 V, generating a porous anodic film (Lemaitre et al., 1987).

The curves of 2 V and 6 V can be divided into 3 stages. The first phase is the first few seconds of the start of the anodic oxidation. Current rises sharply in this stage mainly because of the nature oxide film of the titanium surface dissolved. In the subsequent ten seconds, current with the extension of time dropped sharply to - 12.4 mA because the growth of oxide film occupies the dominant position. A sharp decline in current symbolizes rapid formation of anodic oxide film. Oxide film thickens with the current dropping slowly. Finally, in time were

2400 s and 28 s, the current reached a steady, indicating that dissolution and growth of oxide film achieving a dynamic equilibrium. Oxide film enter the stable growth stage. Observation of 8 V curve can also be found that formation of the oxide film is in the first few seconds, and then maintain a constant current.

The I-t curve reflects the electrochemical reaction process of anodic oxide film formation. The formation of anodic oxide film on TA2 surface is the comprehensive effect of oxide growth and dissolution , the oxide film is formed in the early stage of anodic oxidation. Table 2 is the time of films obtained with different potential to reach the stable current value, it can be found that the higher the anodic oxidation potential, the longer the time required to reach the stable current.

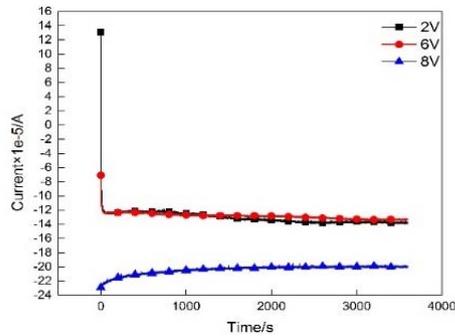


Figure 2: Current-time curves of the anodizing process for Ti anodic films obtained at constant potential

Table 2: Time to achieve the stationary current for Ti anodic films at different potential

Potential/V	2	6	8
Time/s	~2400	~2800	~3000

3.2 Corrosion resistance analysis

The dynamic potential polarization curves of the titanium sheet after anodic oxidation and the untreated titanium sheet in the 3.5 wt% NaCl solution are shown in Figure 3. In the cathodic region, the main reaction is the hydrogen evolution reaction of H_2O or H^+ . In the anode region, the 4 polarization curves have obvious passivation characteristics. All the polarization curves show that the passivation region and the over passivation region. In the range of 0~2 V interval to curve 1, current density keep 12.44 mA/cm² invariant, which is for untreated titanium the passivation region; In the range of 0.1~2.5V interval to the curve 2, 3 and 4, it is anodized titanium passivation region, whose passivation current density remains 1.386 to 1.893 mA/cm² unchanged, suggesting that their corrosion rates are constant. The formation of anodic oxide film and the growth are the passivation region. At the same time, it can be found that the passivation current density of the titanium sheet after anodic oxidation is lower than that of the untreated titanium sheet, which indicates that the corrosion resistance of the titanium sheet after anodic oxidation is better. When the potentials are more than 2 V, 2.5 V, untreated titanium plates and treated titanium sheets will enter into the passivation region. At this time, the current density increases with the increase of the potential, the dissolution rate of the metal increases again, and the pitting corrosion occurs (Rosalbino et al., 2012).

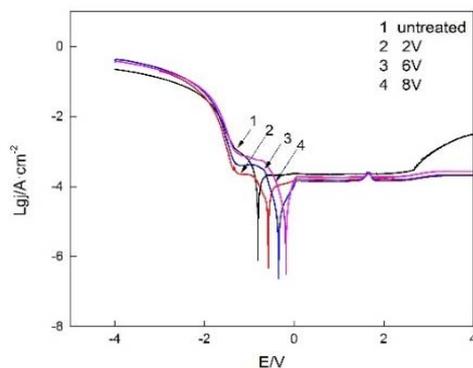


Figure 3: Potentiodynamic polarization curves of untreated and anodized on TA2 in 10% H_2SO_4 solution

The shape of the polarization curves (2V, 6V, 8V) was similar, which indicated that the anodic reaction and cathodic reaction occurred on the surface are similar. Potential rose from 2V to 8V, oxide passivation current density decreases first and then increases. This is due to the potential increased to 8V, the oxide film is porous oxide film. At the same time, the film thickness increases the pore also increased (Liu et al., 2013). The increase of porosity makes the corrosion rate of titanium increase, which shows that the current density decreases. At the same time, it can be found that there is a peak value of the current density in the cathode area of the polarization curve of the titanium material by anodic oxidation when the potential is 1.65V. The study says the occurrence of the peak position may be related to the phase transition on the passive film, and not due to the generation of O₂.

Table 3: Corrosion resistance parameters of TA2 pure titanium before and after anodized

Specimen	E_{corr}/V	I_{corr}/A	I_{pass}/A
No anodized	-0.804	1.174×10^{-4}	2.244×10^{-4}
Anodized(2V)	-0.576	7.42×10^{-5}	1.536×10^{-4}
Anodized(6V)	-0.349	1.572×10^{-5}	1.386×10^{-4}
Anodized(8V)	-0.187	1.888×10^{-5}	1.893×10^{-4}

Self corrosion current density (I_{corr}) and self corrosion potential (E_{corr}) can be obtained by extrapolation of Tafel curve and the passivation current density (I_{pass}) directly is read directly by the polarization curve, specific values as shown in Table 3. As can be seen from table 3, the E_{corr} value of treated titanium is increased, and the I_{corr} value is reduced by an order of magnitude. The increase of E_{corr} value indicates that the titanium sheet is less prone to corrosion after anodic oxidation, and the reduction of I_{corr} value indicates that the corrosion rate of treated titanium is decreased. After anodic oxidation, the corrosion resistance of titanium increases, and with the increase of the potential of oxidation, titanium sheets are less prone to corrosion.

EIS test results of anodic oxidation film of TA2 pure titanium in sulfuric acid solution are shown in Figure 4 and 5. Figure 4 is the Nyquist plot. It can be seen that from the Figure 4 the impedance curves of anodic oxide films have similar characteristics under different voltage, which are an incomplete arc, suggesting that the passivation film has a capacitive loads (Xie et al., 2013). In addition, with the increase of the anode oxidation voltage, the diameter of the circle increases gradually. The diameter of the circle is in direct proportion to the value of the polarization resistance. It shows that the film has better corrosion resistance with the increase of the voltage.

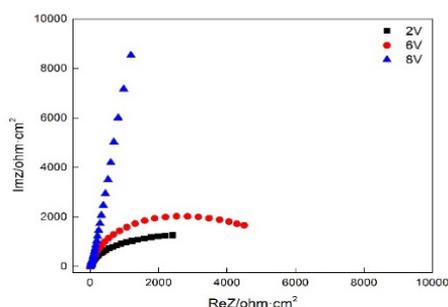


Figure 4: Nyquist curves of anodic films obtained on TA2 pure titanium at different voltages

Figure 5 Bode plots of TA2 oxide film, the Bode plots of oxide films obtained under different treatment conditions are similar. In the high frequency region ($10^5 \sim 10^6$ Hz), the curve is similar to the platform (the curve slope is about 0), which corresponds the solution resistance response.

In the middle and low frequency range, the impedance and frequency are in a linear relationship (the slope is about -1), which indicates that there is a capacitive load (Bhola et al., 2013; Bai et al., 2012). Figure 5 (b) for the Bode phase diagram of the oxide film, in the high frequency area, the phase angle is 0 degrees, which represents the solution resistance. In the mid frequency region, the phase angle is close to 90 degrees, which indicates that there is a capacitive load. And the curves of 6 V in high frequency and low frequency region appear two distinct phase angle peaks, which indicate that the curve has two time constants. According to the literature, the oxide film formed in sulfuric acid solution is a double layer (porous outer layer and a dense inner layer) (Fekry et al., 2009). It is shown that the time constant of the high frequency region is related to the formation of the porous outer layer from the Bode diagram. The low frequency time constant is related to the formation of the dense inner layer film (Kumar et al., 2008).

According to the results of EIS, test data were fitted by using ZSimWin software and the appropriate equivalent circuit was selected to analysis test data, equivalent circuit as shown in Figure 6. In the equivalent circuit of figure 6, R_s represents the solution resistance; Q_p and R_p respectively represent capacitance and resistance of the outer porous film; Q_b and R_b respectively represent capacitance and resistance of the dense inner layer, the C_{dc} and R_{tc} respectively represent the double layer capacitance and charge transfer resistance, respectively.

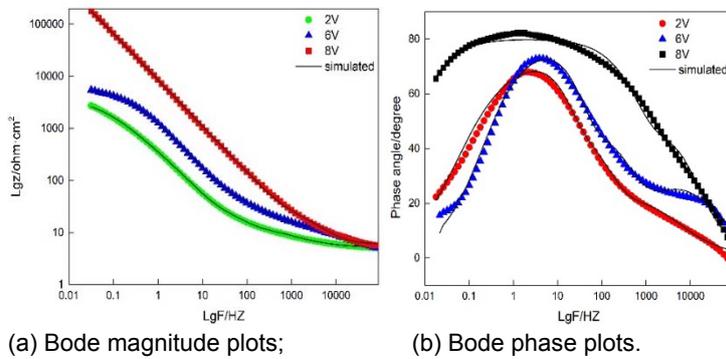


Figure 5: Bode curves of anodic films obtained on TA2 pure titanium at different voltages

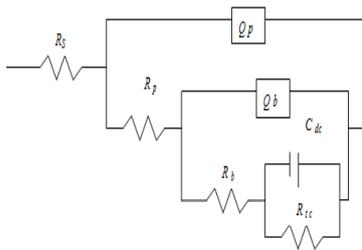


Figure 6: Equivalent circuit model

The electrochemical parameters obtained by equivalent circuit fitting are listed in Table 4. The number of class χ^2 are 10^{-3} , which shows that the test values are in agreement with the fitting values. The value of R_s varies little with different treatment conditions, and the value of R_b is much higher than that of R_p , which indicates that the corrosion resistance of titanium sheet is mainly related to the inner dense film (Assis et al., 2006). The value of n is related to the roughness of the metal oxide interface, the bigger the n value, the more smooth the interface is. When the potential is up to 8 V, the n value is changed greatly (n_p increases, n_b decreases), which indicates that the roughness of the metal oxide interface has changed. C_{dc} value is very small and R_{tc} value is large for different treatment conditions, which shows that the TA2 surface is not easy to produce electrochemical reaction and has a good corrosion resistance (Wang et al., 2012). With the increase of oxidation potential, Q_p and Q_b decreased, and R_p and R_b increased, which indicated that the oxide film obtained under high potential was more difficult to be corroded.

Table 4: Electrical parameters of anodic films obtained on TA2 pure titanium at different voltages by fitting using the equivalent circuit

Electrical parameters provided by the EIS fitting										
	$R_s(\Omega \cdot \text{cm}^2)$	$Q_p \times 10^{-5}(\text{F} \cdot \text{cm}^{-2})$	n_p	$R_p(\Omega \cdot \text{cm}^2)$	$Q_b \times 10^{-5}(\text{F} \cdot \text{cm}^{-2})$	n_b	$R_b(\Omega \cdot \text{cm}^2)$	$C_{dc} \times 10^{-5}(\text{F} \cdot \text{cm}^{-2})$	$R_{tc}(\Omega \cdot \text{cm}^2)$	$\chi^2 \times 10^{-3}$
2V	5.103	49.28	0.67	11.67	10.38	0.98	514.9	8.65	3890	1.63
6V	4.65	10.46	0.67	17.47	3.28	0.97	676.7	3.71	6026	1.93
8V	5.904	0.963	0.89	2868	1.31	0.88	117800	11.51	4.43×10^7	2.20

4. Conclusions

The anodic oxide film with rich color and smooth surface was obtained by using 10% sulfuric acid as the electrolyte on the surface of TA2 pure titanium. TA2 pure titanium oxide film is formed at the initial stage of

anodic oxidation, and the formation of oxide film is the comprehensive effect of oxide growth and dissolution. The corrosion resistance of titanium increases after anodic oxidation and titanium is more difficult to corrode with the increase of the potential of oxidation. When the potential exceeds 0.5 V, pure titanium anodic oxide film in sulfuric acid solution showed n-type semiconductor characteristics. Donor concentration decreases and the corrosion resistance of the film improved after anodic oxidation, and donor concentration decreases with increase of potential, indicating the corrosion resistance of anodization film further improved.

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