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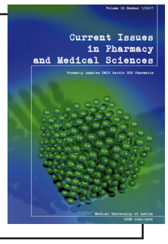

Production of oxide coatings by sol-gel method and electrophoresis

Mariusz Walczak, Kazimierz Drozd*

Department of Materials Engineering, Faculty of Mechanical Engineering, Lublin University of Technology, Nadbystrzycka 36, 20-618 Lublin, Poland

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ABSTRACT

The paper reports the results of depositing SiO_2 and SiO_2-TiO_2 coatings on titanium alloy Ti-6Al-4V ELI (ASTM-grade 5). Oxide coatings were deposited onto the titanium alloy substrate by sol-gel method and by electrophoresis. The produced coatings were chemically uniform, compact and highly dense. We then performed SEM microstructure examination, as well as microhardness and surface roughness measurements for different coating combinations. The significance of the results was assessed by the Shapiro-Wilk and t-Student tests using the STATISTICA software. It has been found that there are statistically significant differences in the hardness of SiO_2 and SiO_2-TiO_2 coatings. The results of roughness parameters reveal significant differences only for individual coatings.

INTRODUCTION

While the release of harmful metal ions to the tissues around the implant [8] is a disadvantage of utilizing titanium implants, their susceptibility to bacteria adhesion and the formation of a bacterial biofilm on their surface [1] is of primary concern. Studies on bacterial adhesion to titanium in the oral cavity have demonstrated that the metal itself does not exhibit antibacterial activity [11], and bacteria cells adhere easily to its surface [1,18]. The adhesion of bacteria to biomaterial surface results in serious complications after surgeries and can pose a particularly huge risk for patients with long-term implants. Therefore, it is necessary to modify the surface layer of titanium biomaterials, assigning them anticorrosive [3], antibacterial [12] and osseointegrational properties [4].

Thin ceramic coatings deposited by the sol-gel method and by electrophoresis are becoming more popular in dental practice and medicine. Currently, implant surface modifications focus on hybrid methods which enable the production of composite structures [1,17]. These methods combine different types of surface treatment in order to shape the properties of biomaterials as desired. As a result, bioceramic composite layers hybrid-produced by the sol-gel method and by electrophoresis have become more important.

The sol-gel method can be regarded as a method of chemically synthesizing non-organic and non-metallic materials (glass, ceramics). It consists in first making colloidal solutions (sols) by hydrolysis and then condensing the applied precursors. The condensation process, often in combination with solvent evaporation, leads to the formation of gels, which, following heating, can be used to produce monolithic ceramics or ceramic coatings for different substrates. The obtained material can have either an amorphous (glass) or crystalline structure [10].

The electrophoretic deposition method is based on electrochemical processes occurring in a colloidal environment under the effect of electric field.

The deposition of ceramic coatings by the sol-gel method and by electrophoresis offers numerous advantages compared to traditional methods. These advantages include: high purity raw materials, good homogeneity of the microstructure, low process temperature (compared to methods such as PVD and CVD), as well as the possibility of using unconventional materials. The sol-gel method and electrophoresis can be used to produce porous, amorphous dense or completely crystalline coatings. However, the high shrinkage of coatings restrains the technological potential of producing monolithic ceramics. Moreover, electrochemical corrosion of such coatings can pose difficulties regarding the use of single- or two-component coating materials exclusively made of soles. As for oxide ceramics, we can produce coatings using oxides of several metals and non-metals. Single-component coatings are usually made of such soles as SiO_2, Al_2O_3, TiO_2, ZnO, Ta_2O_5 and ZrO_2, which can serve as a basis for creating multi-component soles [5]. Oxide coatings, in particular, can be effectively used in orthopedics

* **Corresponding author**
e-mail: k.drozd@pollub.pl

as both implant coatings [1,4] and prosthodontics [2] to increase the adhesion of dental ceramics to metal substrates.

The durability of a biomaterial and its applications greatly depend on the properties of the environment it is used in, its production quality and its surface layer condition. Thus, knowledge of the properties of the surface layer of biomaterials is vital for both the design and selection of material and production technology. Given the above, the purpose of this study was to determine the properties of SiO_2 and SiO_2-TiO_2 coatings deposited on titanium alloy by sol-gel and by electrophoresis methods, with respect to their medical and dental applications.

MATERIAL AND METHODS

The substrate was made of titanium alloy Ti6Al4V ELI – *Extra Low Interstitial* (ASTM-grade 5) manufactured by Daido Steel Co. Ltd. The specimens were in the form of discs with diameters of approximately 25 mm and thicknesses of 0.5 mm. Prior to the deposition of oxide coatings, the metal specimens were subjected to grinding using water abrasive papers with a granularity of 800. After that, they were degreased by an ultrasonic method, and then subjected to etching in a mixture of hydrofluoric and nitric acids. Next, two types of coating: SiO_2 and SiO_2-TiO_2, were applied to the titanium alloy substrate by sol-gel and electrophoretic deposition methods, as listed in Table 1. To that end, two types of sol were prepared: SiO_2 and SiO_2-TiO_2. Silica sol was prepared by the hydrolysis of tetraethoxysilane ($Si(OC_2H_5)_4$; hereafter abbreviated as TEOS) diluted in ethanol with the addition of HCl as a catalyst. The molar composition of H_2O:TEOS:HCl in the silica-sol was 4:1:0.01, while the final concentration of SiO_2 in the silica sol was 3-5 wt.%. Titanium-silica sol was prepared by the hydrolysis of titanium propoxide $Ti(OC_3H_7)_4$ and TEOS, with the addition of HCl as a catalyst. The final concentration of TiO_2+SiO_2 was 7.63 wt.%.

Table 1. Properties of the tested coatings

Coating	Method	Specimen denotation
SiO_2-TiO_2	sol-gel	SiO_2-TiO_2/sol-gel
SiO_2-TiO_2	electrophoretic deposition	SiO_2-TiO_2/EPD
SiO_2	(1) electrophoretic deposition and (2) sol-gel	SiO_2/EPD/sol-gel

The process of electrophoretic deposition (*EPD*) was performed under a voltage of 30V and a time of 10s. In this process, a Ti-6Al-4V ELI alloy plate was used as both an anode and a cathode. The sol-gel coatings were deposited by dip coating with a constant velocity set to 3.3 mm/s, and the coating surface was adjusted by the application of multiple dip coating. Following the application of film, the specimens were dried and soaked in an argon atmosphere at a temperature of 600°C for half an hour, in a pipe furnace.

The surface of the tested materials was examined utilizing the Phenom ProX scanning microscope (manufactured by Phenom-World B.V.). The roughness measurement of the sol-gel coatings was performed on a measuring length L_c= 2 mm, using the Dektak 150 profilemeter from Veeco Instruments. The microhardness measurements were made under a load of 0.49N (HV0.05), employing the Vickers FM-700 microhardness tester provided with the automatic ARS 900 system from Future-Tech Corp. In such work, 15 measurements of roughness profile and microhardness were performed per each specimen group.

RESULTS AND DISCUSSION

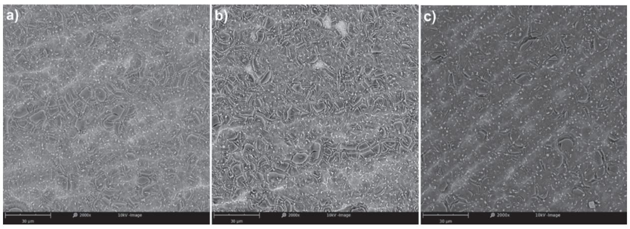

Figure 1. SEM microphotographs of surfaces of different coatings: a) SiO_2-TiO_2/sol-gel, b) SiO_2-TiO_2/EPD and c) SiO_2/EPD/sol-gel (magnified by 2000×)

The SEM microstructures of the SiO_2 and SiO_2-TiO_2 coatings are shown in Figure 1. The examined oxide coatings have a chemically uniform structure; it is compact and has a high density. The thickness of the produced coatings as measured on the microsection is about 3-5 μm. The microstructure of the SiO_2 coating consists of amorphous or very low crystalline SiO_2 particles.

As for the SiO_2-TiO_2 coating, we obtained a composite structure consisting of SiO_2 particles in the TiO_2 matrix. The macroscopic examination reveals that the coatings are uniform: they are thin, shiny, and do not peel off. On the other hand, the SEM results demonstrate that in the SiO_2-TiO_2/EPD coating, the SiO_2 phase spalls off the titanium substrate. In addition, one can see numerous cracks in the region where the SiO_2 phase occurs. The lowest number of such cracks can be observed for the SiO_2/EPD/sol-gel coating. For this reason, the application of the EPD and sol-gel methods for coating deposition is more effective in preventing corrosion and penetration of harmful metal ions. The cracks occur during soaking at a high temperature and on deposition of individual layers. Nonetheless, the cracks do not penetrate through the coating. According to Milell *et al.* [13], microcracks are formed due to the coating's shrinkage at soaking; they can grow and merge to form more extensive areas. Guillèn *et al.* [6] propose that with thicker sol-gel coatings, thinner coatings can be deposited on the sol specimen in several operations, and then the entire metal-coating system be subjected to soaking. As a result, the stresses generated during production of the coating should not accumulated to the same high extent as would be the case if each layer was subjected to soaking separately.

In turn, Szałakowska *et al.* [14] found that the SiO_2-TiO_2 coating exhibits higher barrier properties due to the sealing of pores in the TiO_2 coating by filling them with the SiO_2 phase. This is possible due to the fact that the particles of individual oxide components have different sizes.

Table 2. Comparison of the investigated parameters (mean values) describing roughness of the examined coatings

Coating	Ra (μm)	Rq (μm)	Rv (μm)	Rp (μm)	Rt (μm)	Rz (μm)
SiO_2-TiO_2/sol-gel	0.522	0.757	-3.751	2.833	6.532	3.467
SiO_2-TiO_2/EPD	0.457	0.617	-2.421	1.972	4.341	2.787
SiO_2/EPD/sol-gel	0.389	0.544	-1.873	2.208	4.106	2.522

The results of roughness measurements (Table 2) demonstrate that the SiO_2-TiO_2/sol-gel coating has the highest roughness, which predominantly results from the composite structure of this coating. On depositing the coating film by dip coating, SiO_2 particles merge and form agglomerates which are separated by the structure of TiO_2 oxides. With subsequent operations, depending on the number of deposited layers, this leads to the pile-up of roughness profile regions with a high concentration of the SiO_2 phase. In addition, this coating exhibits the highest values of maximum profile peak height of the roughness profile *Rp,* as well as maximum profile valley depth of the roughness profile *Rv*. This results from the above mentioned susceptibility to microckracking at the last stage of coating formation by thermal treatment. Such roughness properties of coatings are desired in terms of applications for orthopedic implants [4], where, additionally, the presence of TiO_2 particles improves the bonding between the implant and the host tissue during the osseointegration process. The bioactive properties of the surface result from the presence of Ti-OH groups which stimulate the growth of bone structures [10]. Ti-OH hydroxyl groups on the surface of sol-gel coatings can provide space for the nucleation of calcium phosphates, stimulating faster growth of bone structures on the surface of materials in the environment of a living organism [9].

According to the authors of the study [2], the higher development of the surface in the SiO_2-TiO_2 coating is useful in prosthodontics for producing metal crowns with dental ceramics. Dental ceramics penetrate into fine irregularities of the surface, forming micrograftings which ensure a higher durability of the metal-ceramics joint.

As far as the SiO_2/EPD/sol-gel coating is concerned, its roughness parameters are the lowest due to the fact that all surface irregularities and microcracks produced during EPD deposition of the first coating layer are removed during the deposition of the second layer by the sol-gel method. Such properties of the coating will be more effective in applications serving as safety barriers to prevent corrosion processes and the release of harmful metal ions into the surrounding tissues.

Based on the literature [16], statistical analysis was performed using the quadratic mean deviation, Rq, as being most representative for these coatings (Fig. 2a). The Rq parameter is statistically equal to the standard deviation of the profile's ordinates, and it is more affected by a single high profile peak height and valley depth than by the arithmetic mean deviation *Ra*. The results of the Shapiro-Wilk test (Table 3) demonstrate that the specimens have a normal distribution ($p>0.05$), which points to the homogeneity of the produced coatings. Therefore, further significance analysis was performed by t-Student test. The results of the t-Student test (Table 4) indicate statistically significant differences ($p<0.05$) only between the SiO_2-TiO_2/sol-gel and SiO_2-TiO_2/EPD specimens, as well as between the SiO_2-TiO_2/sol-gel and SiO_2/EPD/sol-gel specimens. We did not observe any statistically significant differences regarding the SiO_2-TiO_2/EPD and SiO_2/EPD/sol-gel specimens.

Table 3. The p-values (Shapiro-Wilk) for investigated parameters of the examined coatings

Coating	p-value for parameter	
	Rq	Hardness
SiO_2-TiO_2/sol-gel	0.5295	0.1807
SiO_2-TiO_2/EPD	0.6276	0.0947
SiO_2/EPD/sol-gel	0.2343	0.6306

Table 4. The detailed parameters of significant differences test ($p < 0.05$ for t-Student with Holm-Bonferroni correction p' [7]) for roughness tests of the examined coatings

Coating	SiO_2-TiO_2/sol-gel			SiO_2-TiO_2/EPD			SiO_2/EPD/sol-gel		
	F	p	p'	F	p	p'	F	P	p'
SiO_2-TiO_2/sol-gel				2,512	0.012	0.037	1.713	0.019	0.039
SiO_2-TiO_2/EPD	2,512	0.012	0.037				1.466	0.965	0.965
SiO_2/EPD/sol-gel	1.713	0.019	0.039	1.466	0.965	0.965			

The microhardness results (Fig. 2b) demonstrate that the SiO_2 coatings have the highest mean values of hardness. The lower hardness of the two-component SiO_2-TiO_2 coatings results from the morphology of the examined coatings. The SiO_2-TiO_2 coating contains lower quantities

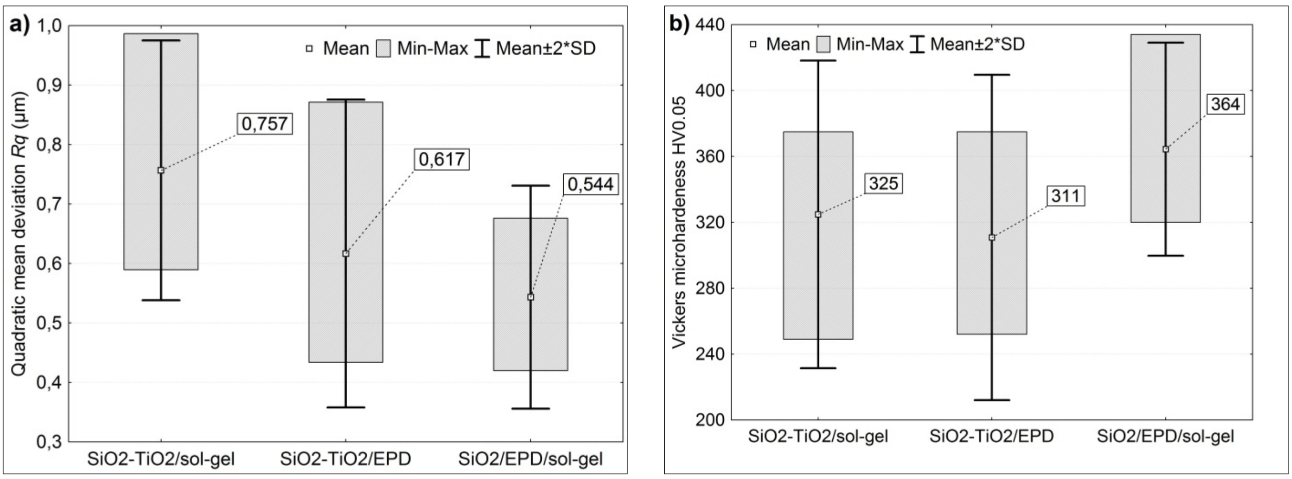

Figure 2. Summary of results of a) quadratic mean deviation *Rq* and b) microhardness

of hard SiO_2 particles surrounded by a soft TiO_2 phase. The statistical analysis of microhardness results was performed by the t-Student test, as the Shapiro-Wilk test results point to a normal distribution ($p>0.05$) for all specimen combinations (Table 3). We observed statistically significant differences between the specimen groups (Table 5): SiO_2-TiO_2/EPD and SiO_2/EPD/sol-gel. No statistical differences between SiO_2-TiO_2/sol-gel and SiO_2-TiO_2/EPD were observed, and, when we take into account Holm-Bonferroni correction [7], no statistical differences between SiO_2-TiO_2/sol-gel and SiO_2 /EPD/sol-gel groups ($p' = 0.081$) were observed as well. Therefore, it can be inferred that the method of production does not affect the hardness of the SiO_2-TiO_2 coating.

Table 5. The detailed parameters of significant differences test ($p < 0.05$ for t-Student with Holm-Bonferroni correction p' [7]) for hardness tests of the examined coatings

Coating	SiO_2-TiO_2/sol-gel			SiO_2-TiO_2/EPD			SiO_2/EPD/sol-gel		
	F	p	p'	F	p	p'	F	P	p'
SiO_2-TiO_2/sol-gel				1.119	0.523	0.523	2.087	0.041	0.081
SiO_2-TiO_2/EPD	1.119	0.523	0.523				2.337	0.010	0.030
SiO_2/EPD/sol-gel	2.087	0.041	0.081	2.337	0.010	0.030			

CONCLUSIONS

The results have led to the following conclusions:

1. SEM examination reveals that the investigated oxide coatings are chemically uniform, compact, and have a high density. As for the SiO_2-TiO_2/EPD coating, we have observed minor defects due to local separation of the ceramic phase SiO_2 from the metal substrate. The highest density can be observed for the SiO_2/EPD/sol-gel coating produced by electrophoresis and by sol-gel methods, despite the fact that the SiO_2 phase is characterized by considerable shrinkage and susceptibility to cracking due to thermal treatment.
2. The highest roughness has been observed for the SiO_2-TiO_2/sol-gel coating. Considerable roughness, combined with the presence of rutile, can facilitate both the living tissue's "anchoring" in the implant, and the adhesion of other coatings, e.g. dental ceramics. The lowest roughness is exhibited by the SiO_2/EPD/sol-gel coating. For this reason, this coating will be most effective for safety barrier applications.
3. The microhardness results demonstrate that the SiO_2 coatings have a higher mean statistically significant value compared to the results of hardness of the two-component SiO_2-TiO_2 coatings. However, no statistically significant differences have been observed regarding the microhardness of the SiO_2-TiO_2 coatings produced by different methods.

The acquired knowledge about the properties of the surface layer of oxide coatings produced by sol-gel method and by electrophoresis will enable the developing of complex criteria of shaping these properties as desired for the design of medical products.

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