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Innovative surface modification of orthopedic implants with positive effects on wettability and in vitro anti-corrosion performance

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Abstract

In this work, sol–gel derived bioactive glass/zirconium titanate coatings were uniformly deposited on stainless steel orthopedic implants, by using carboxymethyl cellulose as a particulate dispersant in the sol. The surface features, wetting, and *in vitro* electrochemical corrosion behavior of the coated samples were evaluated. It was found that, by applying the coating on the substrate, the water contact angle was decreased, which is indicative of an improvement in the implant hydrophilicity. Also, the coating improved the corrosion

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resistance of the metallic implant, as realized by an increase in the corrosion potential and a decrease in the corrosion current density. Indeed, this coating acted as a physical protective barrier which retards the electrolyte access to the metal surface and thereby electrochemical processes.

Keywords: Ceramic coating; Corrosion resistance; Hydrophilicity; Implant

1. Introduction

It has been frequently reported that conventional orthopedic and dental implants do not appropriately bond or integrate to natural tissues. In this regard, bioactive coatings become of interest, in order to improve the bonding quality of implants. When highly bioactive surfaces are needed, bioactive glass materials can be used as coatings on implants. However, their disadvantage lies in their low mechanical strength and often low adhesion to the substrate [1,2]. The development of composite coatings containing bioactive glass materials can be a viable approach to obviating this drawback. For instance, Kamalian et al. [3] synthesized and characterized composites of crystalline magnesium silicate and bioactive glass. They concluded that the addition of magnesium silicate could improve the mechanical strength of the bioactive glass matrix without deteriorating its bioactivity.

On the other hand, zirconia-based and titania-based ceramics have been recently used for biomedical applications, due to their superior characteristics , such as suitable fracture toughness, strength, and biocompatibility. Importantly, zirconium titanate ($ZrTiO_4$) coatings have recently attracted attention for biomedical purposes [4,5]. In this regard, Devi et al. [6] prepared $ZrTiO_4$ coatings by a non-hydrolytic sol–gel method on a metallic substrate, and reported excellent characteristics, such as facilitation of the formation of apatite on the metal.

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In this work, $ZrTiO_4$ was employed as the second component of the above-described bioactive composite coatings. Multilayer bioactive glass/$ZrTiO_4$ thin films were deposited on stainless steel samples using a sol–gel, spin-coating method. Then, the wettability and electrochemical corrosion behavior of the samples were investigated.

2. Materials and methods

Bioactive glass powders with the composition of 60% SiO_2–36% CaO–4% P_2O_5 (in mol%), and $ZrTiO_4$ sol (containing 2 wt. % carboxymethyl cellulose) were prepared according to the method described in Ref. [7]. To prepare bioactive glass/zirconium titanate coatings, a sol containing 50 wt.% of bioactive glass and 50 wt.% of $ZrTiO_4$ was spin-coated on austenitic Type 316L stainless steel substrates at 3000 rpm for 60 sec. The coated samples were dried at 80 °C for 1 h in an oven. Sintering was conducted under a nitrogen atmosphere by raising the temperature at a heating rate of 5 °C/min to 700 °C, holding at that value for 1 h, followed by cooling at the same furnace after turning off. Because of the low carbon level of 316L stainless steel, compared with other common stainless steels like 316 and 304 having high levels of carbon, no carbide precipitation occurred during heat treatment; that is, its structure remained austenitic. The above processes including deposition, drying, and sintering were repeated three times to prepare mono, double, and triple-layered films, where for preparing the miltilayers, the deposition of the upper layer was done on the bottom sintered layer.

A transmission electron microscope (TEM, JEOL JEM-2100) operating at an accelerating voltage of 200 kV and a Veeco multimode atomic force microscope (AFM, Bruker AXS) were used to evaluate the powder particles and the film surface quality,

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respectively. Water contact angles were measured by the sessile drop method at room temperature, using a video camera mounted on a microscope to record drop images. The video signals were transmitted to a Video Pix Framegrabber Sun Microsystems, and a Sun Sparcstation IPC was used to acquire the images from the image processor and to perform the image analysis.

The *in vitro* electrochemical corrosion behavior of the samples was investigated in the simulated body fluid (SBF) [8] at a pH value of 7.4 under the naturally aerated condition. A platinum wire and saturated calomel electrode (SCE) were employed as the auxiliary and reference electrodes, respectively. The samples were first immersed in the SBF for 1 h to obtain a steady-state open circuit potential (ocp). Afterwards, anodic potentiodynamic polarization curves were obtained at a scan rate of 1 mVs^{-1} starting from -0.1 V vs. ocp.

3. Results and discussion

Fig. 1 (a) shows the sedimentation behavior of the sols with and without the carboxymethyl cellulose addition. As can be seen, the addition of carboxymethyl cellulose to the sol creates a physically stable suspension without sedimentation, even after one week of standing. Indeed, carboxymethyl cellulose creates a negative charge around the nanoparticles and depresses their hydrophobicity and aggregation by coulombic repulsion. Due to interactions between the carboxylic groups of carboxymethyl cellulose and the nanoparticles, long chains of anionic polymer layers are created on the surface of the nanoparticles (steric stabilization theory). Accordingly, the strong steric and coulombic repulsion between the particles leads to the development of a high stable and uniform colloidal dispersion of the particles, which is an essential requirement for depositing uniform coatings [9,10].

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Figs. 1(b) and 1(c) show the TEM micrographs of the synthesized bioactive glass and zirconium titanate powders, respectively. As shown, the average particle size of the bioactive glass powder is around 100 nm, while the $ZrTiO_4$ particles have an average size of 5 nm. This difference is attributed to the processing routes used in their synthesis [11-13]. The bioactive glass powder was prepared by a polymeric sol-gel method followed by ball milling, while the $ZrTiO_4$ powder was directly synthesized by a particulate sol-gel route.

According to the two- and three-dimensional AFM images of the triple-layer coated sample (Fig. 2), the coating has the desirable smooth, uniform, and dense features. Also, the multi-layered film comprises nearly globular nanoparticles with an average diameter of 100 nm. Indeed, the lattice mismatch between the different layers leads to the growth of strained layers which energetically tend to show an “island” morphology [14], as observed in Fig. 2.

Surface characteristics are an important condition for the future success of dental and bone implants. The surface quality affects early surface events that usually occur upon implantation into the body. Hydrophilicity is one of the important surface properties, due to its effect on biomineralization and adsorption of proteins and cells onto the implant surface [15,16]. Measuring water contact angles at the solid-air-liquid intersection is widely used to investigate the wettability of solid surfaces, where the results are dependent on the surface tension, surface chemistry, surface topography, and cleanliness of the solid substrate. Fig. 3 shows that the contact angles are changed by depositing the coating. Typically, by increasing the number of the layers, the contact angle values are decreased, which could be interpreted in terms of the surface chemistry of the thin films. Lower contact angles or better spread is indicative of higher hydrophilicity. The hydrophilic nature of the ceramics, compared with the metallic substrates, is attributed to the presence of highly negatively charged hydroxyl

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groups on the surface. Some water molecules are physically and chemically adsorbed on the surface and react with the metal oxide ceramic, forming surface hydroxyl groups. Interactions between H_2O and OH^-, via van der Waals forces and hydrogen bonds, lead to a better spread of water on the surface [17]. In this regard, Abdulmajeed et al. [18] evaluated the effect of exposed bioactive glass particles on the wettability behavior of composite implants. They showed that an increase in the bioactive glass particle content of the samples increased the polar value, while the dispersive value decreased. They finally concluded that composites containing bioactive glass particles were hydrophilic materials that showed good wettability characteristics.

The corrosion resistance of metallic implants is also an essential factor determining their *in vitro* and *in vivo* biocompatibility [19,20]. Fig. 4 indicates the electrochemical potentiodynamic polarization curves of the uncoated and coated samples. Also, Table 1 summarizes the related electrochemical parameters. As can be seen, the corrosion behavior of the coated samples signifies significant differences compared to that of the substrate, while the number of the sol-gel derived layers has no significant influence on the corrosion behavior of the coated samples. Typically, the substrate exhibits no passivity, although 316L stainless steel is essentially an active-passive alloy. This is attributed to the considerable concentration of chloride in the SBF under the naturally aerated condition, which encourages localized corrosion like pitting and avoids passivation. Albeit, it is known that the *in vivo* corrosion resistance of metallic implants is frequently higher than that under in vitro conditions, due to the inhibiting effect of organic species like proteins [21]. However, the film deposition encourages the stainless steel substrate polarized in the SBF to be passivated. In addition, the coatings advantageously increase the corrosion potential and decrease the

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corrosion current density of the substrate, which is indicative of an improvement in the corrosion resistance. Thus, it can be concluded that the coatings act as a physical protective barrier to retard the electrolyte access to the metal surface and thereby electrochemical processes [5,22,23].

4. Conclusions

In this research, bioactive glass/zirconium titanate thin films were successfully deposited on the surface of metallic implants by a sol–gel spin-coating method. The microstructural observations indicated the formation of well-covering homogeneous coatings. In addition, the surface characteristics of the coated implants showed significant improvements in hydrophilicity and corrosion resistance, which can have significant effects on biomineralization and adsorption of proteins and cells onto the implant surfaces.

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Figure:

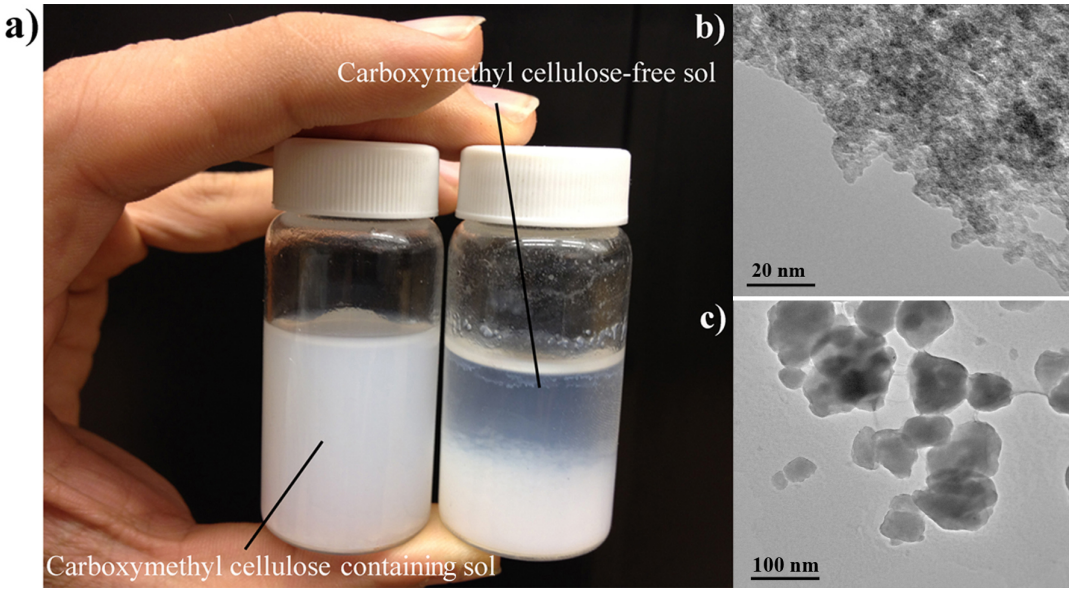

Fig. 1. (a) Optical photograph of the sols, with and without carboxymethyl cellulose, after 2 weeks of standing. TEM micrographs of the (b) zirconium titanate and (c) bioactive glass powders.

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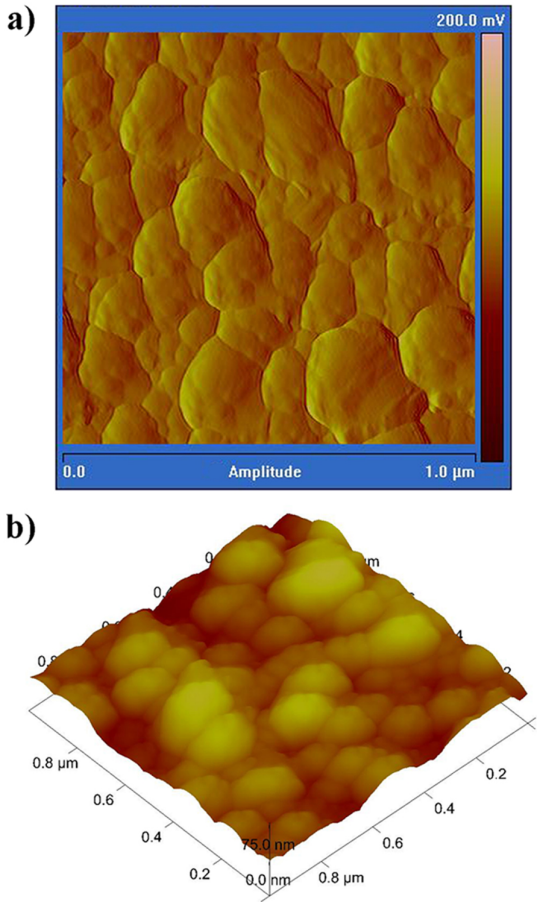

Fig. 2. (a) Two- and (b) three-dimensional AFM images of the triple-layer coated sample.

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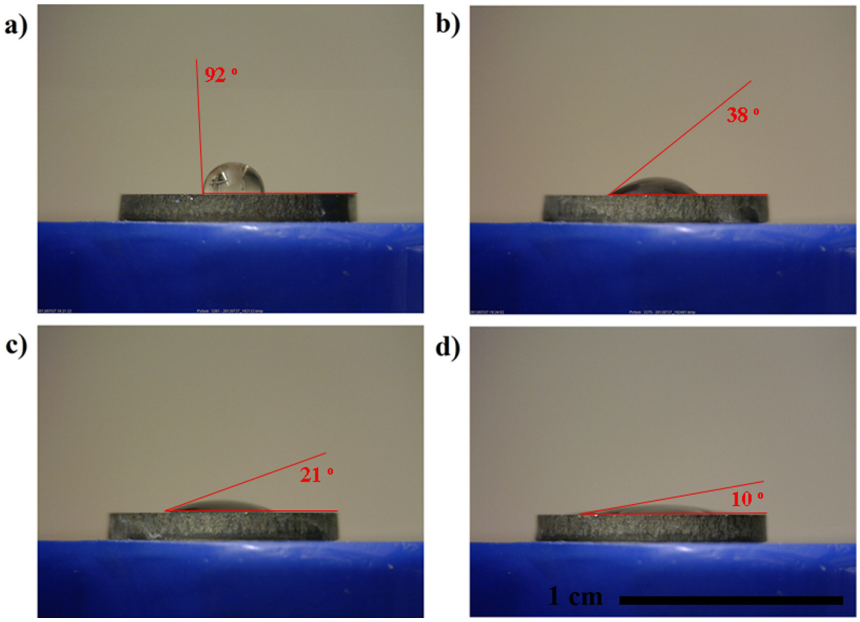

Fig. 3. Contact angle of the surfaces with a liquid droplet for partially wetting of the (a) uncoated, (b) mono-layer, (c) double-layer, and (d) triple-layer coated samples.

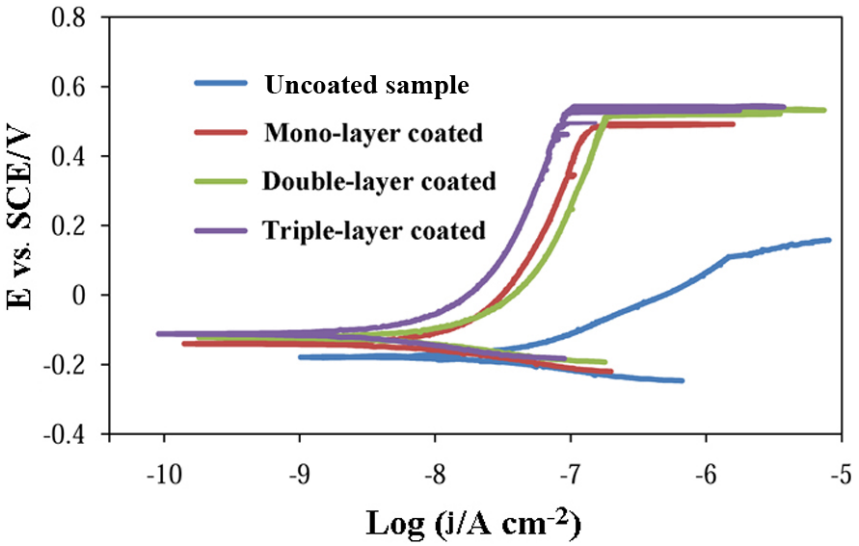

Fig. 4. Potentiodynamic polarization curves of the uncoated and bioactive glass/zirconium titanate coated samples, where *E* is potential and *j* is current density (the testing conditions are electrolyte: SBF, pH = 7.4, and temperature = 37 ˚C).

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Table 1. Corrosion potential (E_{corr}), corrosion current density (j_{corr}), passive current density (j_p), and breakdown potential (E_b) (note that the uncoated sample shows no typical passivity).

Sample	E_{corr} (vs. SCE/mV)	j_{corr} (A/cm^2)	j_p (A/cm^2)	E_b (vs. SCE/mV)
Uncoated	-192	4.8×10^{-8}	-	-
Mono-layer	-130	1.1×10^{-8}	1.3×10^{-7}	485
Double-layer	-114	9.4×10^{-9}	7.9×10^{-8}	518
Triple-layer	-105	8.8×10^{-9}	5.1×10^{-8}	531