METAL OXIDES TiO_2, IrO_2, RuO_2, Ce_2O_3, Ce_3O_4, SnO_2: PROMISING MATERIALS FOR ELECTROCHEMICAL PROCESSES

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Abstract

The work is devoted to the development of technology for obtaining and studying the physicochemical characteristics of oxide coatings of noble (IrO_2, RuO_2), rare earth (Ta, Nb, Ce) metals, and TiO_2, SnO_2 based on a titanium, that has undergone the primary chemistry.

Important technological characteristics (adhesion, roughness) which show the principal possibility of using the obtained samples as anode materials for the electrolysis of aqueous solutions for the purpose of purifying wastewater or the production of sodium hypochlorite as a reagent were determined. Studies conducted by the XPS, obtained microphotographs and surface profiles confirm the prospect of using these oxide coatings as electrode materials.

The electrochemical characteristics we studied make it possible to determine the field of application of the obtained electrodes more accurately for the reaction of chlorine and oxygen evolution with RuO_2 and IrO_2.

Keywords: Ruthenium oxide, cerium oxide, iridium oxide, tin oxide, titanium oxide

1. INTRODUCTION

Because of their chemical resistance in aqueous and non-aqueous electrolytes, catalytic activity, high developed surface and developed production technology, oxides of noble (IrO_2, RuO_2), rare earth (CeO_2) metals and TiO_2, MnO_2, PbO_2, SnO_2, Co_3O_4 have found wide application in high-tech industries (energy sources and energy transducers, electrode materials, catalysis, etc.) [1- 4].

The phase and elemental composition, electrical conductivity, disperse properties, the degree of oxidation of the metal, the presence of impurities and active forms of oxygen in the near-surface layer of the oxide have an influence on the resulting physicochemical and electrocatalytic properties. The electrodes including IrO_2 and RuO_2 arouse interest. They have a high activity in many electrochemical processes. The work on this subject is being carried out around the world [5 - 8].

2. EXPERIMENTAL MATERIALS

The samples were produced in the scientific laboratory "New electrochemical technologies and materials" of the Technopark "Ecohimbiznes-2000" of the D. Mendeleev University of Chemical Technology of Russia. The methodology of production was well-tested earlier [1].

Titanium ingots of BT-1-0 grade were subjected to the **abrasive-jet treatment** in a KSO 60-I to increase the surface roughness and remove titanium oxides. Subsequently, the samples were degreased in a solution of 1M KOH and etched in an 18% solution of hydrochloric acid at 80 °C.

After preparatory processes the samples were thoroughly washed with distilled water and covered with coating solutions containing titanium, tin and noble metal chlorides. Further, the samples were oven-dried in SHS-80-01-SPU/350C, and then calcined for 30 minutes in an electric furnace SNOL at 350 °C. The final layer was calcined for 45 minutes at 420 °C. Thus the oxides of these metals are forming.

The coating solutions were prepared by mixing the chlorides of Ru, Ir, Sn, Ce with 0.9M concentration and a solution of 1.66M titanium chloride within proportions with the addition of a small volume of a mixture solution of butanol and isopropanol.

The adhesion of the obtained coating to the titanium base was determined on the device Elcometer 107 and tested on a PosiTest AT-M 20mm, the gloss was determined by the instrument Elcometer 480, the roughness - with the profilometer mitutoyo Surftest sj-310.

The electrochemical characteristics of the samples were measured on a potentiostat-galvanostat "P-30J".

XPS was conducted in an ultrahigh vacuum of $6.9 \cdot 10^{-8}$ Pa on an X-ray photoelectron spectrometer «PHI Quantera» («Physical Electronics», USA).

The photomicrographs of the surface of the obtained samples were made with a scanning electron microscope JEOL 1610LV (JEOL, Japan) and in the D. Mendeleyev CCU.

The surface morphology was studied using an atomic force microscope INTEGRA Prima (NT-MDT, Russia). ScanMode - semicontact, cantilever - NSG10.

3. EXPERIMENTAL WORK

After testing the manufacturing technology, a pilot batch of electrodes was produced. Further these ones were investigated and tested (samples 2 - 4). The classical ORTA anode was used as a reference sample (sample 1). The composition of the samples is shown in **Table 1**.

Table 1 Effect of the coating composition on the physicochemical characteristics of electrodes based on four-valence metal oxides: titanium, ruthenium, iridium, cerium and tin

№	Coating composition				Roughness	Glossiness		
	RuO_2	IrO_2	SnO_2	CeO_2	**(μm)**	20°	60°	85°
1	35	-	-	-	1.0 - 1.2	0.7	2.5	3.1
2	17.5	17.5	-	-	1.1 - 1.3	0.4	2.2	2.8
3	17.5	-	17.5	-	0.75 - 0.85	0.9	3.5	12.6
4	17.5	-	-	17.5	0.91 - 0.96	0.7	2.5	6.5

The effect of a larger replacement of ruthenium on cerium and tin was studied further in samples 3 and 4. The densification of cerium to 25% (the reducing the concentration of ruthenium up to 10%) contributes to an roughness increase to 0.93-1.08 μm, in contrast to tin which significantly reduces it to 0.53-0.56 μm.

The obtained values of the roughness for reference sample №1 - ORTA (DSA) and manufactured electrode samples were very similar, but values for ruthenium oxide were a bit higher.

The samples had a good adhesion (value - 0), which confirms the reliable adhesion of the metal-oxide coating with titanium base.

It was found that the samples with cerium oxides were similar in reflecting properties with reference sample based on ruthenium oxide, but the sample with tin had differs significantly, especially at a high direction angle of the light ray.

Since an extremely important characteristic of the resulting coatings was the developed surface, the 3D surface studies were performed and photomicrographs were taken. The results are shown in **Figures 1** and **2**.

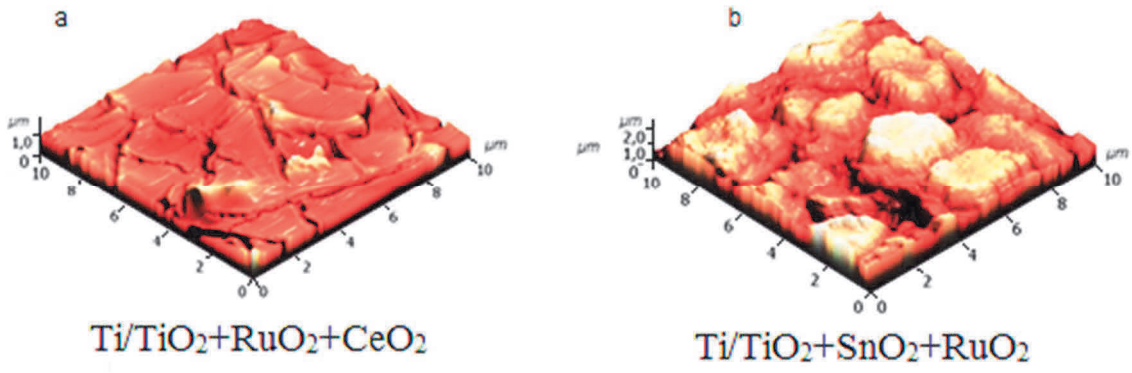

Figure 1 Surface morphology CeO_2 and SnO_2

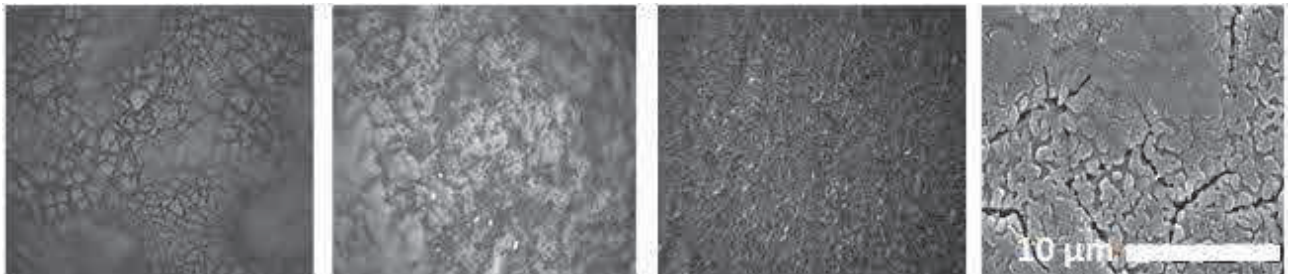

Figure 2 Photographs of SEM of obtained oxide coatings

The electrochemical studies were carried out to confirm that the resulting electrodes have a highly developed surface, and can have catalytic activity [3]. The results are shown in **Table 2**.

Table 2 Electrochemical characteristics

№	Coating composition				Characteristics			
	RuO_2	IrO_2	SnO_2	CeO_2	E_i = 0 in 10 min (mV)		I at E = 1.4 V (mA/cm^2)	
					NaCl	Na_2SO_4	NaCl	Na_2SO_4
1	35	-	-	-	267	362	0.1	0.005
2	17.5	17.5	-	-	247	445	0.5	0.08
3	17.5	-	17.5	-	443	430	0.05	0.01
4	17.5	-	-	17.5	563	380	0.29	0.07

Experimental conditions: C_{NaCl}, C_{Na2SO4} - 1 M, τ - 10 min.

Electrode with RuO_2 and IrO_2 has the highest activity of chlorine and oxygen evolution. The effect of a larger replacement of ruthenium on cerium and tin on the electrochemical parameters was studied in samples 3 and 4. The densification of cerium to 25% (the reducing the concentration of ruthenium up to 10%) increases the currentless potential in a solution of 1M Na_2SO_4, and reduces it in 1M NaCl.

The obtained electrochemical characteristics indicate that it's possible to principally substitution expensive ruthenium for cheaper tin or cerium for some electrochemical processes, which don't possess high aggressiveness (for example**, waste water** treatment). The photoemission spectra of the samples are shown in **Figure 3**.

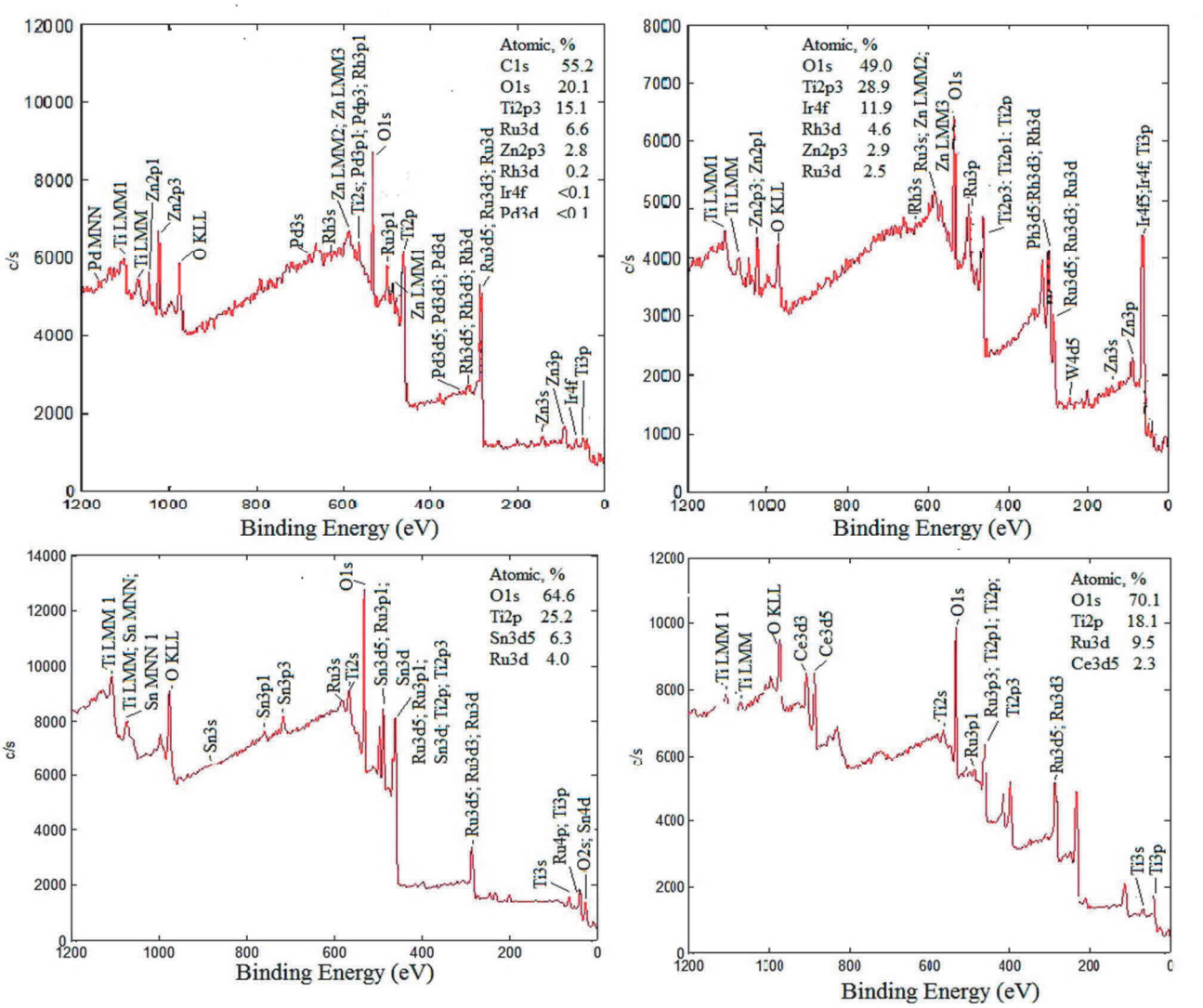

Figure 3 Photoemission spectra of the samples

The data obtained earlier for samples 1 and 2 are presented for comparison [1]. They contain non-stoichiometric titanium oxides, but the degree of titanium oxidation in them is sharply different: in sample №1 is found $TiO_{1,33}$, in sample №2 - $TiO_{1.7}$. The first corresponds to Ti_2O_3, the second corresponds to Ti_3O_5.

In the sample №3 studied in this work a solid solution of Ti_2O_3 with O_2 + RuO_2 non-stoichiometry is located in the layer up to 50 nm. TiO_2 is located on the surface, then Ti^{3+} is seen at a depth of 50 nm, the XPS lines with an energy of 530 eV peak of the presence of RuO_2. Also on the surface Sn^{2+} was found. Sn^{2+} is shifting into Sn^0 at a depth, Sn^{4+} was not detected at all.

In the sample №4 the solid solution of TiO_2 with oxygen and ruthenium oxides non-stoichiometric is placed on the surface. There were no other titanium oxides except (IV). On the surface a mixture of about 90% RuO_4 with an admixture of about 10% RuO_2 is present. With a deepening it splits into a mixture of 52% RuO_4 and 48% Ru^0.

Unlike the sample with tin (№3), where oxygen is not established separately, the oxygen on the surface in hydroxyl group of OH^- passes into O^{2-} at the depth.

There is a doublet of two peaks of 887 and 905 eV from Ce^{4+} on the surface, then they disappear at a depth of 50 nm and there are three peaks (882 eV, 886 eV and 904 eV) from mixture of Ce_2O_3 and CeO_2, in which Ce_2O_3 is predominated.

CONCLUSION

Thus, the studies conducted by the XPS have given a greater understanding of the nature of the formed oxide coating. More interesting mixtures from the catalytic point of view are formed, but not stoichiometric relations (for example, Ce (III) and Ce (IV)) [7].

Researches of physical-chemical and electrochemical properties of titanium electrodes coated with oxides of Ti, Ru, Ir, Sn, Ce were conducted. They showed the potential possibility of their use for the treatment of wastewater by electrolysis [2] and some other electrochemical applications [1, 8]. The obtained data are undoubtedly interest from a practical point of view, because such systems are finding increasing use in chemical engineering and technology [9 - 11].

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