Structure and properties of ruthenium coatings on titanium *

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The paper presents results of tests performed for the ruthenium oxide coating chemically spread on titanium surface of technical grade, and properly heat treated. By means of optical and scanning microscopy as well as X-ray microanalysis it was found that the coating had granular structure with distinctly marked borders of "a slot in dried sludge" type. Such coating is characterized by significantly lower resistance to polarization than that of metallic titanium and titanium with oxygen enriched diffusive layer, and thus ensures good conductance.

1. INTRODUCTION

Coatings composed of mixtures of ruthenium oxide and titanium oxide or iridium oxide and titanium oxide are used as catalysts in electrolysis [1,2,3]. To obtain such coatings the salts of these metals are used, e.g. ruthenium trichloride ($RuCl_3$) or titanium trichloride ($TiCl_3$). Coating application consists in:
- preparation of the mixture with appropriate solvent;
- spreading of mixture on active elements of an anode;
- drying;
- heat treatment in order to reduce salts to oxides.

The most common application of these coatings is chlorine electrolysis, however they can be also applied in other electrolytic processes. Dimensionally stable electrodes [4] having their active element in a form of titanium grid or plate coated with active coating can be applied for metal recovery from anode slime, in production of iodates or zinc where they can replace lead electrodes. Manufacturing costs for dimensionally stable electrodes with active coating are undoubtedly high due to application of very expensive metals (ruthenium, iridium). However, in some cases they can advantageously replace lead electrodes giving product not contaminated with lead or enabling higher output of electrolysis.

2. MATERIALS AND TESTING METHODS

Performed tests refer to titanium of technical quality Grade 1 containing 0.04% Fe, 0.08% O and rest of Ti – in initial state after oxygenation and after application of ruthenium coating. Oxygenation has been performed in temperature of 900°C for 2 hours in surrounding atmosphere with subsequent fast cooling in oil. Ruthenium coating has been applied by immersion in solution composed of ruthenium trichloride and titanium trichloride dissolved in butanol. Two solutions have been prepared for this purpose, the first composed of $RuCl_3 \cdot 3H_2O$ (100 g) dissolved in butanol (1:1); and the second composed of $TiCl_3$ (100g) and butanol (1:1) with addition of hydrochloric acid (0.05 l). Just before application the solutions have been transformed into a lacquer in which the test specimens had been immersed. Then, the volatile solvent has been removed from specimens by drying in temperature of 280 ÷ 300°C for 10 minutes. Entire process has been repeated five times and then the coating has been formed by annealing in temperature of 500°C for 3 hours and cooling down first in furnace to about 200°C and then in ambient temperature. Structural tests have been performed on polished sections as well as on outer surface of coating by means of an optical microscope, electron microscope SEM and X-ray microanalysis. Investigations of resistance to polarization have been done with dynamic-potential method by means of PGP 201 Potentiostat/Galvanostat using three electrode chamber with calomel electrode as reference and platinum electrode as auxiliary one. 3.5% solution of NaCl at room temperature has been used as an electrolyte.

3. RESULTS OF TESTS

Ruthenium layer at outer surface is made up of individual grains with characteristic form of "dried sludge" (Fig. 1). Boundary regions compose visible discontinuities similar to those which appear inside crystallites (Fig. 2). Such type of structure points to necessity of repeated immersion in prepared gel (lacquer) followed by preliminary drying for solvent vaporization. Performed microanalysis shows that the grains contain 45% by weight of both ruthenium and oxygen and 10% of titanium (Fig. 3). Lack of chlorine and decided overbalance of oxygen (81% at) let us make conjectures that the rutile TiO_2 is the main component of the layer, and that from basic ruthenium oxides as ruthenium dioxide RuO_2, ruthenium sesquioxide Ru_2O_3, ruthenium pentoxide Ru_2O_5 and ruthenium octaoxide RuO_4, the latter prevails. Very fine and bright precipitates disposed mainly at grain boundaries are visibly enriched of ruthenium and impoverished of titanium. The layer is bonded with surface mainly by mechanical adhesion. Therefore, it showed tendency to cracking while test specimen was being thermally mounted (Fig. 4). Dynamic-potential tests, especially the shape of anode polarization curve of technical grade titanium let us conclude that the passive state current is very stable (Fig. 5) whereas corrosion potential E_{cor} and current density i_{cor} are low with simultaneously very high resistance to polarization (Table 1). For oxygenated titanium substantial decrease of E_{cor} and i_{cor} with simultaneous rapid decrease of resistance to polarization R_p can be observed. After application of ruthenium coating on specimens made of titanium and oxygenated titanium a significant change of anode polarization curve shapes and numerical results of dinamic-potential tests. Change of curve shape refers to passive state range being limited to about 1000 mV (Fig. 6). In comparison with titanium without ruthenium coating occur an intensive, nearly eightyfold increase of current density and rapid, nearly 250-fold decrease of resistance to polarization.
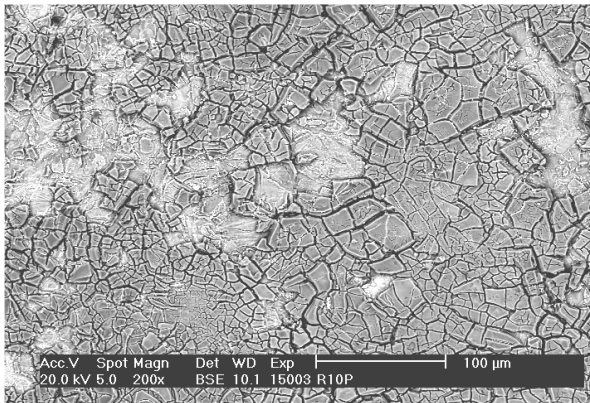
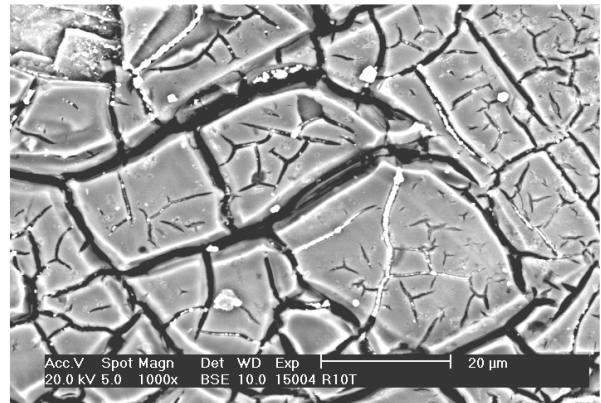Fig. 1. Outer layer of ruthenium coating on titan

Magnification: 200x

Fig. 2. Outer layer of ruthenium coating on superficially oxygenated titanium.

Magnification: 1000x

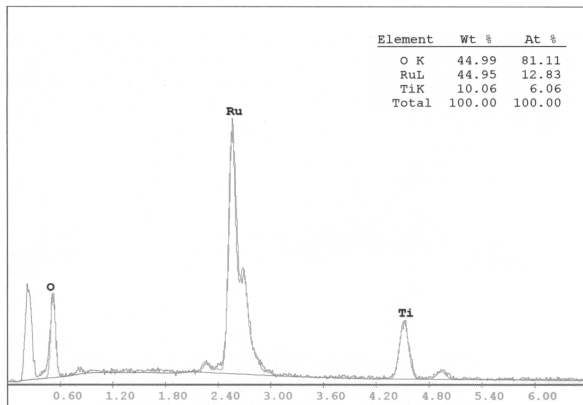| Element	Wt %	At %
O K	44.99	81.11
RuL	44.95	12.83
TiK	10.06	6.06
Total	100.00	100.00

Fig. 3. Spectrum and chemical composition of ruthenium-titanium oxide layer (item 1 acc. to Fig. 2).
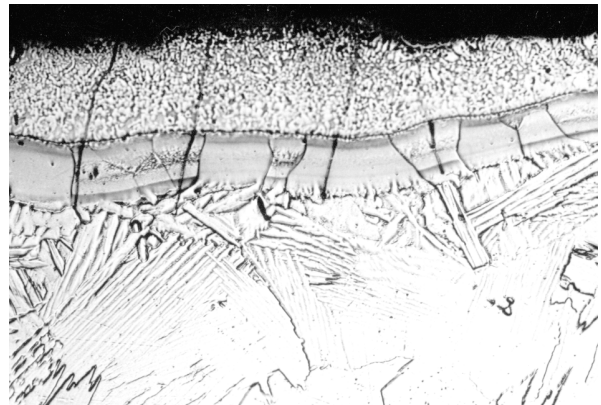

Fig. 4. Intersection through ruthenium layer and superficially oxygenated titanium.
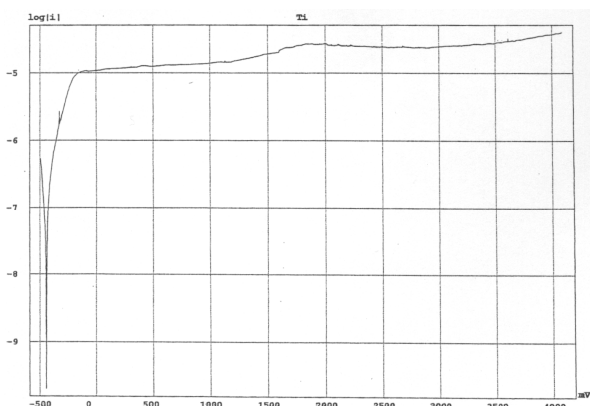
Magnification: 250x

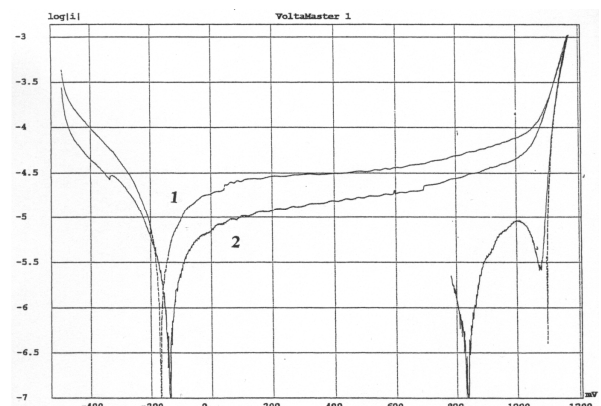Fig. 5. Anode polarization curve for titanium of technical grade.

Fig. 6. Anode polarization curves for titanium with ruthenium layer (1) and oxygenated titanium with ruthenium layer (2).

Table 1
Results of dynamic-potential tests

Specimen	Corrosion potential E_{cor}, mV	Current density i_{cor}, $\mu a/cm^2$	Potential $E_{(i=0)}$, mV	Resistance to polarization R_p, $k\Omega/cm^2$
Titanium	-296	0,047	-366	1520
Titanium (oxygenated)	-180	0,080	-238	220
Titanium (oxygenated) with ruthenium coating	-151	0,826	-160	10
Titanium with ruthenium coating	-118	3,69	-170	6

4. SUMMARY

Ruthenium coating on titanium decidedly changes current characteristics of outer layer. Moreover, taking into account that in none of tested cases the pitting corrosion has been observed, it becomes obvious that ruthenium coating on titanium does not impair its corrosion resistance and gives a layer with good conductance.

REFERENCES

1. B. Tilak, V. Birs, J. Vang, C.P. Chen, S. Rangarajan, J. Electrochem. Soc., 148 (2001) D112.
2. V.A. Alves, L.A. da Silva, J.F.C. Boodts, J. Appl. Electrochem., 28 (1998) 899.
3. V. Panić, A. Dekanski, V.B. Misković-Stanković, B. Nikolić, Eurocorr 2003, Paper No 155, Budapest, 2003.
4. Z. Szulc, S. Król, Proc. Conf. „GRE", Bielsko-Biała, 1988.