

DEVELOPMENT AND CHARACTERIZATION OF 316 L STAINLESS STEEL COATED BY MELT-DERIVED AND SOL-GEL DERIVED 45S5 BIOGLASS FOR ORTHOPEDIC APPLICATIONS

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The 316L austenitic stainless steel (SS) was coated by 45S5 bioactive glass produced by melting and sol-gel techniques to increase the bioactivity and to provide a high mechanical strength for orthopedic and dental applications. The morphologies of coated specimens were investigated by scanning electron microscopy (SEM). Then, the coated specimens were immersed in simulated body fluid (SBF) at 37°C for 14 days, and their microstructures after withdrawal were also investigated by SEM. All the specimens were analyzed by FTIR and XRD in order to survey the formation of hydroxyapatite layer.

INTRODUCTION

Bone rehabilitation depends on many clinical parameters related to dentistry and orthopedics sciences. Bone graft which is produced spontaneously is an ideal standard, but the host tissue is often scarce and hardly can be used for substitution of required tissue successfully. Therefore, the main attentions were concentrated on implants [1]. Metals and alloys are considerably applicable as a part of an artificial implant or rehabilitant materials in dentistry and orthopedics. Besides, orthopedic implants are usually made of metals to be able to undergo mechanical stresses [2].

The most significant alloys that are utilized as orthopedic implants are consisted of titanium and cobalt alloys in addition to some of stainless steels, especially 316L austenitic stainless steel. The main characteristic of metals and alloys is their favorable mechanical properties and on the other hand, the need to low costs in public health services made the stainless steel the best choice for orthopedic implants. However, there are concerns about their corrosion resistance upon the body physiologic fluids and also their bioactivity, since the probability of pitting corrosion is high in stainless steel. Corrosion is constituted of the material loss what causes an implant to become weak and probably the more significant matter is the release of the corrosion products in the body tissues which causes some adverse effects, which increases the

rate of formation of fibrous tissue around the implant. On the other hand, bioinert metals and alloys are not capable of forming a suitable bond between the implant and tissues [3]. For this reason, developing the techniques for increasing their corrosion resistance and bioactivity seems significant. One of the mentioned techniques is the application of coatings prepared by different methods (such as sol-gel) [4-14]. Bioactive glasses are a class of bioactive ceramics that are combinations of silicon, sodium, potassium, calcium, phosphorous and magnesium oxides, that show good adhesion to metals because of their high thermal expansion coefficients and increase the probability of formation of hydroxyapatite (inorganic component of natural bone) [15-18]. Bioactive glasses are successfully used in orthopedic and dentistry operations and as teeth filler. However, some of the disadvantages of these glasses are low mechanical strength and fracture toughness which cases them not to be suitable for under-load applications; while increasing the strength decreases their bioactivity [1].

Therefore, it seems better to use them as powder or other bioactive phases in composites or as coatings. Thus, designing and producing bioactive glasses coated on 316L SS is performed to achieve two simultaneous purposes, containing: improve in corrosion behavior of metallic substrate for biocompatibility and fabrication of a bioactive outer surface for adhesion to living tissues and therefore bone osteointegration.

The purpose of present research is coating 316L stainless steel, which has many applications in biomedical engineering and specially orthopaedy, with bioglass 45S5 prepared by two melting and sol-gel methods, and then evaluating it through in-vitro experiments.

EXPERIMENTAL

Producing 45S5 bioglass with two techniques

The chemical composition of bioglass 45S5 is presented in Table 1. In order to synthesize bioglass 45S5 via sol-gel method, initially, 102.88 ml of tetraethoxysilane (TEOS) was added to 50 ml of 0.1 M nitric acid, and then was placed on a stirrer for the hydrolysis process to be performed. At this stage, nitric acid was used as the sol environment and tetraethoxysilane was utilized as a source to supply SiO_2 . Then, 8.861 ml of triethylphosphate was added to the system as a P_2O_5 supply, which was then stirred for 45 minutes. The process was continued by addition of 63.52 g of calcium nitrate tetrahydrate powder, which was previously solved in distilled water as a CaO supply, and again a 45 min period of stirring. The last stage was adding 25.864 g of sodium carbonate (as Na_2O supply, previously solved in distilled water) and placing the whole system on stirrer for 1 h for complete hydrolysis reactions to be occurred. The molar ratio of water to tetraethoxysilane ($\text{H}_2\text{O}:\text{TEOS}$) was chosen equal to 12:1. Table 2 shows the extent of materials used to synthesize 1 mole of 45S5 bioglass through sol-gel technique. The obtained sol was put in an oven for 6 h at 60°C , in order to approach to the gel state and become suitable for coating the steel surfaces.

Table 1. Chemical composition of bioglass 45S5 in mole & weight percent.

Compound	SiO_2	CaO	Na_2O	P_2O_5
mol %	46.1	26.9	24.4	2.6
wt. %	45	24.5	24.5	6

Table 2. Extent of materials used to synthesize 1 mole of 45S5 bioglass through sol-gel technique.

Compound	Na_2CO_3	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	TEP	TEOS
Extent	25.864 g	63.52 g	8.861 ml	102.88 ml

Table 3. The extent of powders used to synthesize 100 g of 45S5 bioglass through melting technique.

Compound	SiO_2	CaCO_3	Na_2CO_3	P_2O_5
Extent (g)	45	43.75	41.89	6
Molecular weight (g/mol)	60	100	106	141.9

Trying to use melting technique to produce the bioglass 45S5 with the chemical composition mentioned in table 1, SiO_2 , P_2O_5 , CaCO_3 and Na_2CO_3 powders were blended homogenously. The obtained blend was decarburized at 900°C for 2 h, melted using an alumina plant at 1350°C for 2.5 h and then quenched in water at room temperature. Afterwards, the produced 45S5 bioglass by melting technique was milled using a planetary mill for 12 h with a 1500 rpm velocity in order to gain the bioglass powder. The fabricated powder was screened to achieve a maximum particle size of $38 \mu\text{m}$. Table 3 presents the extents of powders used to synthesize 100 g of 45S5 bioglass through melting technique.

Test-specimens' preparation

In this research, stainless steel 316L sheets in $2 \text{ cm} \times 2 \text{ cm} \times 0.3 \text{ cm}$ dimensions were used as substrates. The specimens were shot blasted before coating to obtain a suitable surface roughness for coating. Afterwards, they were cleaned by immersing in ethanol to become ready for coating.

In order to coat the SS 316L using the melting method, a suspension of the powder of bioglass 45S5 was prepared. The suspension was made from 1 mole of the powder, 10 mole of distilled water and citric acid (0.1 mole %) as dispersant, and then stirred for 1 h. The prepared suspension was sprayed on the surface of stainless steel 316L specimens. During the coating procedure, steel specimens were kept at 300°C to evaporate the water of suspension. After the precipitation (coating) process finished, the coated specimens were heated up to 500°C in 3 h and 20 min (with $1^\circ\text{C}/\text{min}$ rate) and kept there for 2 h. They were then heated up to 700°C in 3 h and 20 min (with $1^\circ\text{C}/\text{min}$ rate) and kept in this point for 40 min. The specimens were cooled slowly in furnace until the room temperature.

Following the purpose of coating SS 316L using sol-gel technique, the specimens were immersed in the prepared sol for 30 min. After the immersion period, specimens were withdrawn from the sol with a constant velocity of $4 \text{ cm}/\text{min}$ to let a thin homogenous coating form on the steel surface. The coated specimens were kept at room temperature for 30 min and then heated in furnace up to 500°C in 8 h (with $1^\circ\text{C}/\text{min}$ rate) and kept there for 2 h. Afterwards, they were heated from 500°C to 700°C in 3 h and 20 min (with $1^\circ\text{C}/\text{min}$ rate) and kept at this point for 40 min. The specimens were cooled slowly in furnace until the room temperature. Because of required maximum tensile strength of 150 MPa for a cortical bone, there is no concern about sensitization of stainless still in high temperatures [19, 20].

However, if the best mechanical conditions were required for the steel substrate, substituting paths of heat-treatment could be used [21].

Identification analyses

X-ray diffraction (XRD) technique (Philips X'Pert-MPD system with a Cu K_{α} wavelength of 1.5418\AA) was used to analyze the crystal structure and phase present in the coated samples after immersing in SBF. The diffractometer was operated at 40 kV and 30 mA at a 2θ range of $20\text{--}55^{\circ}$ employing a step size of $0.02^{\circ}/s$.

FTIR analysis (Bomem, MB-100) was used to observe functional groups developed in the specimens and specially investigate the formation of apatite layer on the surface of SS 316L coated by bioglass 45S5 which was immersed in SBF at 37°C . The FTIR spectrum was investigated in $400\text{--}4000\text{ cm}^{-1}$ range. Furthermore, scanning electron microscope (SEM, Phillips XL 30) was used to observe the structure and morphology of the bioglass 45S5 coating produced by both melting and sol-gel techniques on SS 316L.

In-vitro bioactivity evaluation

The (simulated body fluid) SBF solution was prepared by dissolving reagent-grade NaCl, KCl, NaHCO_3 , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 and KH_2PO_4 into distilled water and buffered at $\text{pH}=7.25$ with 50 mM of TRIS (trishydroxymethyl aminomethane) and approximately 45 mM of HCl at 37°C . Its composition is given in Table 4 and is compared with the human blood plasma.

Table 4. Ion concentrations of simulated body fluid (SBF) and human blood plasma.

Ion	Plasma (mM)	SBF (mM)
Na^+	142.0	142.0
K^+	5.0	5.0
Mg^{+2}	1.5	1.5
Ca^{+2}	2.5	2.5
Cl^-	103.0	103.0
HCO_3^-	27.0	27.0
HPO_4^{2-}	1.0	1.0
SO_4^{2-}	0.5	0.5

Investigating the bioactivity of metallic implants made of SS 316L coated by bioglass 45S5 was performed using a SBF. The coated specimens were immersed in 100 ml of SBF for 14 days in an incubator at 37°C . They were then brought out from the incubator and desiccated at room temperature.

RESULTS AND DISCUSSION

Structure and bioactivity

The XRD patterns of coated specimens' surfaces are shown in Figure 1. XRD results indicated the formation of hydroxyapatite on the surface of stainless steel specimens according to 26° and 32° peaks that are assigned to be (211) and (002) apatite due to the standard JCPDS cards (09-0432).

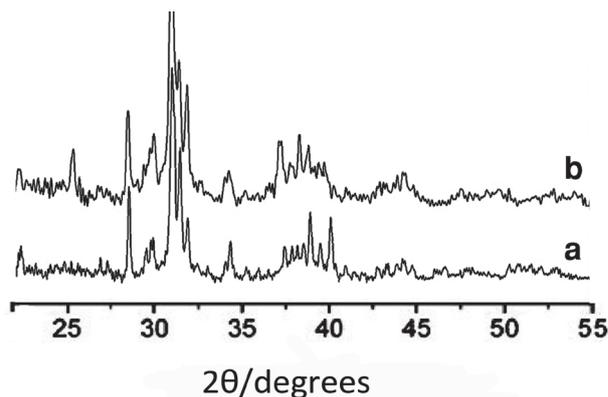


Figure 1. XRD pattern of the hydroxyapatite layer formed on 316L stainless steel coated by 45S5 bioglass produced by (a) melting and (b) sol-gel techniques, after 14 days of immersion in SBF.

Biological properties (the formation of HAP layers) were also investigated through FTIR analysis, which is presented in figure 2 and 3 for melting and sol-gel techniques, respectively.

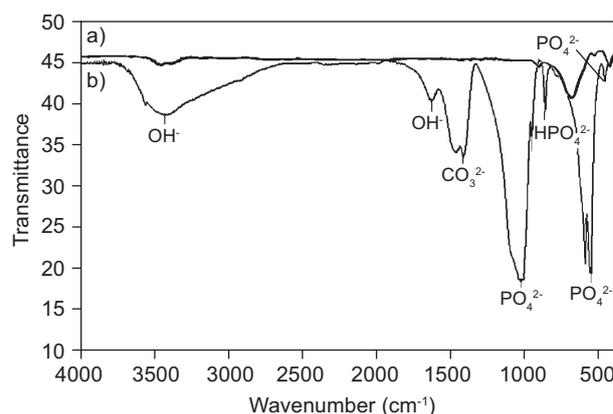


Figure 2. FTIR spectra showing the apatite layer formed on stainless steel 316L coated by bioglass 45S5 produced by melting technique (a) before and (b) after 14 days of immersion in SBF.

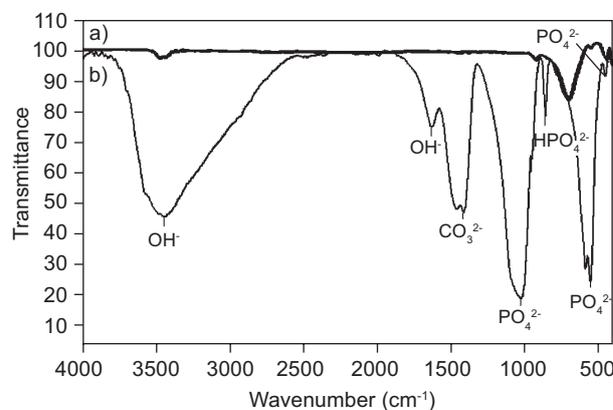


Figure 3. FTIR spectra showing the apatite layer formed on stainless steel 316L coated by bioglass 45S5 produced by sol-gel technique (a) before and (b) after 14 days of immersion in SBF.

Comparing between before and after 14 days of immersing the specimens in SBF, the FTIR spectroscopy pattern of both of them (including SS 316L coated by bioglass 45S5 produced by melting and sol-gel techniques) shows a large peak at the wave numbers range of 1000-1200 cm^{-1} , that confirms the formation of an amorphous layer rich of CaO and P_2O_5 . In addition, a peak related to P-O bond is observed at the wave numbers range of 500-600 cm^{-1} , that shows the formation of hydroxyapatite layer on the specimens' surfaces [18]. The obtained peak at the range of 3400-3500 cm^{-1} is associated with the absorbed water of the system.

As it can be seen, the intensities of bands associated to phosphate group and the spectrum were similar to that of Hap (Figures 2 and 3). The characteristic bonds exhibited in the sample's spectra are as follow:

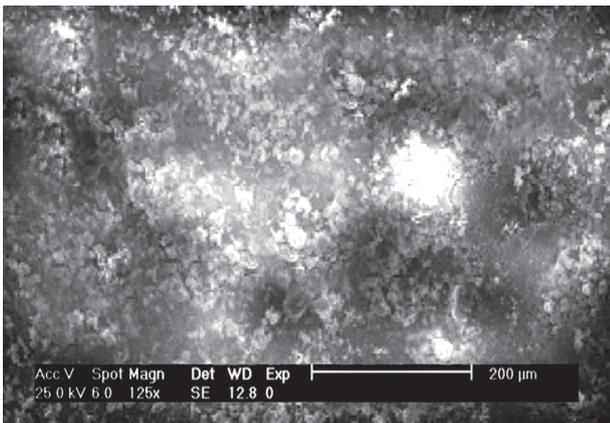
- Two bonds were observed at 3460 and 673 cm^{-1} due to stretching mode of hydrogen-bonded OH^- ions and librational mode of hydrogen-bonded OH^- ions, respectively.

- The bond at 1131 cm^{-1} arises from $\nu_3 \text{PO}_4$ and the bond at 604 arises from $\nu_4 \text{PO}_4$ [22,23].

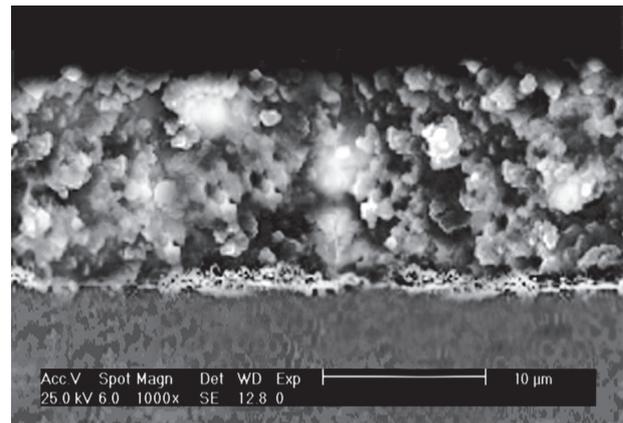
Another noticeable point is the larger peak of P-O bond for SS 316L coated by bioglass 45S5 produced by sol-gel technique in comparison with the same peak for SS 316L coated by bioglass 45S5 produced by melting technique, which implies more formation of hydroxyapatite layer on sol-gel prepared surface than its formation on the surface coated by the bioglass produced by melting technique, the suspension of powder of which was sprayed on the hot surface of metal.

IDENTIFICATION RESULTS

At this stage, the morphology and microstructure of the specimens were investigated. Therefore, images from surfaces and cross sections of the specimens were taken after coating (before immersing in SBF and after 14 days of immersion), as shown in Figures 4, 5 and 6.

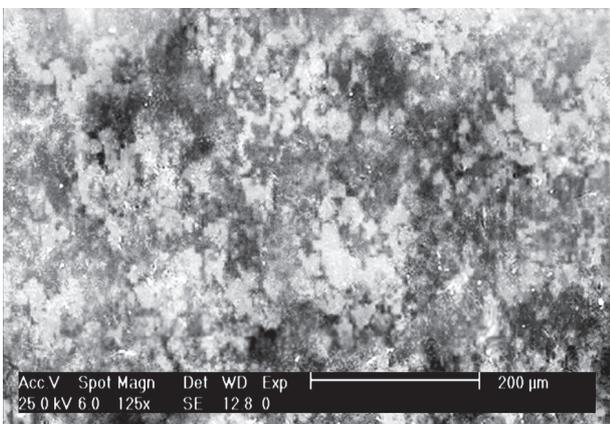


a)

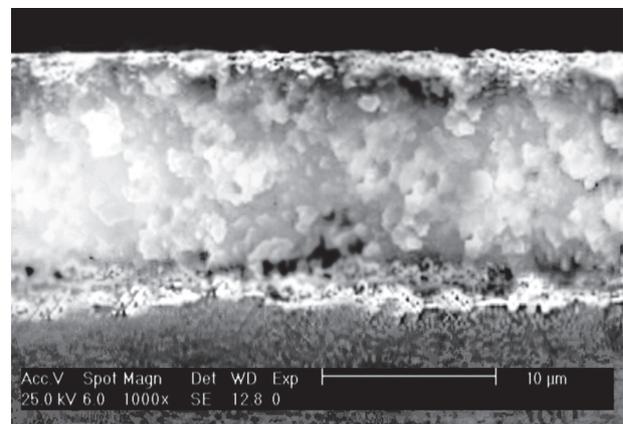


b)

Figure 4. SEM images of (a) the surface and (b) cross section of SS 316L coated by bioglass 45S5 produced by melting technique before immersion in SBF.



a)



b)

Figure 5. SEM images of (a) the surface and (b) cross section of SS 316L coated by bioglass 45S5 produced by sol-gel technique before immersion in SBF.

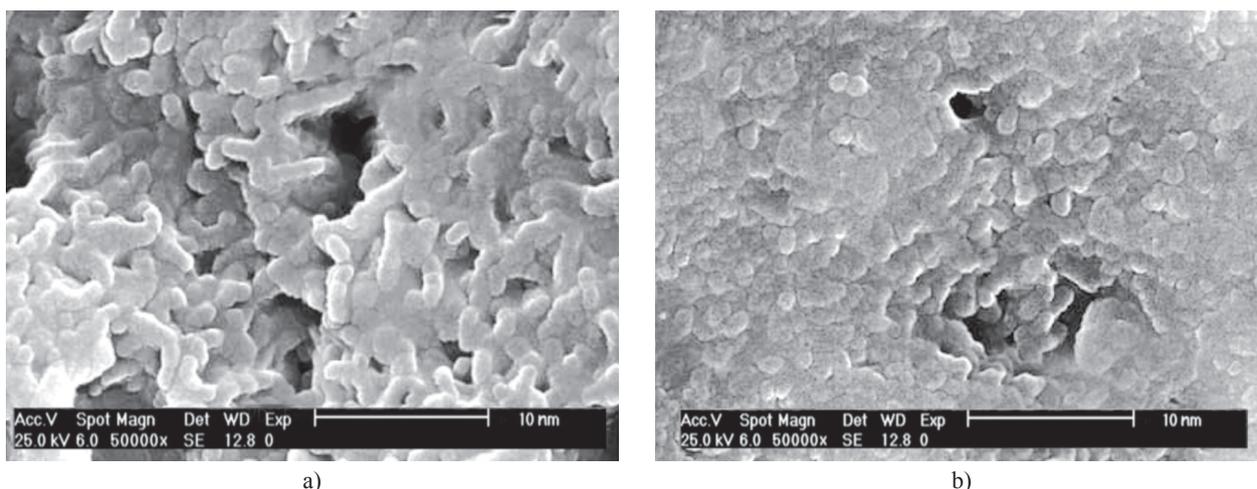


Figure 6. SEM images of the surface of SS 316L coated by bioglass 45S5 produced by (a) melting and (b) sol-gel techniques after immersion in SBF.

Comparing the SEM images of coated surfaces before immersing in SBF shows that the specimens coated by sol-gel method have more homogenous and uniform surfaces than the specimens coated by a bioglass produced by melting technique. Furthermore, some pores and cracks could be observed on the specimens coated by the bioglass produced by melting technique, while it seems that the specimens coated by sol-gel method show surfaces less pores and cracks. Also, SEM images of the surface of SS 316L coated by bioglass 45S5 using both sol-gel and melting techniques after 14 days of immersion in SBF are presented in Figure 6.

In addition, a comparison between the SEM images of the cross sections of specimens before immersion in SBF indicates that the coating thickness of the specimens coated by sol-gel technique is more homogenous and uniform than the same property of the other specimens. Although, the coating thickness on all specimens is about 10-15 μm .

CONCLUSION

This study revealed the capability of 45S5 bioglass coating produced by melting and sol-gel techniques to adhere on the surface of 316L stainless steel. However, the sol-gel coatings showed more homogeneity and yielded a more uniform thickness in comparison with the coatings of bioglass produced by melting technique. All the coated specimens demonstrated an interesting bioactivity after 14 days of immersion in SBF; although the coated specimens by sol-gel method indicated more formation of hydroxyapatite layer.

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