# Surface Morphology and Chemical Composition of Thermally Prepared $(RuO_2)_x(Ta_2O_5)_y$/Ti Coatings

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## Abstract

A binary coating with the nominal composition $(RuO_2)_x(Ta_2O_5)_y$/Ti deposited on a Ti substrate has been prepared by thermal decomposition of $RuCl_3.xH_2O$ and $TaCl_5$ solutions at 450 °C. Surface morphology and microstructure of the coatings were investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDS). The aim of this work is to analyze the effect of the replacement of $TiO_2$ by $Ta_2O_5$ in a binary composition with ruthenium oxide. The influence of the addition of $Ta_2O_5$ on the morphological properties of the surface film is discussed.

**Keywords:** DSA, Ruthenium oxide, Tantalum oxide, SEM, EDS.□

## Introduction

The need of a new technology for removal of organics from aqueous effluents is widely recognized and electrochemistry offers an approach to develop such technology (1). Metal oxide coating consisting of ruthenium and titanium oxides thermally prepared on titanium substrates have received much attention as a catalyst for electrochemical oxidation of organic pollutants. Such coating is generically denominated DSA-type electrodes. In previous studies, it has been shown that the organic oxidation at DSA-type material occurs under simultaneous $O_2$ evolution (2). Under this condition, the service life of a DSA-type material is relatively low, mainly due to the anodic passivation of the titanium substrate (3). The replacement of titanium dioxide ($TiO_2$) by $Ta_2O_5$ enhances the electrode lifetime; in fact the commercial electrode for oxygen production is based on $30\%IrO_2/70\%Ta_2O_5$ (4). Another advantage of changing titanium oxide by tantalum oxide is based in the fact that the later one has lower specific resistivity (13 μΩ cm) compared with titanium oxide (42 μΩ cm) (5). The aim of this work is to analyze the effect of the replacement of $TiO_2$ by $Ta_2O_5$ in a binary composition with ruthenium oxide, named: $(RuO_2)_x(Ta_2O_5)_y$/Ti. The influence of the addition of $Ta_2O_5$ on the morphological properties of the surface film is discussed.

## Materials and Methods

Electrodes of nominal composition $(RuO_2)_{0.1}(Ta_2O_5)_{0.9}$/Ti and $(RuO_2)_{0.5}(Ta_2O_5)_{0.5}$/Ti) were prepared from appropriate mol ratio by thermal decomposition at 450 °C from alcoholic (isopropanol (Aldrich)) solutions of the precursors mixtures ($RuCl_3.xH_2O$ and $TaCl_5$ (Aldrich)). The corresponding inorganic salts solution was dropped on a pre-treated Ti-support base as described previously (6). A solution layer formed on the Ti electrode was dried at low temperature (80 – 90 °C) in order to evaporate the solvent, then fired at 450 °C for 5 min. in a 5 $dm^3$ $min.^{-1}$ $O_2$-flux. This procedure was repeated until the desired nominal oxide loading surface layer (2 μm or 10 μm) was reached. The electrode was finally annealed for 1 h at the same temperature and under $O_2$-flux. Duplicate samples were prepared for each electrode composition.

Surface morphology, microstructure and elemental composition of the deposited oxide films were analyzed by scanning electron microcopy (SEM) and energy-dispersive X-ray spectrometry (EDS) in a Leica-Zeiss LEO 440 model SEM coupled to an Oxford 7060 model analyzer.

## Results and Discussion

Figure 1 shows the comparative scanning electron micrographs of the different $RuO_2/Ta_2O_5$ films prepared. The oxide surface morphology shows a clear relationship with the coating composition and thickness investigated. For instance, thinner films (2 µm) containing high amounts of $RuO_2$, i.e., 50% mol, shows compact and not very rough surface with small portions of fissures and cracks (Figure 1a). As the thickness of the oxide loading is increased (10 µm, Figure 1b) the amount of fissures and cracks increase and the coating shows a rough morphology with the typical mud-flat cracking (2 - 7 µm) (6, 7). As the Ru loading is lowered (10% mol) and nominal thickness is kept at 2 µm, the crack-mud aspect of the surface vanishes and a more compact structure is observed (Figure 1c and 1d). In fact, this later oxide composition presents a fine microstructure and the micrograph presents a smoother microstructure not affected by cracks, even for the thicker film (Figure 1d).

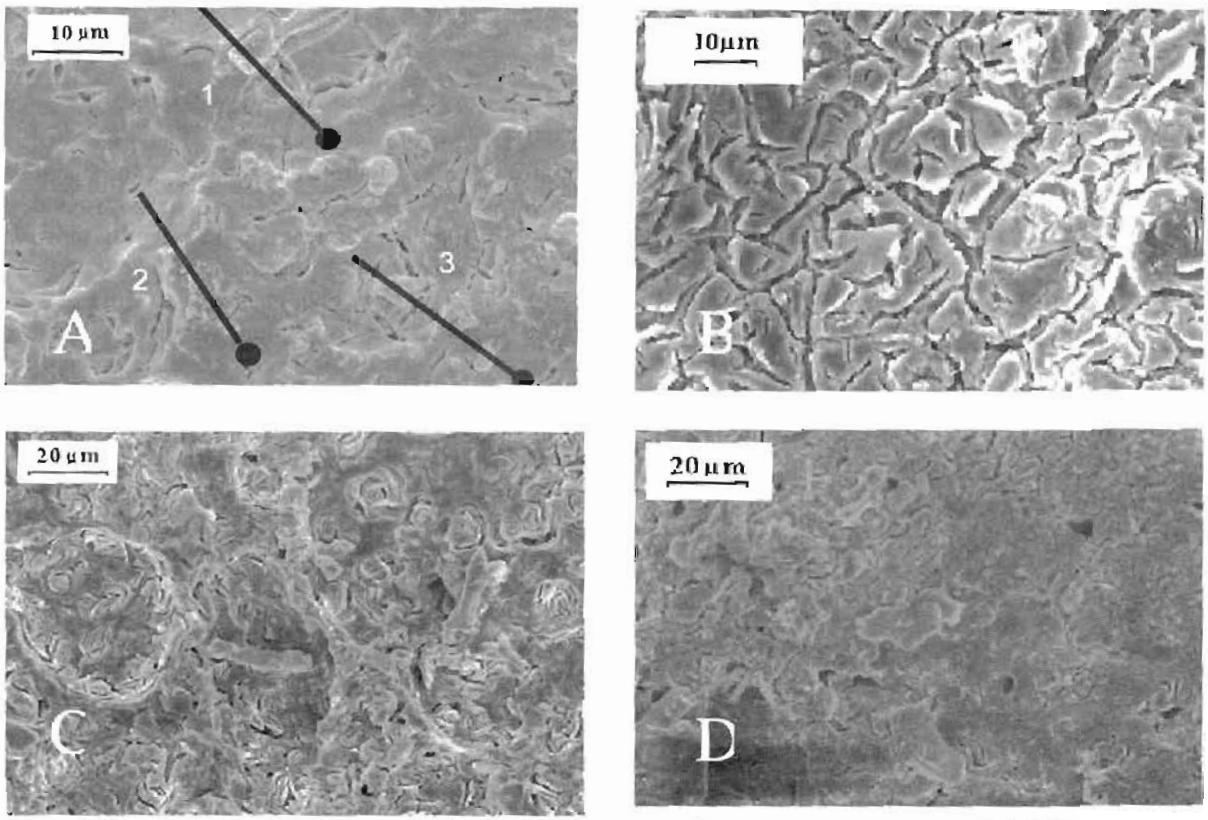


Figure 1. SEM pictures of $(RuO_2)_{0.5}(Ta_2O_5)_{0.5}$ oxide layer: (a) $(RuO_2)_{0.5}(Ta_2O_5)_{0.5}/Ti$, nominal thickness 2 µm, (b) $(RuO_2)_{0.5}(Ta_2O_5)_{0.5}/Ti$, nominal thickness 10 µm, (c) $(RuO_2)_{0.1}(Ta_2O_5)_{0.9}/Ti$, nominal thickness 2 µm and (d) $(RuO_2)_{0.1}(Ta_2O_5)_{0.9}/Ti$, nominal thickness 10 µm. $T_{dec}$ 450 °C; $O_2$-flux 5 dm$^3$min$^{-1}$.

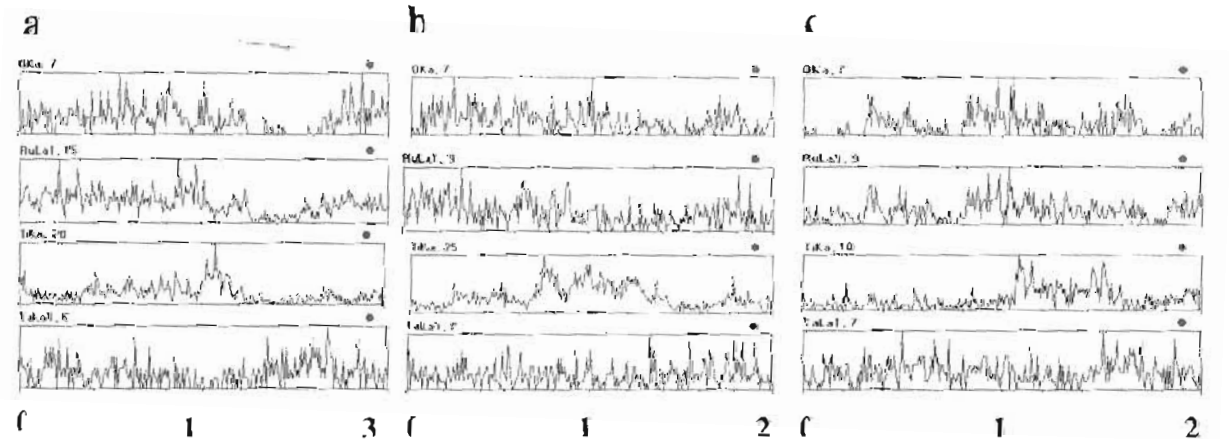


Figure 2. EDS line analyzes for O, Ru, Ti and Ta in the $(RuO_2)_{0.5}(Ta_2O_5)_{0.5}/Ti$ oxide layer. (a) line 1, (b) line 2 and (c) line 3 from figure 1a.

In order to check the homogeneity of the oxide coating it was done EDS line analyzes in three distinct regions of Fig. 1a. Figure 2 shows the qualitative variation of the atomic concentration of the elements analyzed (O, Ru, Ti and Ta). The circles sign in Fig. 1a indicates the beginning of the analysis scan. The composition of three analyzed elements (oxygen, ruthenium and tantalum) present almost homogeneous distributions along the lines. Nevertheless, titanium composition shows a suddenly increase as the scanning cross a fissure or a crack on the oxide layer. Additionally, the Ti-signal almost vanishes when the EDS probe scans region whit low porosity or non-cracked surface.

Table 1 shows the EDS semi-quantitative analizes for the four film investigated. The experimental and the theoretical composition of the studied surfaces show an excellent agreement. The exception is only observed for the thick oxide layer (10 μm) containing the nominal composition of 50% mol of $RuO_2$ that shows a depletion of the Ru amount when compared with the nominal composition and, a consequent enrichment of Ta is also observed. This suggests that for this specific coating there is a Ta-rich outermost surface layer that segregates from the innermost $RuO_2$. It is important to stress out that Ti signal was not observed when the nominal thickness was 10 μm. Nevertheless, in thinner layers Ti was detected from the Ti-base. Therefore, the data shown in Table 1 for 2 μm of nominal thickness was calculated without considering the Ti-atomic percentage.

Analyzes performed at random points (Figure 3) showed an excellent relationship between the experimental and the expected amounts of Ru and Ta, and are similar to the values shown in Table 1. The dot mapping showed no phase segregation on a sub-micrometer level for the analyzed elements in all investigated $RuO_2/Ta_2O_5$ systems, as shown in Figure 4.

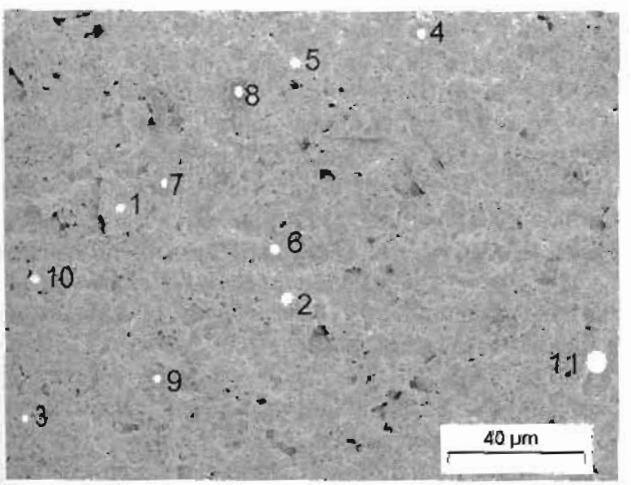


**Figure 3.** SEM picture of $(RuO_2)_{0.5}(Ta_2O_5)_{0.5}$ oxide layer with nominal thickness of 10 μm; $T_{ox}$: 450°C; $O_2$-flux: 5 dm$^3$min$^{-1}$

Table 1. Nominal and experimental EDS composition of $(RuO_2)_x(Ta_2O_5)_{1-x}$ oxide layers.

| Atomic percentage, nominal and experimental / % | | | |
|---|---|---|---|
| 2 (20) μm | | 10 (70) μm | |
| Ru | Ta | Ru | Ta |
| 10 (11) | 90 (88) | 10 (13) | 90 (87) |
| 50 (54) | 50 (46) | 50 (29) | 50 (71) |

( ) Experimental data

The data shown in Table 1 were obtained by the matrix interference, atomic number, absorbance and fluorescence (ZAF correction) (8).

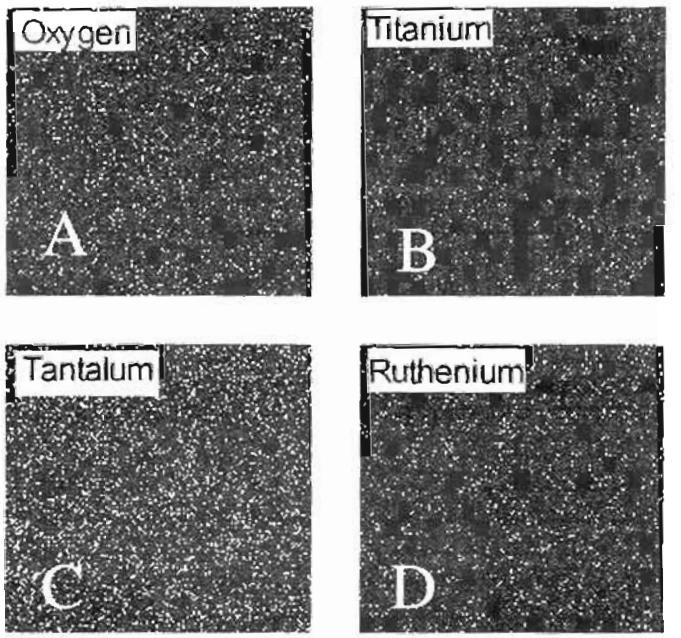


**Figure 4.** Dot maps for: (a) Oxygen, (b) Titanium, (c) Tantalum and (d) Ruthenium obtained focusing Figure 3.

Figure 5 shows a representative side picture of the oxides deposited on Ti-base. The transversal section analyses of a nominal 10 μm thick sample containing 50% mol of $RuO_2$, shows three different regions: (i) the first one contains the oxide layer with an average value of approximately 70 μm (7 times greater than the nominal thickness); (ii) one second intermediate region with 60 μm; and (iii) the third region is related to the metallic titanium base. A EDS line analysis was performed over the line displayed in Figure 5, covering the whole transversal surface of the sample (200 μm). These data confirm the three region observed in the corresponding SEM picture and, shows that at the intermediate region, located between the rich oxide layers and the Ti-base, the Ti amount decreases smoothly as one moves away from the metallic base. The Ta and Ru amounts increase in the opposite direction. In the pure oxides layer it was not observed Ti incorporation. These results suggest that the presence of titanium observed focusing the electrode from

the side position is due to the metallic base instead of it incorporation into the Ru-Ta oxides layer.

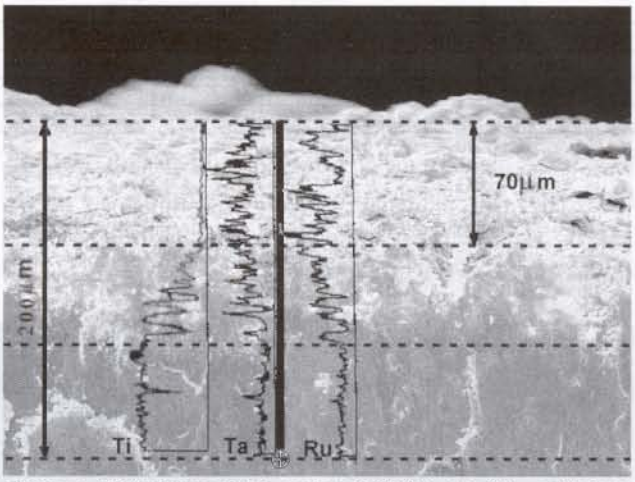


**Figure 5**. SEM picture of side section of $(RuO_2)_{0.5}(Ta_2O_5)_{0.5}$ oxide layer with nominal thick of 10 µm. $T_{calc.}$ 450 °C; $O_2$-flux, 5 $dm^3min^{-1}$. EDS data for Ti, Ta and Ru performed in the thicker dark line.

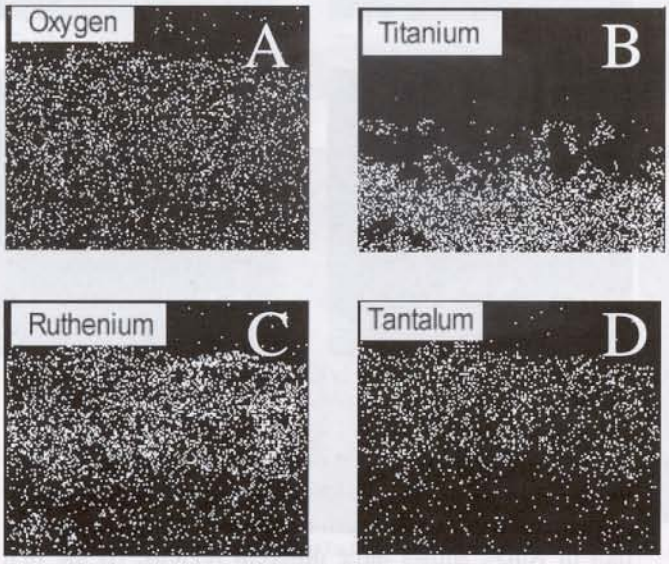


**Figure 6**. Dot maps for: (a) Oxygen, (b) Titanium, (c) Ruthenium and (d) Tantalum obtained focusing Figure 5 picture.

The transversal section shows an apparent inter-diffusion of ruthenium and tantalum into the titanium substrate. The dot map profile (Figure 6) suggests that it contains larger amount of ruthenium than tantalum. This can be explained due to the better interaction between ruthenium and titanium atoms, which favors the formation of solid solution (9).

The EDS analysis also reveals the presence of oxygen into the titanium base, suggesting that the substrate can be oxidized during the calcination process. From the other samples analyzed may conclude that the experimental thickness of the $(RuO_2)_{0.1}(Ta_2O_5)_{0.9}$/Ti oxide coating has an average of 10 times greater than the nominal thickness. Furthermore, it is suggested that a deep oxidation of the Ti-substrate during the process of preparing the oxide layer have provoked the increase of its thickness, or formation of low-density material.

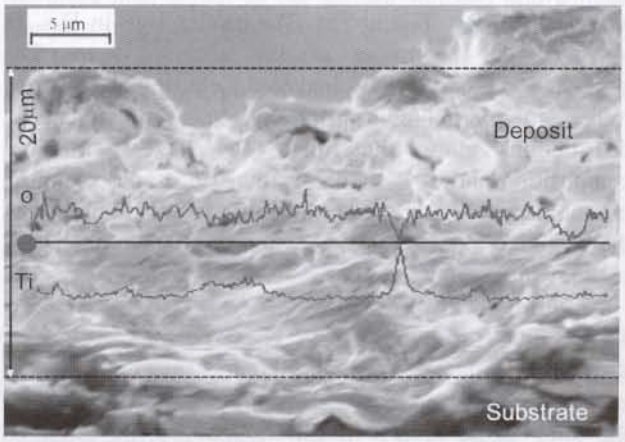


**Figure 7**. SEM micrograph of the layer 10% $RuO_2$ 2 µm with the elemental line scan microanalysis. $T_{calc}$, 450 °C; $O_2$-flux, 5 $dm^3min^{-1}$.

Figure 7 shows the SEM and the EDS analysis for Ti and O atoms of $(RuO_2)_{0.1}(Ta_2O_5)_{0.9}$/Ti oxide coating with nominal thickness of 2 µm. It is possible to observe that the Ti signal increase with simultaneous depletion of the O-one, under this thickness condition. This suggests that the titanium substrate in the region close to the oxide layer is not present in a pure oxide form, indeed it is only partially oxidized. Further confirmation about the oxidation state of the elements in the mixture it is only possible with more detailed characterization e.g., X-ray photoelectron spectroscopy (XPS) and electron spin resonance.

## Conclusions

The preparation and characterization of $(RuO_2)_x(Ta_2O_5)_y$/Ti mixed oxide system has been studied by SEM and EDS techniques. The SEM micrographs show that the oxide surface morphology has a clear relationship with the coating composition and loading thickness. Rich Ru-containing films show the typical mud-flat crack morphology. An increase of the thickness promotes enhancement of the roughness of the sample. Low amount of ruthenium coating shows more compact and smooth morphology independently of the nominal thickness of the layer deposited.

The EDS analyses shows a good relationship between the nominal and the experimental composition of Ru and Ta, the exception is for the thicker layer with 50% mol of $RuO_2$ which shows the Ta outermost surface enrichment.

The dot mapping of Ru and Ta oxides showed that the elements Ta, Ru and O are homogeneously distributed along the surface of the oxides coating.

The EDS microanalysis performed in the transversal section of the film shows the occurrence of an important concentration gradient in the interlayer region. The side dot mapping of the interlayer shows enrichment of ruthenium in the titanium substrate.

## Acknowledgments

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