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THE INFLUENCE OF HEAT TREATMENT TEMPERATURE ON THE MORPHOLOGY OF TiO_2 SOL-GEL COATINGS

ABSTRACT

In the present work an influence of heat treatment temperature on the morphology of TiO_2 sol-gel coatings is presented. The sol-gel TiO_2 coatings were deposited onto Co-Cr-Mo alloy substrate. Scanning electron microscopy examination revealed very good quality of the coatings treated up to 600°C temperature. For higher heat treatment temperature cracks and pores appeared. The pores size increased with increasing heat treatment temperature.

Key words: *sol-gel, titania, morphology, coating*

1. INTRODUCTION

Recent years brought a significant growth of interest in ceramic coatings deposited on different substrates and having different applications [1]. The sol-gel method is especially interesting among existing methods. This comes from specific properties of this method – in particular an ease of its application in practice.

The sol-gel method consists in preparing the colloidal solutions (sols) as a result of the hydrolysis and condensation of precursors used. Next advanced process of condensation bond with solvent vaporization leads to gel formation and after burning the monolithic ceramics or ceramics coating on the solid body is formed [2].

The most important aspect of the sol-gel method is the fact that the liquid sol can be deposited on almost every substrate in the very easy way e.g. by immersing or spraying. Thanks to this the process technology is not complicated in comparison to other methods.

The coating deposition by dipping in sol runs in five stages: dipping, emerging start, deposition, liquid excess dripping, and vaporization [2]. Important parameters effecting a thickness of the coating are: sol viscosity and speed of the substrate withdrawal from the sol. Next stages are: drying (vaporizing) and burning. Drying temperature never exceeds 100ºC: usually the process is carried out at room temperature. Burning runs at temperature range 400-1000ºC (typically 500-750ºC). Therefore this method doesn't require any complicated instrumentation and devices and can be realized at relatively low costs.

Advantages of the sol-gel method, against other methods of ceramics coating deposition, are as follows:

- possibility of deposition on shape-complicated parts
- heat treatment temperature of obtained coatings is usually lower than in other methods
- water electrolysis does not occur in the process, what eliminates oxygen bubbles presence inside the coating, what can conduce the disadvantageous phenomena during exploitation
- deposited coatings are well adherent to the substrate
- practical usage of the method is relatively simple and inexpensive.

The sol-gel method can be used for the deposition of different coatings, among others, oxides as e.g. Al_2O_3, TiO_2, ZrO_2 and other kinds. The oxides coatings on different kind of substrates are widely used as a corrosion and heat protection [2,3].

Investigations of sol-gel coatings focus mostly on the corrosion resistance of coated substrate. This is the main property of these coatings from the viewpoint of most applications which can not be considered without morphology compliance. This is very important taking under consideration the fact that properties of the sol-gel coatings can be widely controlled by process parameters selection as well as heat treatment [4]. Thus the aim of this work was to analyze the influence of the thermal parameters of the sol-gel oxide coating deposition on its morphology.

2. EXPERIMENTAL

The Vitallium alloy specimens were used as substrates for sol-gel TiO_2 coating. This alloy widely applied in implantation, is characterized by high corrosion resistance and structure and mechanical properties stability in a wide range of temperatures.

Chemical composition of substrates used is presented in Table 1

Table 1. *Chemical composition of the substrates*

Alloying component	Co	Cr	Mo	Si
Content [%]	61,25	30,39	7,38	0,98

The chemical composition was determined with use of X-Ray diffractometer Siemens D-500. Results satisfy standard Vitallium composition.

Before the process the substrates were ground and polished to obtain glossy surface. Next they were washed in ultrasonic cleaner using ethanol and tetrachloromethane.

The sol was prepared from $Ti[O(CH_2)_3CH_3]_4$. The precursor was mixed with absolute ethanol and with diluted acetic acid as a catalyst. The sol had been aged for three weeks, and before it was used for deposition.

Sol was deposited by dip-coating. The substrate was immersed in sol for 2-3 minutes each time, to set the balance between sol and surface, and then it was withdrawn with constant speed.

The parameters were the same in each case: withdrawing speed – 10 mm/min, drying time (in the air, at ambient temperature) – 15 minutes. The substrates were heat treated for 15 minutes at different temperatures: 400, 500, 600, 700, and 800ºC. This procedure was repeated twice for each substrate. The next step was a surface examination by means of scanning electron microscope (SEM) HITACHI S-3000M.

3. RESULTS

The microstructure of the surface of the TiO_2 coating heat treated at 400ºC is shown in Fig. 1

The coating burnt out at 400^{o}C does not show any cracks or porosity, it is dense and smooth, well projecting the substrate surface.

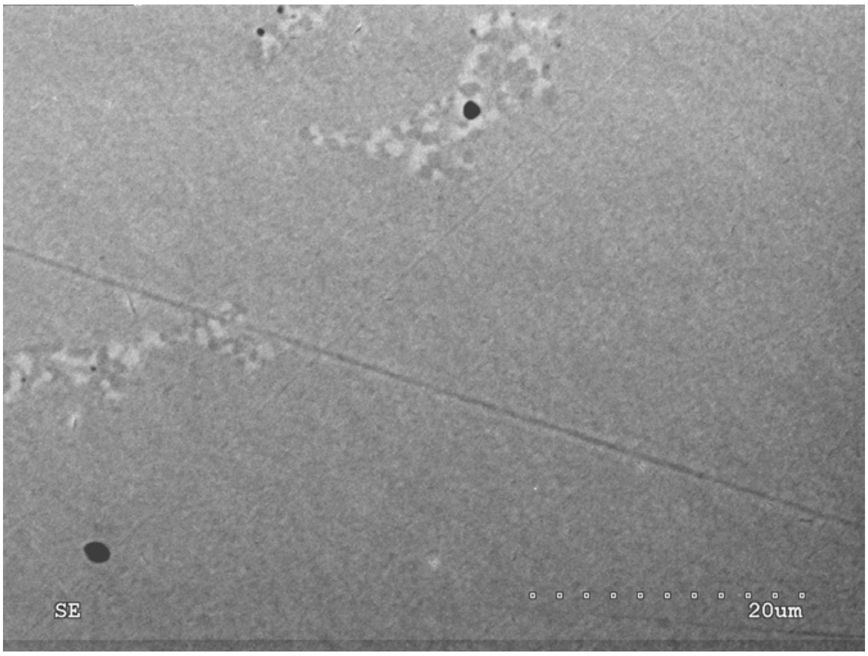

Fig. 1. SEM image of double layer TiO_2 coating heated at 400°C. Magnification 2000x

The coating heated at 500ºC is similar to the previous one. There are no significant changes against coating burnt out at 400ºC, what is shown in Fig. 2

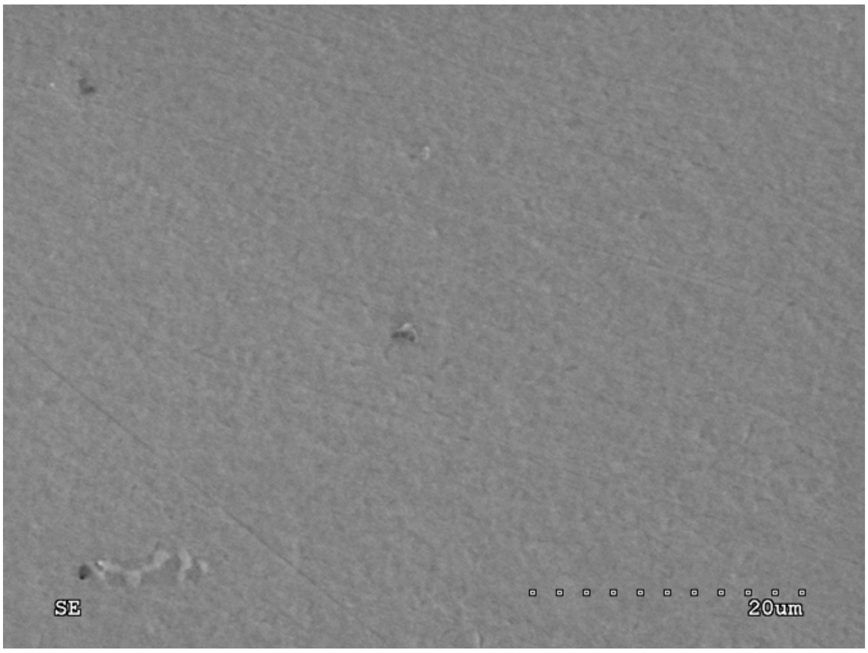

Fig. 2. SEM image of double layer TiO_2 coating burnt out at 500°C. Magnification 2000x

Some changes can be observed for specimen heat treated at 600ºC – a weakly visible micro cracks occur – Fig. 3

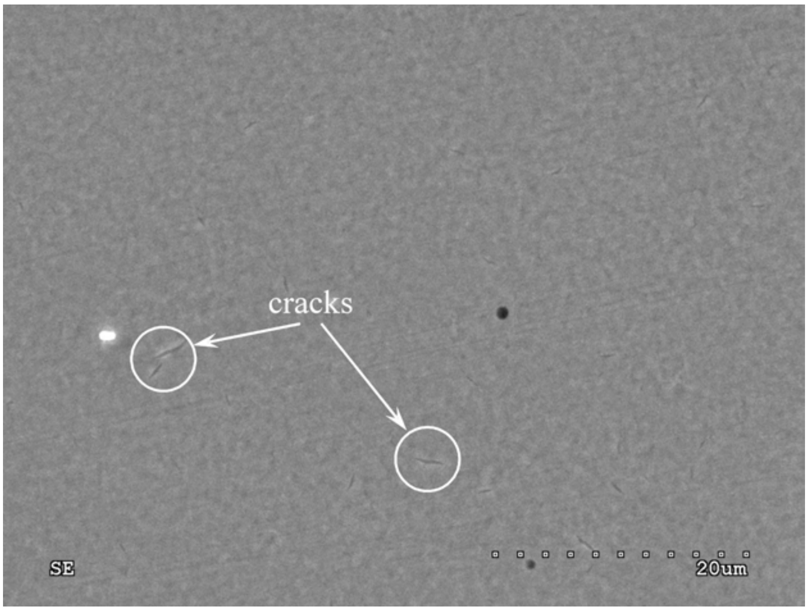

Fig. 3. SEM image of double layer TiO_2 coating treated at 600°C. Magnification 2000x

The size and amount of cracks increased in the specimen heat treated at 700ºC, which can be seen in Fig. 4. Moreover, small pores appeared, well detected in Fig. 5

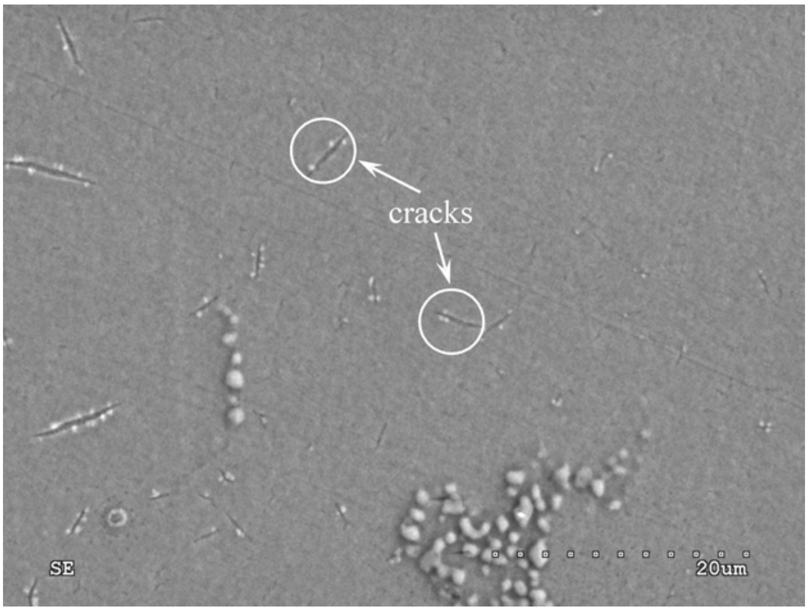

Fig. 4. SEM image of double layer TiO_2 coating burnt out at 700°C. Magnification 2000x

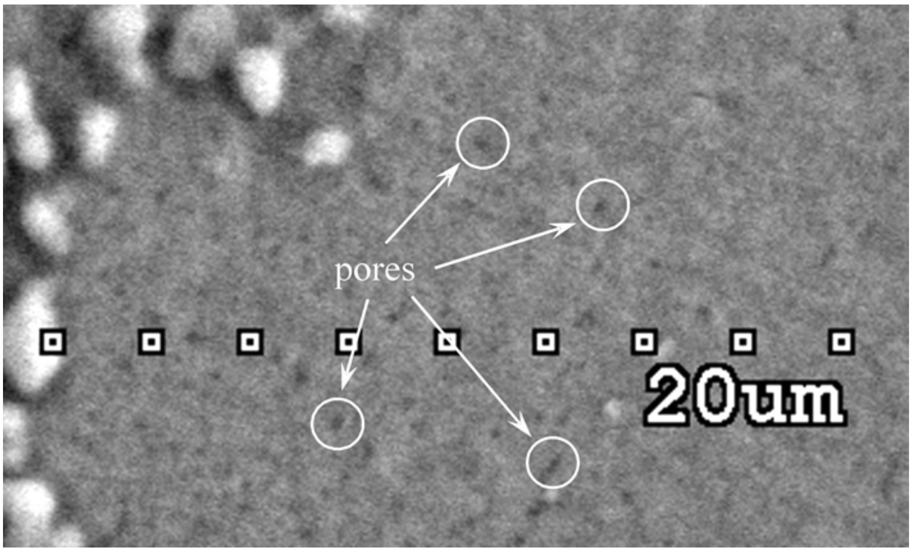

Fig. 5. Digitally magnified part of Fig. 4 with visible pores in the coating.

The last substrate was burnt out at 800ºC and demonstrates high porosity, perfectly visible in Fig. 6

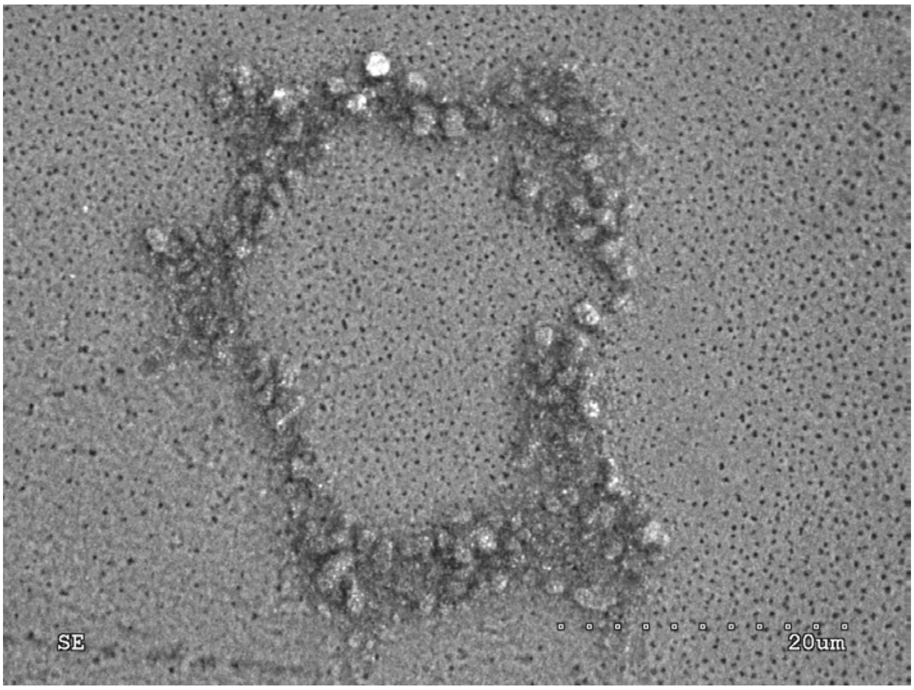

Fig. 6. SEM image of double layer TiO_2 coating burnt out at 800ºC. Magnification 2000x

The porosity seen in Fig. 6 appears on the whole surface. Additionally the pore dimensions increased, and achieve 0,5μm what is shown in Fig. 7

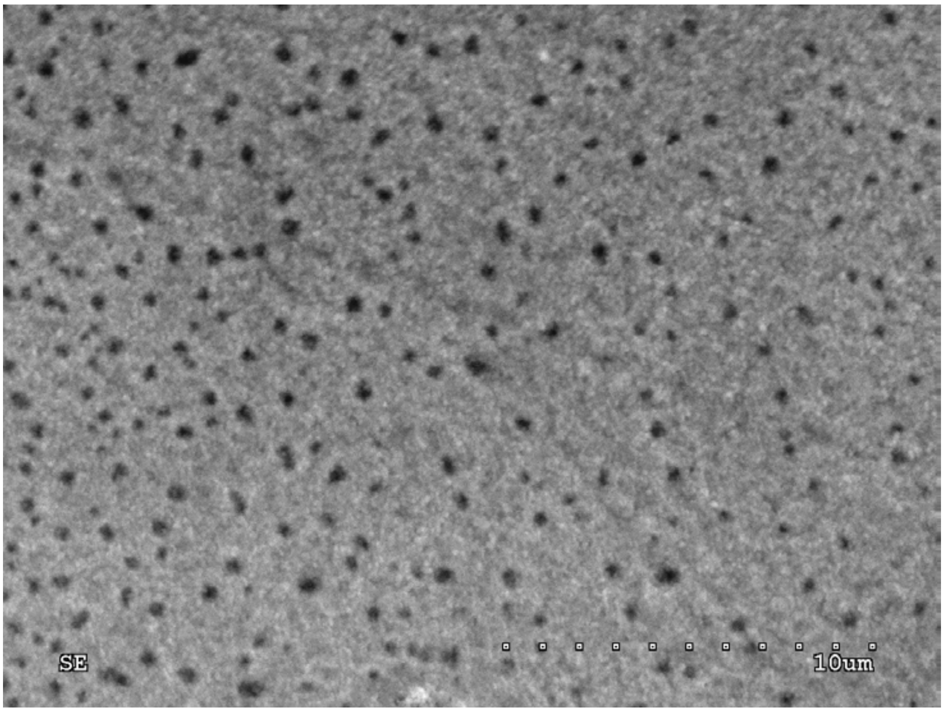

Fig. 7. SEM image of double layer TiO_2 coating burnt out at 800ºC. Magnification 5000x

4. SUMMARY

The dense, flawless coatings of TiO_2 can be obtained with a use of sol-gel method on condition of well selected process parameters. Heat treatment temperature plays the main role. Obtained results prove that this temperature determines the amount of defects in the coating. This amount increases with temperature – discontinuities (cracks) and visible pores occur in coatings. This phenomenon appears at temperatures above 600ºC – coatings treated below this value don't show such defects.

In the coating annealed at 700ºC, local cracks are visible, which result from the tensile stresses arising during heat treatment. Moreover, the pores appear, what is probably the repercussion of rapid vaporization of the remains of the sol solvent. The amount and size of the pores increase in the sample heated to 800ºC. However the cracks don't occur in this sample – probably the amount and sizes of pores cause the stresses relaxation preventing cracks.

The above phenomena limit application of such coatings as temperature resistant coatings. They can find application at working temperature not higher than the burn-out temperature of the good quality coating. It can be assumed that such coating will make a very good protection against corrosion and temperature below the level of 600ºC.

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