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PROCEEDINGS

Editors:
Ljubiša Balanović
Dejan Tanikić

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PREFACE

On behalf of the Organizing Committee, it is a great honor and pleasure to welcome all esteemed participants of the 54th International October Conference on Mining and Metallurgy (IOC 2023), scheduled to take place at the picturesque Bor Lake, Serbia, from October18th to 21st 2023.

The collaborative efforts of the University of Belgrade, the Technical Faculty in Bor, and the Mining and Metallurgy Institute Bor have meticulously organized this year's IOC. Our focus remains unwavering on showcasing the latest research findings and advancements in geology, mining, metallurgy, materials science, technology, environmental protection, and other engineering disciplines. Our primary objective is to foster a dynamic environment where academics, researchers, and industry professionals can come together to share their knowledge, experiences, and innovative ideas while exploring opportunities for collaborative research endeavors.

Our conference agenda is rich and diverse, encompassing plenary sessions, engaging invited lectures, technical presentations, enlightening oral and poster sessions, informative technical tours, a diverse exhibition, and memorable social gatherings. At the heart of this event lies our strong commitment to sustainable development within the mining and metallurgy sector. We are dedicated to exploring ecologically conscious methodologies, responsible resource extraction practices, and cutting-edge technologies that reduce the industry's environmental impact and enhance the well-being of local communities.

The conference proceedings comprise 129 papers authored by individuals from universities, research institutes, and industries in 22 countries. We are proud to welcome participants from Bosnia and Herzegovina, Bulgaria, Canada, China, Croatia, Germany, Greece, India, Iran, Kazakhstan, Libya, North Macedonia, Montenegro, Morocco, Romania, Russia, Slovakia, South Africa, Spain, Turkey, United States, and, of course, Serbia.

We are excited to host the 8th International Student Conference on Technical Sciences (ISC 2023) as part of IOC 2023. This event offers students from Serbia and the wider region a unique chance to showcase their research and discuss the future of their fields with experts.

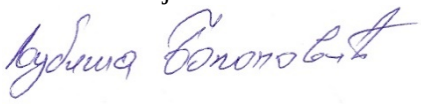
We sincerely thank the Ministry of Science, Technological Development, and Innovation of the Republic of Serbia for their generous financial support. In addition, we express our profound gratitude to all our sponsors, exhibitors, and friends of the Conference for their contributions and unwavering support for playing a pivotal role in ensuring the success of IOC 2023.

We would like to express our heartfelt thanks to all authors, committees, reviewers, speakers, and chairpersons for their invaluable contributions in shaping IOC 2023.

We look forward to welcoming you to the 55th International October Conference on Mining and Metallurgy (IOC 2024), which will be held in October 2024.

On behalf of the 54th IOC Organizing Committee,

Prof. dr Ljubiša Balanović



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ELECTROCHEMICAL CHARACTERISTICS OF THE ANODIZED TITANIUM OXIDE FILMS IN SULFURIC ACID

Branka Pešovski[1], Milan Radovanović[2], Vesna Krstić[1,2], Danijela Simonović[1], Silvana Dimitrijević[1]

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Abstract
We presented some research into titanium electrode anodizing in H_2SO_4 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 H_2SO_4 concentrations. Voltammetric tests showed the passivation of the Ti-surface in all cases. XRD and SEM-EDS measurements confirmed the existence of TiO_2 species in a crystalline form on the Ti surface after anodizing in 3M H_2SO_4 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]

$$TiO_2 + 3H^+ + e^- \rightarrow Ti(OH)^{2+} + H_2O \quad (1)$$

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]

$$TiO_n + H_3O^+ + e \rightleftarrows TiO_{n-1}(OH)(H_2O) \quad (2)$$

for $1.5 \leq n \geq 2$

The XRD obtained data indicates the presence of Ti_3O_5 in a dominant TiO_2 matrix. The following reactions of TiO_2 film dissolution in H_2SO_4 solutions occur: [3]

$$TiO_2 + 4H^+ \rightarrow Ti^{4+} + 2H_2O \quad (3)$$

2. EXPERIMENTAL

The concentrations of H_2SO_4: 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 H_2SO_4 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 H_2SO_4 solutions; Passivizing TiO_2 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 TiO_2 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 H_2SO_4 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 % H_2SO_4 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 TiO_2 structure. The first peak may occur due to the formation of the Ti oxides with the lower Ti-valence. These would probably be Ti^{2+} and Ti^{3+} (TiO and Ti_2O_3), while the second and third peaks correspond to the forming of TiO_2 films [4]. Unstable Ti_2O_3 oxide rapidly oxidizes to TiO_2 in contact with water.

3.2 Open circuit potential

Open circuit measurements of Ti- and (Ti+TiO_2)-electrodes had performed for 60 min in different concentrations of H_2SO_4 solutions and the results obtained are presented in Fig. 3, and Table 1. In Figure 1 it can see that in the H_2SO_4 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.

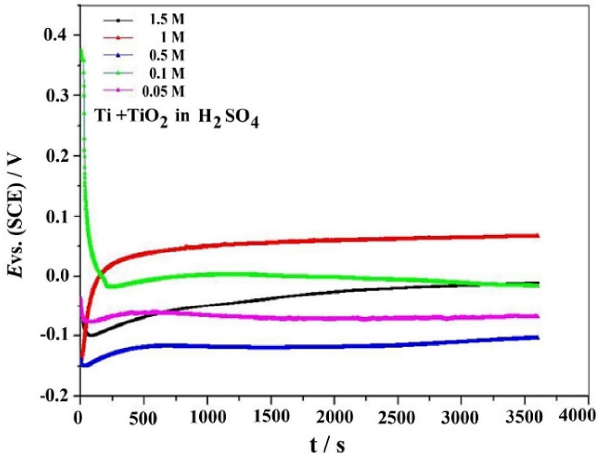

Figure 1 - The plot of the open circuit potential of (Ti+TiO_2)-electrode in different concentrations of H_2SO_4 solutions.

Table 1 - The potential values for a Ti-electrode on OCP in different H_2SO_4 concentrations

Potential on t = 3600 s	H_2SO_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 H_2SO_4 solutions of the Ti- and (Ti+TiO_2)-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.

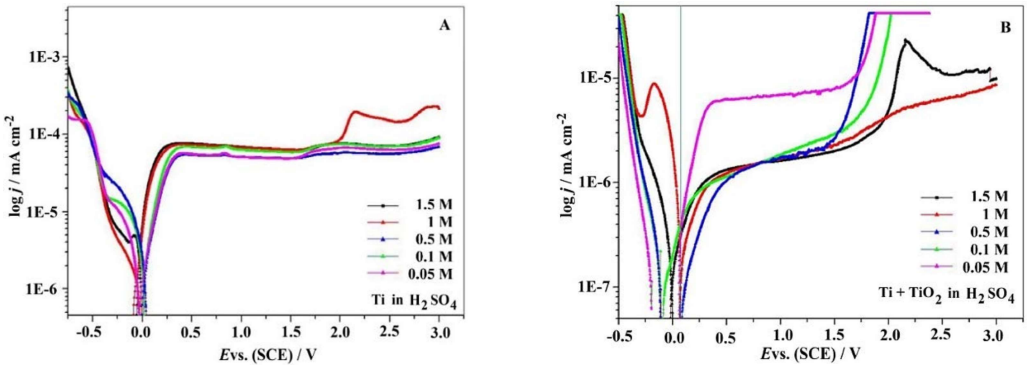

Figure 2 - The potentiodynamic polarization curves in H_2SO_4 solutions: A) Ti electrodes, and B) (Ti+TiO_2)-electrode. The scan rate is 1 mV s^{-1}.

The kinetic parameters of electrochemical processes have been determined: the corrosion potential (Ecorr), 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+TiO_2)-electrode.

H_2SO_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 H_2SO_4 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 H_2SO_4 solutions on constant potentials

H_2SO_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 H_2SO_4

Figure 3 shows the XRD image of the Ti substrate after anodization in 3 M H_2SO_4 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 TiO_2 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.

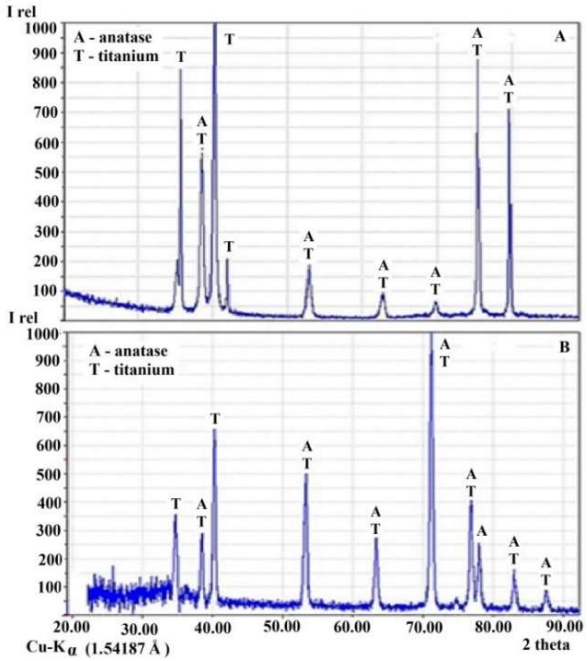

Figure 3 - XRD patterns of Ti electrode: A) after anodizing in 3M H_2SO_4, B) after annealing anodized Ti electrode, at 400 °C in the the airflow.

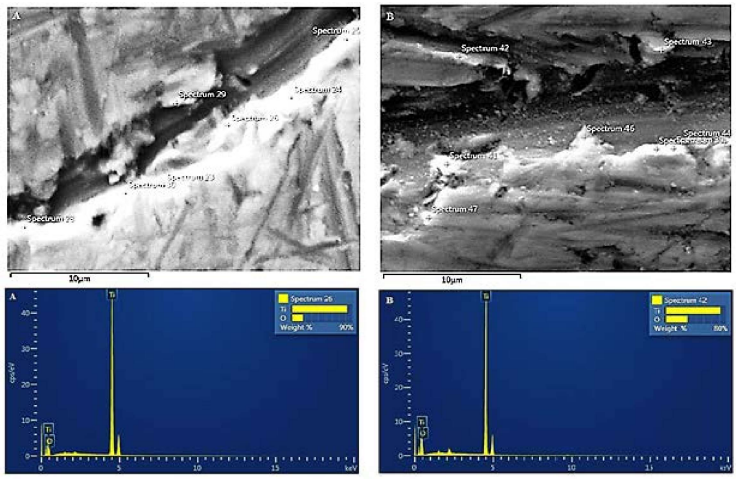

Figure 4 - SEM-EDS images of A) Ti electrode after anodizing in 3M H_2SO_4, B) annealed Ti electrode at 400 °C 1 h after anodizing in 3M H_2SO_4

SEM-EDS analyses confirm the results obtained by XRD measurements. It can also observe that after anodization on the titanium surface Ti and O_2 species exist. According to chemical analysis, after annealing of titanium, the content of O_2 species increase indicating thicker TiO_2 oxide films (Table 4).

Table 4 - Chemical composition of titanium surface after anodization in 3 M H_2SO_4 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 TiO_2 is the most stable oxide formed, besides TiO and Ti_2O_3 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.

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