IMEKO TC15 - Experimental Mechanics - Proceedings of the
11th Youth Symposium on Experimental Solid Mechanics
Brasov, ROMANIA, 2012, May 30-June 2

SILICA AND TITANIUM OXIDE THIN FILMS FOR MEDICAL IMPLANTS

DONESZ-SIKORSKA A.[1] KRZAK-ROŚ J.[1] GRYGIER D.[1] KALETA J. [1]

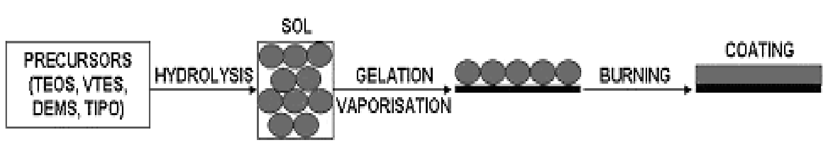
Abstract:. Metals and their alloys are the basic materials using for bone implants. Unfortunately all metallic biomaterials contain an elements which may cause metallosis or corrosion, and their surface may not promote colonization by cells of the surrounding tissue. In this paper, we describe obtaining of new coating materials on commercial available steal that can work as bio functional and well-protecting coatings for medical implants. Thin silica and titanium films were synthesis using the sol–gel method that is based on the hydrolysis of alkoxide precursors at room temperature. The results of our previous study and described in this work show possibility to synthesis by sol-gel method stable, continuous and biocompatible coating for metallic implants.

Key words: thin films, sol-gel method, surface modification

1. Introduction

The rapid progress of modern medicine entails the need for improvement of commercial available metallic implant materials. Metals and their alloys are the basic materials using for bone implants. Unfortunately all metallic biomaterials contain an elements which may cause metallosis or corrosion, and their surface may not promote colonization by cells of the surrounding tissue.

The sol-gel method is very popular as a method of coatings synthesis allowing to modify the medical implants surface properties [9,7, 11]. The sol–gel method based on the hydrolysis of alkoxide precursors and policondensation at room temperature. An advanced condensation process combined with solvent evaporation allows gels to be obtained. The metallic surfaces are covered using hydrolysates obtained in sol-gel method which after burning become ceramic coatings [3, 10], Figure 1.



[1] Institute of Materials Science and Applied Mechanics, *Wroclaw* University of Technology.

Fig. 1. *Sol-gel method [3,10]*

The interest of sol-gel method grown in the field of preparing surface layers designed for implants, e.g., dental, orthopaedic or traumatologic [6, 12].

Silica and titanium oxides layers increases the steel 316L corrosion resistance [2] and the same protecting the tissue surrounding implant from the toxic effects of ions released from the steel and exhibit biocompatibility enabling a positive recipient response to the implant [1,4,8]. The main advantages of sol-gel method are [5]: low temperature of process (ability to obtain a solid material at room temperature), strictly controlled chemical composition of layers, high biocompatibility of synthesized coatings in tissue environment, possibility of synthesis active coatings (with specified properties) and relatively low cost of manufacturing.

In this method coatings can be applied in several ways (dip-coating, spin-coating, meniscus coating, painting, spraying etc.). The advantages of dip-coating technique are: (i) no restrictions on the shape and size of discs, (ii) opportunity to reduce pollution, (iii) independency of the properties of using solvents and solutions and (iv) simplicity and low cost.

2. Objectives

The main aim of this work was to obtain using sol-gel method silica and titanium oxide thin films witch could be used for medical implants.

3. Material and methods

We have chosen the stainless steel 316L in the form of plates (50mm×10mm×1mm) for deposition thin films prepared by sol-gel method. We used tetramethylortho-silicate (TEOS) as basic silica precursor and titanium(IV) isopropoxide (TIPO) as titanium precursor, ethanol (EtOH) and isopropanol (izoPOH) as the solvents, acetyloacetone (AcAc) as titanium stabilizer and HCl_{aq} as catalyst. Two different silica precursors: phenyl-trimethoxysilane (TPhOS) and diethoxy-dimethylsilane (DEMS) were added to basic silica precursor (TEOS). During synthesis we used the principle saying that the ratio of precursor to solvent is 1:2. We synthesizes of two silica and one titanium sols (Figure 2). Obtained solutions of sols were dip-coated with controlled parameters onto the cleaned metallic substrate. The deposited films were dried at room temperature in air and then annealed at a temperature 250°C for 12 hr.

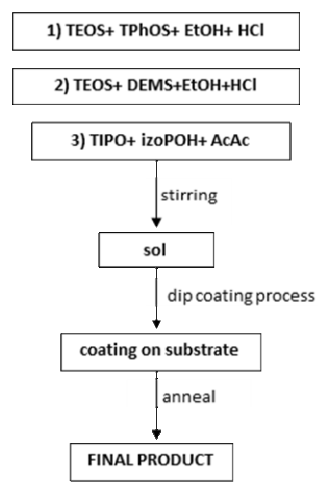


Fig. 2. *Procedure of obtaining by sol-gel method silica (1-2) and titanium (3) oxides layers*

4. Results and Discussions

The study on the Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX) were carried out to observe the surface (SE1 detector), structure (BSE detector) and mapping of the distribution of elements at four different magnifications (50÷1000)x. Titanium and silica oxides layers are transparent, homogeneous and uniformly cover the substrate- steal 316L (Figure 2-3). SEM-EDX mapping image of titanium (Figure 3) and silica (Figure 5,7) layer at 500x magnification shows the uniform distribution obtained coatings on steal.

Pure substrate- steal 316L was characterized by fine-grained structure (Figure 3). Unfortunately we have seen in pictures (Figure 4) and on SEM-EDX mapping image corrosion centers (Figure 5) which were characterized by increased amounts of oxygen. **SEM-EDX** analysis of stainless steel (Figure 6) showed a basic elemental composition of 316L steel whose main components are: chromium (Cr), nickel (Ni) and molybdenum (Mo).

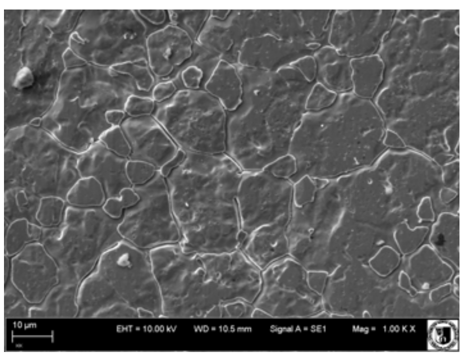


Fig. 3. *SEM image of pure steal 316L in 1000x magnification*

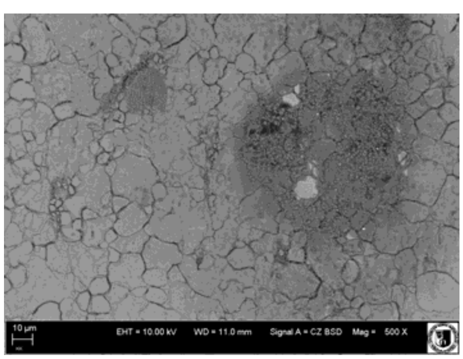


Fig. 4. *SEM image of corroded steel 316L at 500x magnification*

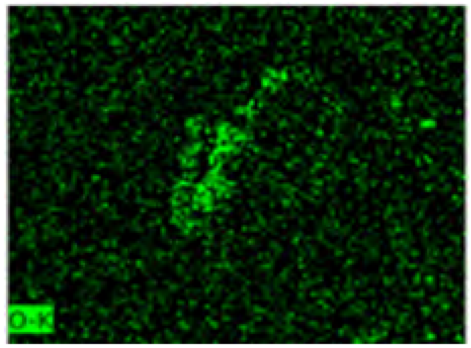


Fig. 5. *SEM-EDX mapping image of corroded steel 316L at 500x magnification*

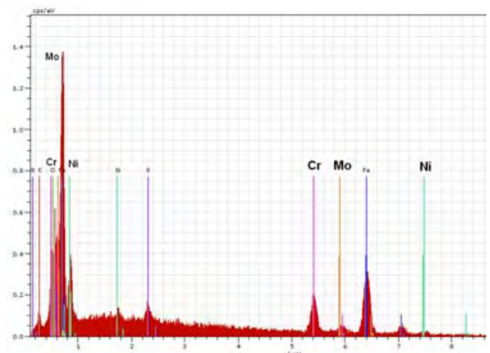


Fig. 6. *SEM-EDX image of pure steel 316L at 500x magnification*

Titanium oxides layers are transparent, homogeneous and uniformly cover the substrate- steal 316L (Figure 7-8). SEM-EDX mapping image of titanium layer at 500x magnification (Figure 8) shows the uniform distribution of titanium on steal. Image at angle of 60º shows the scaly structure of the titanium layer (Figure 9).

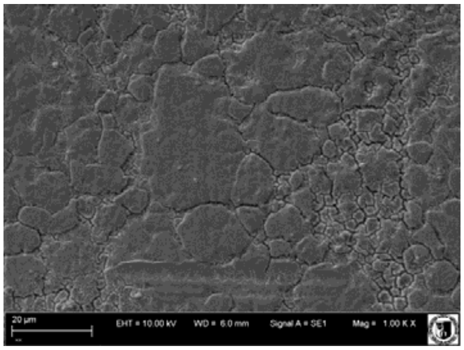


Fig. 7. *SEM image of titanium coating at 1000x magnification*

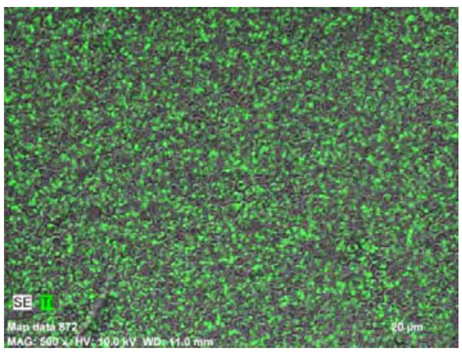


Fig. 8. *SEM-EDX mapping image of titanium coating at 500x magnification*

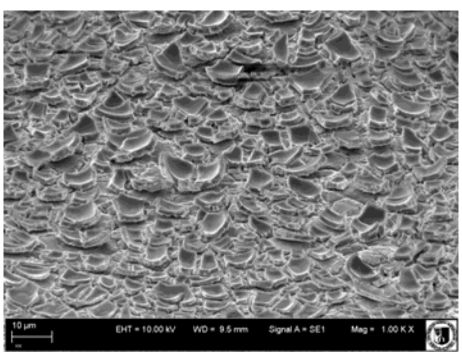


Fig. 9. *SEM image of titanium coating at angle of 60° at 1000x magnification*

Both of silica oxides layers on steal 316L were also transparent, homogeneous and uniformly cover the substrate (Figure 10-13). On SEM images of both silica coatings at 1000x magnification (Figure 10-11) clearly seen grain boundaries of steel 316L that are covered by a layer. SEM-EDX mapping image of silica coatings at 500x magnification (Figure 12-13) show uniform distribution of silicon in coating. Silica coating (TEOS+DEMS), Figure 12 contains less silicon than second silica coating (TEOS+TPhOS), Figure 13. This difference results from various number of used silica precursors for the synthesis by sol-gel method.

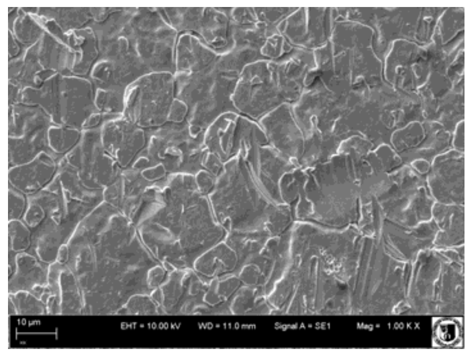


Fig. 10. *SEM image of silica (TEOS+DEMS) coating at 1000x magnification*

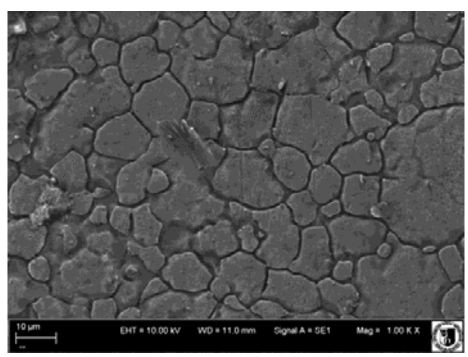


Fig. 11. *SEM image of silica (TEOS+TPhOS) coating at 1000x magnification*

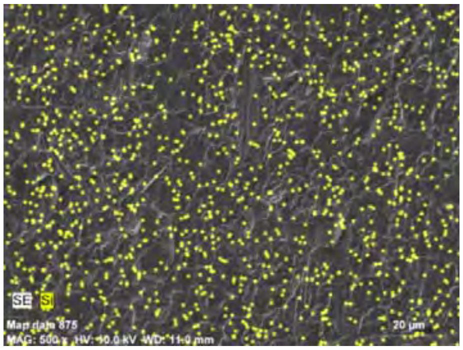


Fig. 12. *SEM-EDX mapping image of silica (TEOS+DEMS) coating at 500x magnification*

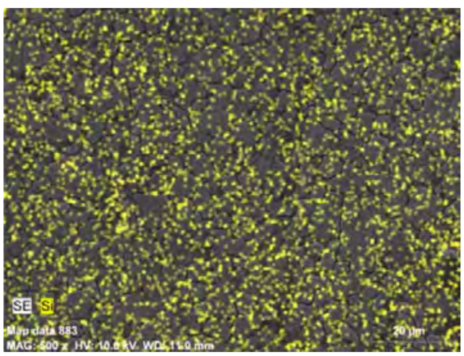


Fig. 13. *SEM-EDX mapping image of silica (TEOS+TPhOS) coating at 500x magnification*

The adherence of the coatings to the base was evaluated by the cross-cutting method according to EN ISO 2409. The examination procedure consisted in making cuts in two perpendicular directions and next in performing the pull-off test using a special adhesive tape. The six-blade cutter was used in this test (Figure 14). After the test, the adherence of the layers was evaluated by macro- and microscopic examinations. Tests were performed three times on each sample, at 23 ± 2°C and a relative humidity of 50 ± 5%.

Qualitative evaluation of the results was performed according to EN ISO 2409:1999 which relies on the assignment of the resulting grid cuts a specific parameter, among the six described in the standard. Based on microscopic observation was selected parameter "0" corresponding to the description: the edges of the cuts are completely smooth, and in any of the grid squares occur splinters The results showed good adhesion of most sol-gel layers to the substrate. The edges of the cuts were completely smooth in the macro- and micro- scale. Neither cracks nor spalls were observed in any area, but only uniform wear of the coating.

Fig. 14. *Macroscopic view of a gri d on titanium coating deposit on steal 316L after adherence test*

The results showed good adhesion of most sol-gel layers to the substrate. Observations of the macro-edge cuts showed no cracks or splinters. It has been found only a uniform wipes of coating in analyzed areas.

Summarizing, sol-gel method allows synthesize in easy and cheap way oxide materials witch composition we can planned.

Obtained silica and titanium coatings are continuous and exhibit strong adhesion to the substrate.

Our previous studies have shown that silica and titanium oxides layers anneal in 250°C are free from potentially toxic methyl and hydroxyl groups also *in vitro* tests confirmed these results.

5. Conclusion

This paper presents huge potential of the sol-gel method, which allows synthesis of continuous and chemically designed coatings for medical implants.

Acknowledgements

We wish to thank Krzysztof Kaliński from Electron Microscopy Laboratory at the University of Environmental and Life Sciences in Wroclaw, who played an important role in obtaining the SEM-EDX results submitted within the paper.

References

1. Będziński, R., Krzak-Roś, J., et al.: *Investigation of the Bone Tissue and Implant Surface Interaction*. In: Strain, Volume 46, Issue 6, p.518–525, 2008.
2. Galliano, P., et al.: *Sol–gel coatings on 316L steel for clinical applications*. In: Journal of Sol–Gel Science and Technology 1998; 13:723–727.
3. Głuszek, J., *Oxide protective coatings obtained by sol-gel method*. Publishing House Of Wrocław University Of Technology, Wrocław, 1998.
4. Jokinen, M., et al.: *Influence of sol-gel and surface properties on in vitro bioactiv of so l-gel-derived TiO_2 and TiO_2+SiO_2 film d eposited by di p-coating method*. In: Journal of Biomedical Materials Research 1(998); 42(2) p. 259-302.
5. Klein, L.C., *Sol-gel technology for thin films, fibers, preforms, electronics and specilaty shapes*. Noyes Publications, New Jersey, 1988.
6. Koubo, T., Kim H., et. al.: *Novel bioactive materials with different mechanical properties*, Biomaterials, 2003, 24, 2161–2175.
7. Krzak-Roś, J., Filipiak, et. al.: *The effect of substrate roughness on the surface structure of TiO_2, SiO_2, and doped thin films p repared by the sol–gel method*. Acta of Bioengineering and Biomechanics 2009; 11(2): 21-29.
8. Li, P., Kokubo, T., Nakanishi, K., et al.: *Induction and morphology of hydroxyapatite, precipated from metastable simulated body flui ds, on sol-gel prepared silica*. Biomaterials 1993; 14: 963-968
9. Li, R., Clark, A.E., et. al.: Effect of structure and surface area on bioactive powders made by sol-gel process. In: Hench LL, West JK, editors. *Chemical processing of advanced materials*. New York: John Wiley & Sons, Inc. 1992; 627–633.
10. Łaskawiec, J., Michalik, R. *Theoretical and app lication problems of implants*. Publishing House Of Silesian Technical University, Gliwice, 2002.
11. Peltola, T., Jokinen, M., et al.: *Effect of againg time of sol on structure and in vitro calcium phosphase formation of sol-gel-derivied titania films*. Journal of Biomedical Materials Research 2000; 51(2): 200-208.
12. Tadashi, K., Hyun-Min, K., et. al.: *Novel bioactive materials with different mechanical properties*. Biomaterials, 2003, 24, 2161–2175.