

ELECTROCHEMICAL CHARACTERISTICS OF THE ANODIZED TITANIUM OXIDE FILMS IN SULFURIC ACID

**Branka Pešovski¹, Milan Radovanović², Vesna Krstić^{1,2},
 Danijela Simonović¹, Silvana Dimitrijević¹**

¹Mining and Metallurgy Institute Bor, Zeleni Bulevar 35, 19210 Bor, Serbia

²Technical Faculty in Bor, VJ 12, 19210 Bor, Serbia

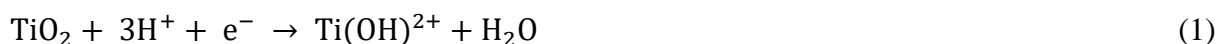
Abstract

We presented some research into titanium electrode anodizing in H₂SO₄ solutions in the potential range – 1 to 5 V at different scan rates (10, 50, 100 mV s⁻¹) by cyclic voltammetry measurements. Linear potentiodynamic measurements had used before and after the oxide layer formed on the Ti- surface. Three characteristic oxide peaks appeared at 0.2 V, 2.3 V, and 3.5 V on CV curves at all scan rates for all H₂SO₄ concentrations. Voltammetric tests showed the passivation of the Ti-surface in all cases. XRD and SEM-EDS measurements confirmed the existence of TiO₂ species in a crystalline form on the Ti surface after anodizing in 3M H₂SO₄ and annealing the anodized Ti electrode at 400 °C in the airflow.

Keywords: titanium oxides, cyclic voltammetry, XRD, linear voltammetry, polarization

1. INTRODUCTION

The exact nature of formed oxide films on the Ti surface during the anodization process is still not well known, even though, in the study of surface modifications, many of the latest techniques for the investigating properties of such films have been used. A series of different oxides of low-valent titanium is present in the oxide film. Electrochemical dissolution of the passive film occurs at the boundary of the oxide-solution phase, according to eq. (1), where the dissolution is not localized [1]



The quantities of non-stoichiometric oxides obtained within the electrochemically formed oxide film depend on the potential and pH solution. This anodization can be represented according to the reaction (2): [2]



for $1.5 \leq n \leq 2$

The XRD obtained data indicates the presence of Ti₃O₅ in a dominant TiO₂ matrix. The following reactions of TiO₂ film dissolution in H₂SO₄ solutions occur: [3]



2. EXPERIMENTAL

The concentrations of H₂SO₄: 1.5 M, 1 M, 0.5 M, 0.1 M, and 0.05 M were used. The following measurements into the electrochemical behavior of Ti electrodes were done:

- Scanning of the Ti electrode cyclic voltammograms in H₂SO₄ solutions at different scan rates (10, 50, and 100 mV s⁻¹); Scans were carried out for five cycles in the potential range of –1 to 5 V; Linear potentiodynamic measurements had taken after measuring the open circuit potential in various concentrations of H₂SO₄ solutions; Passivizing TiO₂ layer is applied by cyclic voltammetry at a scan rate of 50 mV s⁻¹;

Linear potentiodynamic measurements were performed on a Ti electrode on which a passive TiO₂ film has previously been applied at a scan rate of 1 mV s⁻¹; Anodic oxidation of a Ti electrode has performed in a 3 M H₂SO₄ solution before XRD and SEM-EDS measurements in a CV range of – 1 to 5 V at a scan rate of 100 mV s⁻¹ during five cycles. The working electrode was a Ti plate, the reference electrode was a saturated calomel electrode (SCE), and the auxiliary electrode was a Pt electrode. The working electrode was polished with grinding paper from 280 to 2000 grit and washed with distilled water. The IVIUMSTAT.xRe instrument provided hardware and software support. X-ray analysis had performed on the instrument „Rigaku MiniFlex 600”. The surface appearance and mineralogical composition investigation of the samples SEM (JEOL, JSM IT 300LV) and EDS (OXFORD Instruments) analyses were applied.

2.1 Materials and Solutions

The working electrode was made of a titanium plate Grade II, like a spatula shape in the lower part, and dimensions of 1.5 × 1.5 × 0.2 cm, with a handle length of 15.0 cm. The working solution was sulphuric acid, 96 % H₂SO₄ p.a. quality.

3. RESULTS & DISCUSSION

3.1 Cyclic Voltammetry

Based on the CV measurements, the growth of the oxide film was usually in the form of a TiO₂ structure. The first peak may occur due to the formation of the Ti oxides with the lower Ti-valence. These would probably be Ti²⁺ and Ti³⁺ (TiO and Ti₂O₃), while the second and third peaks correspond to the forming of TiO₂ films [4]. Unstable Ti₂O₃ oxide rapidly oxidizes to TiO₂ in contact with water.

3.2 Open circuit potential

Open circuit measurements of Ti- and (Ti+TiO₂)-electrodes had performed for 60 min in different concentrations of H₂SO₄ solutions and the results obtained are presented in Fig. 3, and Table 1. In Figure 1 it can see that in the H₂SO₄ solutions, immediately after the electrode immersion, there is a sudden drop in the value of the open circuit potential, which most likely indicates titanium oxide dissolution on the electrode surface.

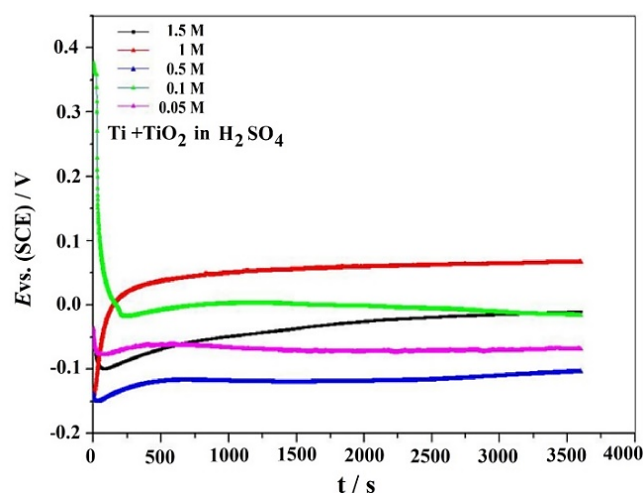


Figure 1 - The plot of the open circuit potential of (Ti+TiO₂)-electrode in different concentrations of H₂SO₄ solutions.

Table 1 - The potential values for a Ti-electrode on OCP in different H₂SO₄ concentrations

Potential on $t = 3600$ s	H ₂ SO ₄ concentration				
	1.5 M	1 M	0.5 M	0.1 M	0.05 M
E / V_{SCE}	-0.0636	-0.0926	0.0166	-0.0205	-0.0363

3.3 Linear potentiodynamic measurements

Figure 2 shows polarization curves in the various concentrations of H₂SO₄ solutions of the Ti- and (Ti+TiO₂)-electrodes. A rapid formation of the oxide film observes at the beginning of the polarization process. On potentials higher than 1.5 V, there is an increase in the current density that undoubtedly indicates further oxidation of titanium.

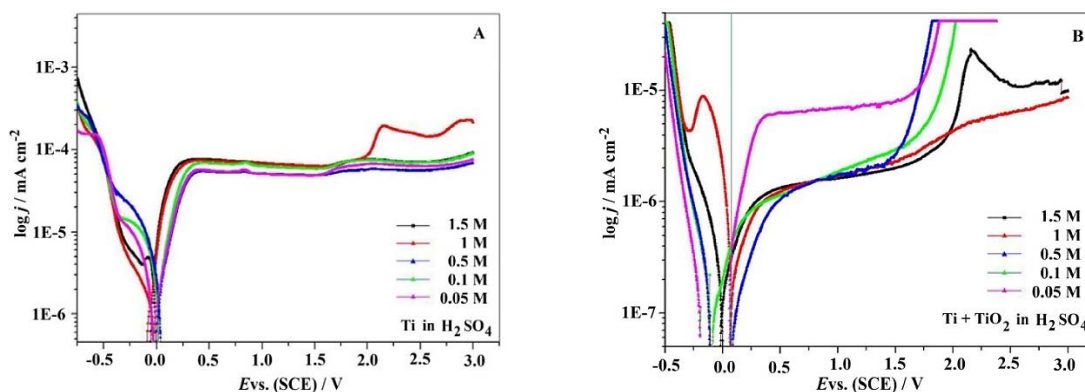


Figure 2 - The potentiodynamic polarization curves in H₂SO₄ solutions: A) Ti electrodes, and B) (Ti+TiO₂)-electrode. The scan rate is 1 mV s⁻¹.

The kinetic parameters of electrochemical processes have been determined: the corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic (b_a), and cathodic (b_c) Tafel's slopes are presented in Table 2.

 Table 2 - Electrochemical parameters of (Ti+TiO₂)-electrode.

H ₂ SO ₄	E_{corr}/mV	$i_{corr}/mA\ cm^{-2}$	b_a	b_c
1.5 M	$-0.44 \cdot 10^{-2}$	$1.74 \cdot 10^{-4}$	545.26	-283.53
1 M	$7.84 \cdot 10^{-2}$	$1.57 \cdot 10^{-4}$	359.59	-106.90
0.5 M	$-8.86 \cdot 10^{-2}$	$1.18 \cdot 10^{-4}$	597.20	-332.40
0.1 M	$-1.44 \cdot 10^{-2}$	$3.29 \cdot 10^{-5}$	111.98	-671.43
0.05 M	$-7.32 \cdot 10^{-2}$	$2.70 \cdot 10^{-5}$	357.21	-428.33

The influence of the H₂SO₄ concentration on the coverage degree of the titanium surface with Ti-oxide was presented in Table 3.

 Table 3 - Coverage degree of titanium electrode surfaces with oxide in various concentrations of H₂SO₄ solutions on constant potentials

H ₂ SO ₄ concentration	Coverage degree, θ (%)		
	$E=0.5$ V	$E=1.0$ V	$E=1.5$ V
1.5 M	98.24	97.62	96.78
1 M	98.32	97.43	96.32
0.5 M	98.32	97.04	94.95
0.1 M	98.04	96.54	94.58
0.05 M	88.60	86.11	83.44

4. XRD and EDS analyses of anodized and annealed Ti substrates in H₂SO₄

Figure 3 shows the XRD image of the Ti substrate after anodization in 3 M H₂SO₄ and after annealing the sample at 400 °C in the airflow, previously prepared in the same way. The intensity of peaks for the anatase type of crystals also suggests a thin TiO₂ film formation. The height of the same peaks increases after the annealing titanium electrode at 400 °C, which indicates that the oxide film of anatase becomes thicker after heat treatment.

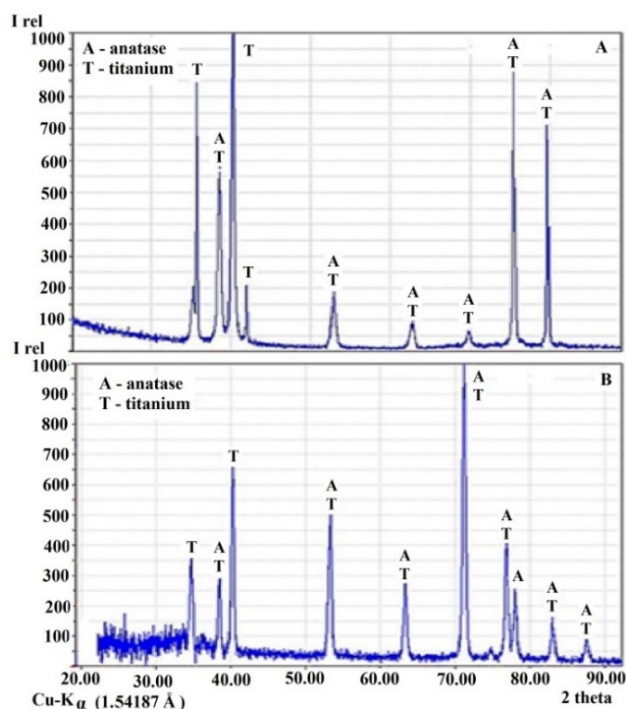


Figure 3 - XRD patterns of Ti electrode: A) after anodizing in 3M H₂SO₄, B) after annealing anodized Ti electrode, at 400 °C in the the airflow.

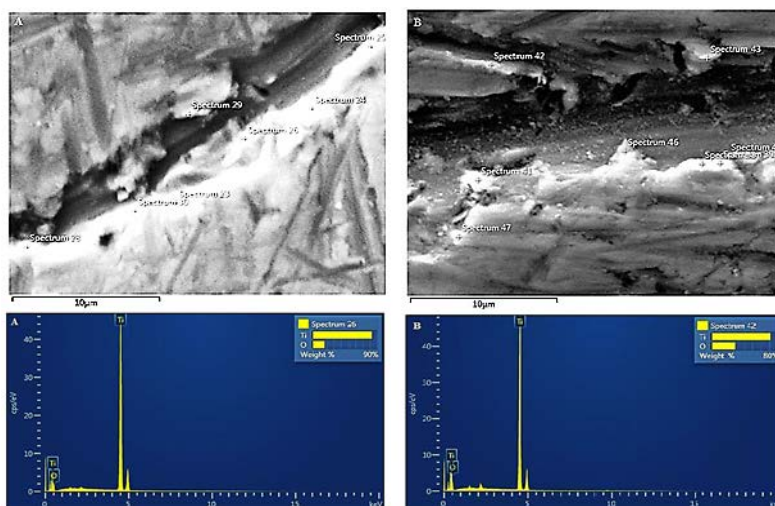


Figure 4 - SEM-EDS images of A) Ti electrode after anodizing in 3M H₂SO₄, B) annealed Ti electrode at 400 °C 1 h after anodizing in 3M H₂SO₄

SEM-EDS analyses confirm the results obtained by XRD measurements. It can also observe that after anodization on the titanium surface Ti and O₂ species exist. According to chemical analysis, after annealing of titanium, the content of O₂ species increase indicating thicker TiO₂ oxide films (Table 4).

Table 4 - Chemical composition of titanium surface after anodization in 3 M H₂SO₄ and after annealing at 400 °C at a time of 1 h.

Atomic species	O %	Ti %	Total %
after anodization	17.30	82.70	100.00
after thermal treat.	28.40	71.60	100.00

5. CONCLUSIONS

It was observed that TiO₂ is the most stable oxide formed, besides TiO and Ti₂O₃ oxides. CV measurements indicate the rapid formation of an oxide layer with variations in stoichiometry and morphology. After thermal treatment of the electrode, XRD patterns showed a higher intensity of anatase peaks in the anodized oxide films. SEM-EDS images also confirmed the higher presence of oxides in the heat-treated titanium electrode.

ACKNOWLEDGEMENTS

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Grant No. 451-03-47/2023-01/ 200052 and No. 451-03-47/2023-01/ 200131.

REFERENCES

- [1] T. Ohtsuka, M. Masuda, N. Sato, J Electrochem Soc, 134(10) (1987) 2406-2410.
- [2] O.R. Camara, C.P. De Pauli, M.C Giordano, Electrochim. Acta, 29(8) (1984) 1111.
- [3] D.J. Blackwood, L.M. Peter, D.E. Williams, Electrochim. Acta, 33(8) (1988) 1143.
- [4] G. Blondeau, M. Froelicher, M. Froment, A.H. Le Goff, J. less-common met, 5(2) (1977) 215-222.