

Sol-gel prepared active ternary oxide coating on titanium in cathodic protection

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Abstract: The characteristics of a ternary oxide coating, on titanium, which consisted of TiO₂, RuO₂ and IrO₂ in the molar ratio 0.6:0.3:0.1, calculated on the metal atom, were investigated for potential application for cathodic protection in a seawater environment. The oxide coatings on titanium were prepared by the sol-gel procedure from a mixture of inorganic oxide sols, which were obtained by forced hydrolysis of metal chlorides. The morphology of the coating was examined by scanning electron microscopy. The electrochemical properties of activated titanium anodes were investigated by cyclic voltammetry and polarization measurements in a H₂SO₄- and NaCl-containing electrolyte, as well as in seawater sampled on the Adriatic coast in Tivat, Montenegro. The anode stability during operation in seawater was investigated by the galvanostatic accelerated corrosion stability test. The morphology and electrochemical characteristics of the ternary coating are compared to that of a sol-gel-prepared binary Ti_{0.6}Ru_{0.4}O₂ coating. The activity of the ternary coating was similar to that of the binary Ti_{0.6}Ru_{0.4}O₂ coating in the investigated solutions. However, the stability in seawater is found to be considerably greater for the ternary coating.

Keywords: ruthenium-oxide-based coatings, sol-gel procedure, iridium oxide, cathodic protection, stability.

INTRODUCTION

Due to the good activity of RuO₂-based anodes for the chlorine evolution and oxygen reaction,^{1–3} they are commercially widely applied in cathodic protection processes.⁴

The most often employed electrochemical protecting systems for steel constructions sunk in seawater include organic protective coatings and cathodic protection.^{5,6} Although protection by sacrificial anodes is also an aspect of cathodic protection, the concept of impressed-current technology relates to the cathodic

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polarization of the species requiring protection, which are coupled to an anode over an appropriate power source. The protecting procedure by impressed current is one of most efficient since it allows highly automated control of the protection process. Also, it is desirable for the anode material to show high activity for the reactions which occur during protection in a given corrosion medium. In addition, cathodic protection process in seawater should also provide protection against overgrowth by biomaterials, which is realized by the use of anodes possessing a good activity for the chlorine evolution reaction.

Activated titanium anodes are commercially available for application in the cathodic protection of steel constructions in seawater, soil and concrete, as well as pipelines exposed to an aggressive environment.⁴ Recently, investigations have considered alternative applications of ruthenium oxide in corrosion protection.^{7–10} Darowicki and Janicki⁸ improved the properties of a carbon/polyethylene/vinyl acetate composite material as an anode in cathodic protection by the addition of ruthenium oxide. The improvement was related to the increase in activity for the oxygen evolution reaction. Shibli *et al.*⁹ increased the erosion stability of Al and Al–Zn sacrificial anodes and their anticorrosion characteristics in NaCl solution by activation of the surface with ruthenium oxide.

In addition to the commercially available activated titanium anodes named LIDA[®] and LIDA TSA[™],⁴ platinized titanium anodes (protection of ship hulls),¹¹ as well as Pb–Ag, Al–Zn and Fe–Si alloys (protection of offshore docks) are used for cathodic protection in seawater.^{12–14} However, Ti/Pt anodes are expensive, while anodes made of alloys are of very limited service life due to side reactions of alloy dissolution. Anodes coated with RuO₂ also undergo degradation due to the electrochemical oxidation of Ru species. Since the products of oxidation are soluble, the anode coating is gradually enriched in insulating TiO₂, which leads to passivation of the anode surface. The anode activity for the oxygen evolution reaction, however, appears to play a key role in the process of anode degradation.^{15–20} It is known that activated titanium anodes containing iridium oxide are more stable against passivation in the electrolysis of NaCl solutions than a binary RuO₂–TiO₂ coating.^{16,21–24} This is due to the slower corrosion rate of IrO₂ with respect to RuO₂, especially when a considerable portion of the current is related to the oxygen evolution reaction.²⁵ For this reason, activated titanium anodes, commercially available for cathodic protection purposes, contain iridium oxide in small amounts, in addition to ruthenium and titanium oxide. It is to be mentioned that previous studies^{18,19,26} postulated the higher activity for the chlorine and oxygen evolution reaction, as well as stability to passivation of Ti_{0.6}Ru_{0.4}O₂ coatings on titanium prepared by the sol-gel procedure, when compared to the coating prepared by the usual thermal decomposition of metal chlorides.^{1,17} This effect was mostly due to the larger real surface area of the sol-gel prepared coating.

The aim of this work was to investigate the activity and stability of a ternary Ti_{0.6}Ru_{0.3}Ir_{0.1}O₂ coating on titanium, prepared by the sol-gel procedure, under

the conditions of the chlorine and oxygen evolution. The anode characteristics were investigated in NaCl and H₂SO₄ solutions as well as in seawater, and compared to the characteristics of a binary Ti_{0.6}Ru_{0.4}O₂ coating.

EXPERIMENTAL

Coating Preparation

Colloidal monodispersions of ruthenium, iridium and titanium oxide were obtained by the forced hydrolysis of metal chlorides in boiling 0.27 mol dm⁻³ HCl.²⁷ The dispersions of RuO₂, IrO₂ and TiO₂ (oxide sols) were formed during 46, 20 and 10 h (ageing times), respectively. These distinct ageing times were chosen to prepare the sols since coatings with the best electrochemical properties were formed from them.¹⁸ The prepared oxide sols were mixed to form ternary or binary dispersions for the preparation of a coating with the desired composition of Ti_{0.6}Ru_{0.3}Ir_{0.1}O₂ or Ti_{0.6}Ru_{0.4}O₂. The dispersions were painted over Ti plates (1 cm×1 cm×0.89 mm), previously sand-blasted, degreased in saturated NaOH/ethanol solution and etched in hot 20 mass% HCl for 20 min. The coatings were applied in two layers, each converted into the gel phase at 90 °C and annealed at 450 °C, the first layer for 10 min and the second for 20 min, which developed the crystal structure of the oxide and provided good coating adhesion. The total coating mass was 1.0 mg cm⁻² (calculated to the overall oxide).

Coating morphology

The microscopic appearance of the prepared coatings was examined before and after an accelerated stability test (AST) by scanning electron microscopy (SEM), using a JEOL microscope, model JSM-T20 ($U_w = 20$ kV).

Basic electrochemical properties

The capacitive behavior of the prepared anodes was investigated by cyclic voltammetry in 1.0 mol dm⁻³ H₂SO₄, 0.50 mol dm⁻³ NaCl and in mixtures of these two solutions, at room temperature and a sweep rate of 20 mV s⁻¹. A Pt plate electrode was used as the counter electrode, while the reference electrode was a SCE, and all potentials are referred to the SCE scale.

The polarization characteristics of the prepared oxide coatings, in the solutions used in the cyclic voltammetry measurements and additionally in seawater sampled in the harbor of Tivat, Montenegro, were registered by anodic linear sweep voltammetry at a scan rate of 0.50 mV s⁻¹. The electrochemical cell was the same as that used in the cyclic voltammetry measurements.

Anode stability

The stability of the prepared anodes was investigated in seawater by AST at a current density of 0.60 A cm⁻² and a temperature of 16 °C. The end of anode service life was seen as a sudden increase in potential, which is a measure of the anode stability to passivation under the given conditions.

RESULTS AND DISCUSSION

SEM microphotographs of the Ti_{0.6}Ru_{0.3}Ir_{0.1}O₂ and Ti_{0.6}Ru_{0.4}O₂ coatings prepared by the sol-gel procedure on titanium are shown in Fig. 1. The surfaces of the coating appear like “cracked mud” consisting of islands separated by cracks, with a uniform crack width independent of the coating composition. The island border zone appears brighter than the bulk of islands, which is usually assigned to edge segregation of titanium oxide.^{17,28} This effect is more pronounced for Ti_{0.6}Ru_{0.4}O₂ than for Ti_{0.6}Ru_{0.3}Ir_{0.1}O₂ coating, which indicates more uniform composition (less pronounced TiO₂ edge segregation) of the ternary coating. How-

ever, the main difference in microscopic appearance between the binary and ternary coating should be addressed to the ubiquitous presence of sub-micron-sized spherical grains in the $\text{Ti}_{0.6}\text{Ru}_{0.3}\text{Ir}_{0.1}\text{O}_2$ coating (Fig. 1a), which occupy preferentially the hills of the coating (the coating is apparently not of uniform micro-thickness; the microphotograph in Fig. 1a was taken with a 45° incidence angle). The origin of grains could be assigned to the formation of a separate iridium oxide phase within the ternary coating, since the composition is the single qualitative difference between the binary and ternary coating.

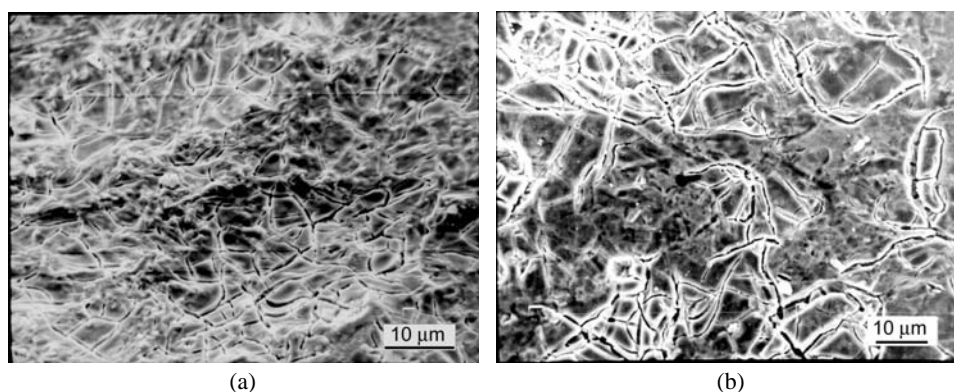


Fig. 1. SEM Microphotographs of the surface of sol-gel prepared: (a) $\text{Ti}_{0.6}\text{Ru}_{0.3}\text{Ir}_{0.1}\text{O}_2$ and (b) $\text{Ti}_{0.6}\text{Ru}_{0.4}\text{O}_2$ coatings on titanium.

Cyclic voltammograms of the prepared anodes, registered in H_2SO_4 , $\text{H}_2\text{SO}_4/\text{NaCl}$ and NaCl electrolyte are shown in Fig. 2. The voltammetric curves are of the characteristic shape for RuO_2 -based electrodes,^{1,17,18,29} which demonstrates the almost pure capacitive behavior of the anodes within the potential region of electrolyte stability.³⁰ A broad reversible peak appears around the potential of 0.60 V in the proton-containing solutions (Figs. 2A and 2B), which is assigned to the solid state surface redox transition (SSSRT) of Ru with participation of protons.^{29,30} The injection/ejection of protons involved in the following SSSRT²⁹ is seen at potentials below 0.10 V, which causes a pseudocapacitive energy storage (PCES) behavior of the coating in the potential region below 0.10 V (Figs. 2A and 2B). However, both capacitive features SSSRT and PCES are considerably suppressed in pure NaCl electrolyte (Fig. 2C), due to the lack of protons.

The capacitive behavior for the ternary and binary coating in the proton-containing electrolytes were similar (Figs. 2A and 2B). However, the voltammetric currents were lower in NaCl electrolyte for the ternary coating (Fig. 2C), due to the lower pseudocapacitive ability of IrO_2 with respect to RuO_2 .^{1,30,31}

The voltammogram in H_2SO_4 solution of the binary coating is more tilted due to a higher ohmic resistance (Fig. 2A). This could be caused by the more pronounced non-uniform composition of the binary coating, as seen in Fig. 1. The

coating parts with TiO_2 segregation (island edges) are regions with poor conductivity, since TiO_2 is known for its semi-conductive or insulating properties.¹ Through these regions, the current is carried preferentially by ions which fill the pores of the regions, making the total coating resistance dependent on the electrolyte resistance. As can be seen in Fig. 2B, the voltammograms are less tilted in $\text{H}_2\text{SO}_4/\text{NaCl}$ solution, due to the higher ion concentration and, consequently, lower resistance.

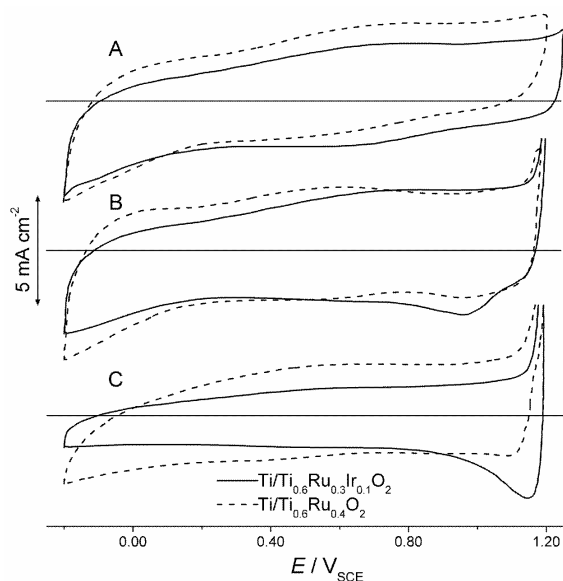


Fig. 2. Cyclic voltammograms of sol-gel prepared $\text{Ti}/\text{Ti}_{0.6}\text{Ru}_{0.3}\text{Ir}_{0.1}\text{O}_2$ and $\text{Ti}/\text{Ti}_{0.6}\text{Ru}_{0.4}\text{O}_2$ anodes registered in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ (A), $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 0.50 \text{ mol dm}^{-3} \text{ NaCl}$ (B) and $0.50 \text{ mol dm}^{-3} \text{ NaCl}$ (C) at room temperature and sweep rate of 20 mV s^{-1} .

An increase in the anodic currents is seen in the voltammograms registered in Cl^- -containing electrolytes at potentials more positive than 1.15 V (Figs. 2B and 2C), which corresponds to the onset of the chlorine evolution reaction (CER). The increase is followed by the appearance of a cathodic counterpart, assigned to the desorption of chlorine species,³² at potentials increasing with increasing chloride concentration. The counterpart is more pronounced for the ternary coating. Since the CER commences on the ternary coating at even more positive potential than on the binary one, the more pronounced counterpart could be assigned to the larger surface area of the ternary coating available for chloride oxidation. It is known that IrO_2 -containing coatings are more porous than those in which this oxide is not present.²¹ Note that the larger surface area of the ternary coating is not visible in the capacitive region due to its already mentioned lower pseudocapacitive ability with respect to the binary coating.

The polarization curves registered in different solutions and in seawater for the $\text{Ti}/\text{Ti}_{0.6}\text{Ru}_{0.3}\text{Ir}_{0.1}\text{O}_2$ anode are shown in Fig. 3, while those of the $\text{Ti}/\text{Ti}_{0.6}\text{Ru}_{0.4}\text{O}_2$ anode are presented in Fig. 4.

The currents of oxygen evolution were registered at the most positive potentials in H_2SO_4 solution (curve 1, Figs. 3 and 4). The Tafel slopes are close to

60 mV, which is the usual value for this type of anodes.^{33,34} When chloride ions were introduced into the H_2SO_4 solution, the Tafel plot for the chlorine evolution reaction was registered in the region of lower potentials (curve 2, Figs. 3 and 4). The slopes for both the ternary and binary coating are close to 35 mV, indicating the high activity of oxide coatings for this reaction.³⁵ The slope in NaCl solution (curve 3) was almost doubled when compared to the $\text{H}_2\text{SO}_4/\text{NaCl}$ solution. This is the consequence of the different reaction mechanisms. In acid chloride solution, protons are involved in the oxidation of the active sites, which makes the sites suitable for the adsorption of chlorine species.³⁶ The chlorine evolution reaction in such circumstances occurs at a lower overvoltage compared to the case in NaCl electrolyte.

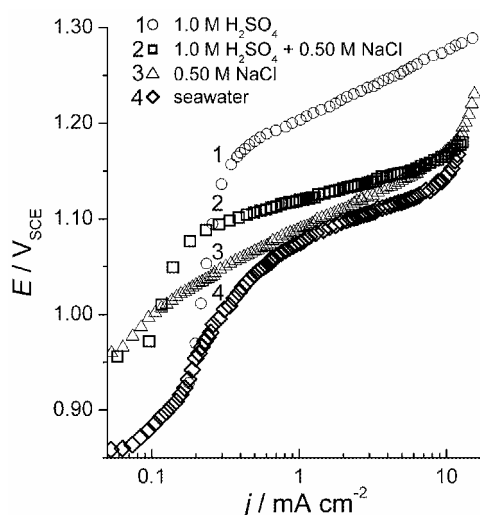


Fig. 3. Polarization curves for a $\text{Ti}/\text{Ti}_{0.6}\text{Ru}_{0.3}\text{Ir}_{0.1}\text{O}_2$ anode registered in different solutions and in seawater.

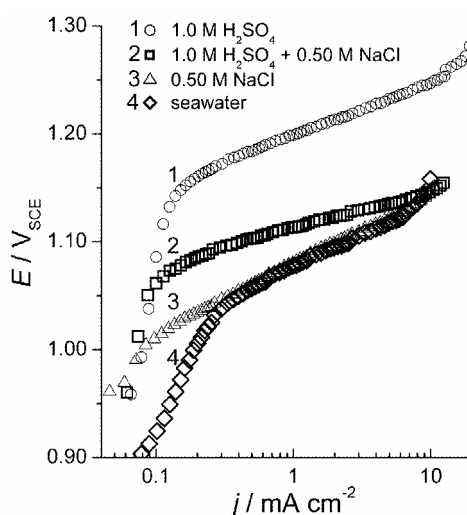


Fig. 4. Polarization curves for a $\text{Ti}/\text{Ti}_{0.6}\text{Ru}_{0.4}\text{O}_2$ anode registered in different solutions and in sea water.

The values of the current densities at potentials near the middle of the Tafel region, as registered in different solutions (Figs. 3 and 4), are given in Table I. Almost two times higher values were obtained for the binary coating in proton-containing solutions, while similar values for the binary and ternary coating were registered in NaCl solution and in seawater.

These results can be interpreted from two points of view: one is the dependence of the current on the real surface area and the other is the destruction rate of the oxide. It has already been mentioned in the discussion of the voltammetry results that the ternary coating should be more porous and of larger real surface area than the binary one. This makes the ternary coating more active at low overvoltages, as seen in Figs. 2B and 2C. It is seen also in the polarization curves from Figs. 3 and 4 that the currents were higher for the ternary coating up to

1.05 V_{SCE} and even up to 1.08 V_{SCE} in $H_2SO_4/NaCl$ solution. However, evolved gas fills the coating pores at high overvoltages, which causes a reduction in the charge transfer availability of the coating surface. Since the ternary coating was more active at low overvoltage and particularly because of its more porous structure, the reduction in charge transfer availability should be more pronounced for the ternary than for binary coating. Also, this reduction is more evident in the solution favorable for oxygen evolution, due to the lower solubility of oxygen in comparison to chlorine.

TABLE I. Current densities at given potentials registered for $Ti/Ti_{0.6}Ru_{0.3}Ir_{0.1}O_2$ and $Ti/Ti_{0.6}Ru_{0.4}O_2$ anode in different solutions

Solution	E / V_{SCE}	$j / mA\ cm^{-2}$	
		$Ti/Ti_{0.6}Ru_{0.3}Ir_{0.1}O_2$	$Ti/Ti_{0.6}Ru_{0.4}O_2$
1.0 mol dm^{-3} H_2SO_4	1.23	2.30	4.45
1.0 mol dm^{-3} H_2SO_4 + 0.50 mol dm^{-3} NaCl	1.13	1.73	3.02
0.50 mol dm^{-3} NaCl	1.10	1.86	2.00
Seawater	1.10	2.46	2.56

At higher overvoltages appreciable partial currents of the electrochemical dissolution of active oxide are to be expected.^{15,22,23} It is known that the destruction rate and, consequently, the partial currents of dissolution in anodic polarization are lower for IrO_2 when compared to those of RuO_2 .^{22,23} This was registered as lower overall current densities at high overvoltages (Figs. 3 and 4).

The good activity of the prepared anodes in seawater is important for their application in cathodic protection. The AST results for both the ternary and binary coating are shown in Fig. 5 as the time dependence of the anode potential at a constant current density. Since IrO_2 is more stable during the simultaneous evolution of oxygen and chlorine, the durability of the ternary coating is longer than that of the binary coating.

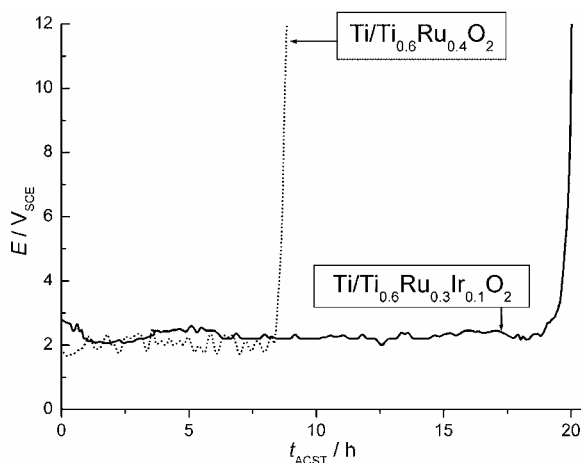
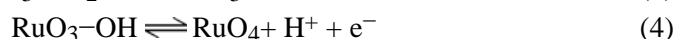
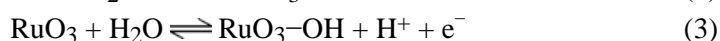
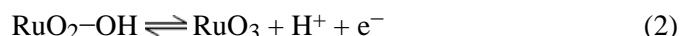
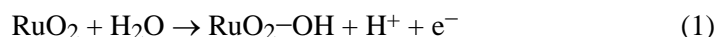


Fig. 5. Time dependences of the potential of a $Ti/Ti_{0.6}Ru_{0.3}Ir_{0.1}O_2$ and $Ti/Ti_{0.6}Ru_{0.4}O_2$ anode during the accelerated stability test in seawater at a current density of $0.60\ A\ cm^{-2}$.

A tentative explanation for considerably larger stability of the ternary coating could be as follows. The reactions of RuO_2 dissolution and oxygen evolution precede in parallel.¹⁵ The mechanism for RuO_2 dissolution could be:



while for oxygen evolution reaction proposed mechanism¹⁵ suggests that steps (3) and (4) should be replaced by:



The steps (1) and (2) are the same for the two reactions, with the formation of $\text{RuO}_2\text{-OH}$, step (1), as the rate-determining step. The species in the subsequent steps (3)–(5) decompose giving either oxygen or RuO_4 , which is soluble in acid solutions. However, when IrO_2 is present in the coating, oxygen evolution occurs mainly at the IrO_2 active sites. This hinders the decomposition reactions on the RuO_2 active sites and considerably extends the service life of the coating.

The effect of selective coating dissolution can be seen on SEM microphotographs given in Fig. 6, which illustrates the typical appearance of the ternary and binary coating after AST. Fig. 6a illustrates the appearance of the ternary coating along the hills at which the segregation of IrO_2 was seen on the freshly prepared coating (Fig. 1a). Complete depletion of the active material can be seen in the valleys of the coating, while it is retained to a great extent on the hills. This supports the conclusion that IrO_2 grains suppress the corrosion of the active material, while RuO_2 -rich regions corrode faster. On the other hand, the binary coating corrodes uniformly, with depleted regions appearing from place to place.

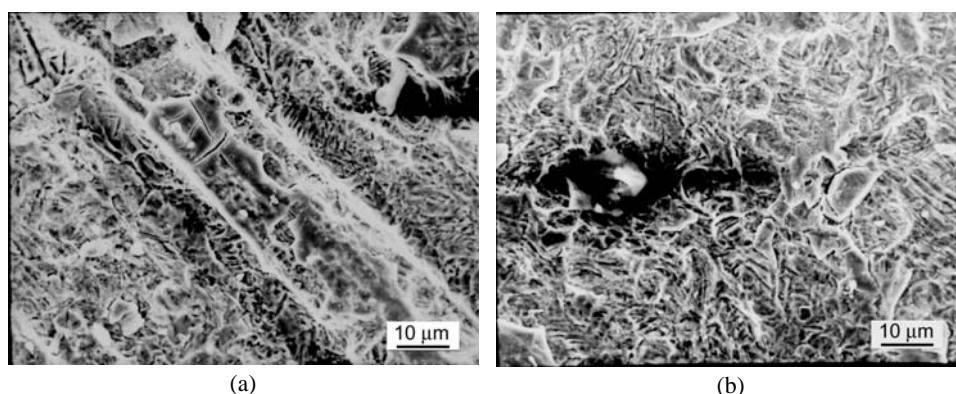


Fig. 6. SEM Microphotographs of the surface of sol-gel prepared: a) $\text{Ti}_{0.6}\text{Ru}_{0.3}\text{Ir}_{0.1}\text{O}_2$ and b) $\text{Ti}_{0.6}\text{Ru}_{0.4}\text{O}_2$ coatings on titanium taken after the accelerated corrosion stability test.

CONCLUSIONS

The properties of sol-gel prepared ternary $Ti_{0.6}Ru_{0.3}Ir_{0.1}O_2$ and binary $Ti_{0.6}Ru_{0.4}O_2$ coatings on titanium with respect to their possible application for cathodic protection in seawater environments were investigated by scanning electron microscopy, cyclic voltammetry, polarization measurements and accelerated stability test in H_2SO_4 and NaCl solutions as well as in seawater.

The microscopic appearance of the ternary coating indicates segregation of IrO_2 in the sub-micron grains in the region of the hills in the coating.

Cyclic voltammetry investigations showed similar capacitive behavior of the ternary and binary coating, while the ternary coating seemed to be more active for chlorine evolution.

The polarization characteristics of the prepared coatings indicated similar activity of the ternary and binary coating in H_2SO_4 , $H_2SO_4/NaCl$ and NaCl solutions, while the partial currents related to the dissolution of the active material of the ternary coating was less pronounced than in the case of the binary coating at high overvoltages.

The results of an accelerated stability test of the prepared coatings showed that the ternary coating was considerably more stable during exploitation in seawater than the binary one, which is the consequence of the greater stability of IrO_2 under vigorous oxygen and chlorine evolution in comparison to RuO_2 . This fact makes the ternary coating a better candidate as the anode in real applications.

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ИЗВОД

АКТИВНА ОКСИДНА ПРЕВЛАКА НА ТИТАНУ ДОБИЈЕНА СОЛ-ГЕЛ ПОСТУПКОМ
КАО АНОДА ЗА КАТОДНУ ЗАШТИТУ У МОРСКОЈ ВОДИВЛАДИМИР ПАНИЋ¹ и БРАНИСЛАВ НИКОЛИЋ²

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Карактеристике тројне оксидне превлаке на титану, која се састоји од TiO_2 , RuO_2 и IrO_2 у молском односу 0.6:0.3:0.1 рачунато на атом метала, испитиване су са циљем потенцијалне примене за катодну заштиту у морској води. Оксидна превлака на титану формирана је сол-гел поступком из смеше неорганских оксидних солова, који су добијени форсираном хидролизом хлорида метала. Морфологија превлаке је испитивана скенирајућом електронском микроскопијом, док су електрохемијска својства активираних титанких анода испитивана методом цикличне волтаметрије и поларизационим мерењима у растворима H_2SO_4 , NaCl и у реалним условима, у морској води узоркованој из Јадранског мора (Тиват, Црна Гора). Стабилност аноде током рада у морској води испитивана је галваностатски, убрзаним тестом стабилности. Добијене превлаке упоређене су са двојном $Ti_{0.6}Ru_{0.4}O_2$ превлаком, у погледу морфологије и електрохемиских карактеристика. Показано је да су тројна и двојна превлака сличне активности у испитиваним растворима. Међутим, у морској води стабилност тројне превлаке је знатно већа.

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