

Double-layer Bioactive Glass Coatings Obtained by Pulsed Laser Deposition

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Abstract. Pulsed laser deposition was used to obtain functionally graded bioactive glass coatings on titanium substrates. An UV KrF* ($\lambda=248$ nm, $\tau>7$ ns) excimer laser was used for the multi-pulse irradiation of the targets. The depositions were performed in oxygen while keeping substrate temperature at 400°C. We used sintered glass targets in the system SiO₂-Na₂O-K₂O-CaO-MgO-P₂O₅ that differed in SiO₂ content, which was either 57 wt.% (6P57) or 61 wt.% (6P61). A glass 6P61 was used as the first layer in direct contact with the metallic substrate, while the outer bioactive layer was made of glass 6P57. Both the bioactive coatings and the bulk glasses were analyzed by Fourier transform infrared spectrometry (FTIR), grazing incidence X-ray diffraction (GIXRD), and scanning electron microscopy (SEM). The FTIR spectra of the glass powders and glass coatings showed the main vibration modes of the Si-O-Si groups. GIXRD analysis confirmed that the glass coatings had an amorphous structure. The SEM micrographs of the glass coatings showed the films to consist of droplets with diameters ranging from 0.2 to 5 μ m. SEM was used to determine the rate of apatite formation on the coating when exposed to simulated body fluid (SBF) solution for 7 days. We demonstrated that pulsed laser deposition leads to good glass-metal adhesion on the substrate and well attached bioactive particles on the surface. We consider therefore this method appropriate for forming implants that can develop an apatite layer after immersion in SBF.

Introduction

Bioactive glasses are a class of biomaterials that can be used as surgical bone replacement material in otorhinolaryngology, oral surgery, orthopedics, and dentistry [1]. Silica based glasses in the system SiO₂-Na₂O-K₂O-CaO-MgO-P₂O₅ have active surfaces and can form mechanically strong bonds with bone. When exposed to biological fluids, bioactive glasses form a silica gel and calcium phosphate layer on their surface due to the alkali and alkali earth cations (Na⁺, Ca²⁺) inside silica network. These cations cause the Si-O-Si bonds to break locally, releasing silica in the form of silic acid in the solution and promoting the formation of non-bridging silicon-oxygen groups (Si-O-NBO) [2]. The dissolution rate of silica is controlled by the concentration of these groups [3].

An optimal composition of the silica based glasses results in a suitable compromise between bioactivity and solubility in which the percentage of silica content plays a key role. It is well known that bioactive glasses are typically silicate glasses with less than 60 wt.% SiO₂ content [4].

However, bioactive glasses are relatively brittle and have poor mechanical strength which makes them suitable only in non- or low-load bearing applications. In high stress implant applications, bioactive glasses can be used as coatings for prosthetic metallic implants. Bioinert metals and alloys (Ti, Ti6Al4V, Co-Cr alloy, and others) have been used as implant materials as they can bear loads while causing only minor reactions in the body [5]. Preparing glass coatings is a way to combine the mechanical properties of the base material with the bioactive properties of

bioglasses [6]. To coat Ti substrates with bioglasses that retain bioactivity and provide enhanced glass-metal adhesion, functionally graded bioactive glass coatings have to be fabricated [5].

Different coating techniques, such as sputtering, plasma spraying, enameling, and electrophoretic deposition have been applied to produce bioactive glass coatings [7-10]. Among them, pulsed laser deposition (PLD) has yielded good results in preparing coatings of different calcium phosphate and bioglass compositions by changing the parameters of deposition [11-13]. Compared with other methods, PLD has several advantages, such as helping to grow materials with high melting points, being free of contamination, and ensuring a stoichiometric transfer of the target composition to the substrate [1, 6, 13].

The aim of this work was to pulsed laser deposit functionally graded bioglass coatings on Ti substrates using a glass containing 61 wt.% silica in direct contact with Ti and a bioactive glass containing 57 wt.% silica as surface coating. An intermediate bioinert glass layer was introduced in order to improve the substrate adhesion of the multistructures.

Materials and methods

Functionally graded bioactive glass coatings were grown on Ti substrates using glasses in the system $\text{SiO}_2\text{-Na}_2\text{O-K}_2\text{O-CaO-MgO-P}_2\text{O}_5$ containing 61 wt.% (6P61) and 57 wt.% (6P57) silica. Pulsed laser deposition was applied to make the coatings. The composition of the glass powder 6P61 was: SiO_2 61.1%, Na_2O 10.3%, K_2O 2.8%, CaO 12.6%, MgO 7.2%, P_2O_5 6%. The composition of the glass powder 6P57 was: SiO_2 57%, Na_2O 11%, K_2O 3%, CaO 15%, MgO 8%, P_2O_5 6%.

The glass powders were prepared by mixing the required amounts of SiO_2 , CaCO_3 , MgCO_3 , Na_2CO_3 , K_2CO_3 and NaH_2PO_4 . All chemicals were p.a. grade. The mixtures were dried at 100 °C for 24 h, then calcinated in air at 850 °C for 1h, and then heated up to 1500 °C over 3 h in a Pt crucible at a rate of 10 °C/min. The melt was quenched, and the glasses were separately milled in a planetary agate ball mill (Fritsch, Germany) at radial velocity 273 min^{-1} for 90 min. The grinding was performed using ZrO_2 grinding balls. The glass to balls ratio was 50 g: 250g.

The glass targets, which were prepared by pressing the base powder material at 3 MPa and sintering at 650 °C for 6h, were ablated with an excimer laser in a stainless steel deposition chamber. The beam generated by an UV KrF* laser source ($\lambda=248$ nm, $\tau \geq 7$ ns) was focused on the target at an energy density of 2.8 J/cm^2 and repetition rate of 2 Hz. The laser beam attacked the target at an angle of 45 ° to the substrate surface. During film growth, the target was rotated in order to improve film quality and avoid piercing. The distance between target and substrate was 40 mm. For the deposition of each layer, 25000 subsequent laser pulses were applied. As deposition substrate, we used chemically-etched, high-purity (97 %) Ti disks of 15 mm diameter and 1.5 mm thickness. The temperature of substrates was kept at 400 °C during the deposition. The glass thin films were deposited in oxygen at 13 Pa and then cooled down at the same pressure.

The first layer in contact with the Ti substrate was always 6P61, whose thermal expansion behavior is similar to that of Ti. Next, a second layer glass 6P57 was deposited. The depositions were performed without opening the chamber by simply changing the target with a carousel.

Information about the bonding configuration of the coatings was acquired by FTIR spectrometry in mid-IR within the range (4000 to 400 cm^{-1}). These studies were conducted with a Nicolet 380 equipped with a smart orbit ATR (diamond crystal). The crystallinity and composition of the samples were analyzed by grazing incidence XRD with a Bruker AXS D8 advance diffractometer. The grazing incidence angle was varied within a (1° - 2.5°) range. The surface morphology of the coatings was investigated by scanning electron microscopy (SEM) with a Jeol JSM-6460LV.

In-vitro tests were performed by soaking the coatings in 25 ml simulated body fluid (SBF) for 7 days at a constant temperature of 37° C, without stirring. The solution was replaced every 48 hours. The SBF was prepared by dissolving the appropriate amounts of salts in distilled water to reach the following composition (in mM): Na^+ 142, K^+ 5, Ca^{2+} 2.05, Mg^{2+} 1.5, Cl^- 148, HCO_3^- 4.2,

HPO_4^{2-} 1.0. After soaking in SBF, the coatings were removed from the solution, washed in distilled water, dried at room temperature, and examined by SEM.

Results and discussion

Fig.1. shows typical FTIR spectra recorded in the case of a) 6P61 glass powder, b) 6P57 glass powder, and c) coating. All spectra contain the bands characteristic of the Si-O-Si groups. We were able to identify: i) the Si-O (s) stretching mode assigned at ($1300\text{--}1000\text{ cm}^{-1}$), ii) the Si-O (b) banding mode around 800 cm^{-1} , and iii) a band attributed to Si-O (r) rocking vibrations at approximately 460 cm^{-1} . As can be seen in Fig.1 (b, c), a band at $950\text{--}900\text{ cm}^{-1}$ was associated to the Si-O (s) with one non-bridging silicon-oxygen (Si-O-NBO) per SiO_4 tetrahedron [13]. Additionally, the intensity of the Si-O (b) band decreased, and the intensity of the band associated to the Si-O-NBO groups increased and became sharper. Comparing the FTIR spectra of the bulk glasses and those of the coating, we found the coatings had the same structure and composition as the starting powders.

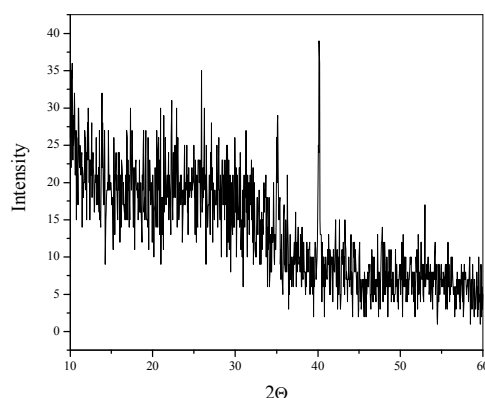
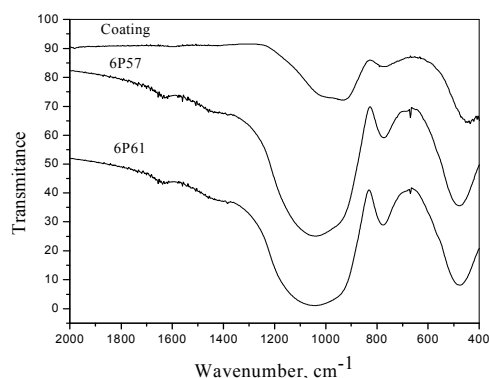


Fig.1. FTIR spectra of a) 6P61 glass powder, b) 6P57 glass powder, and c) coating

Fig. 2. Grazing X-ray diffraction pattern of the coating at a grazing angle of 2.5°

The XRD spectrum of a synthesized coating is given in Fig. 2. The X-ray diffraction patterns of the coating on Ti substrate showed clearly visible peaks that belong to Ti at $2\theta = 35.1$, 38.4 and 40.2 , while the increase in background revealed the presence of an amorphous structure of the deposited film.

Typical SEM micrographs of the coating surface are shown in Fig.3 (a). As an important feature, we noticed that the deposited film mainly consisted of spherical droplets of different dimensions ranging between $0.2 - 5\text{ }\mu\text{m}$. According to Bao *et al.* [14], these droplets are produced by multiple mechanisms that are mainly induced during laser ablation due to the brittle nature of the target material. The geometrical shape of the deposited layers generally followed the surface relief of the Ti substrate. The pinholes that can be noticed on the coating originated from the existing pitting on the Ti surface. This droplet-and-pinhole microrelief of the coating is appropriate for the growth and proliferation of cells which can more easily and deeply implant their roots into such surface imperfections [15].

The evolution of the coating surface microstructure after immersion in SBF was observed by SEM (Fig. 3(b)). The SEM analysis indicated changes in the surface morphology of the deposited layers. The micrograph showed that the surface of the deposited layers was covered by precipitated new phase with a high degree of interconnectivity between the primary spherical particles. Nevertheless, voids between the primary particles were still visible. The microstructural changes seen on the micrograph of the coating after 7 days in SBF were probably due to the Si content of bioglass 6P57. The lower silica glass had a more open network structure that facilitated ion exchange with the solution, and the coating showed bioactivity [16].

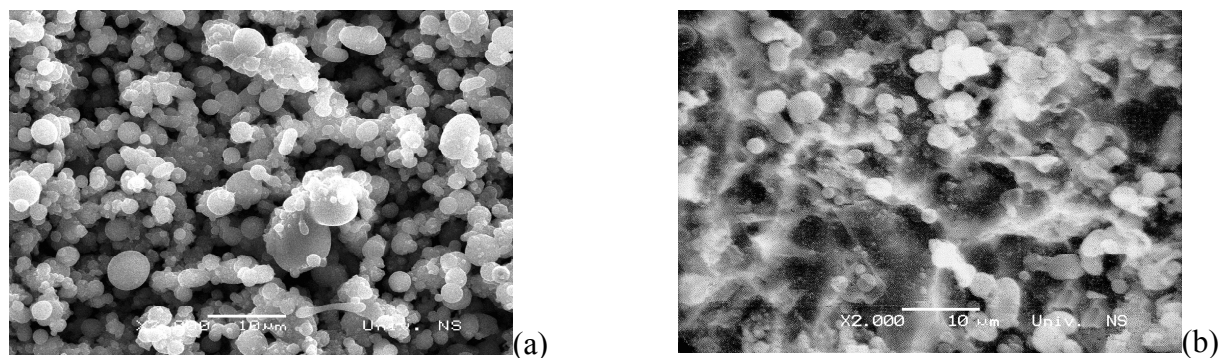


Fig. 3. SEM micrographs of the coating (a) before and (b) after 7 days of immersion in SBF

Conclusions

Pulsed laser deposition was used to coat Ti substrates with double-layer bioactive glass thin films. The depositions were performed in oxygen keeping the deposition temperature at 400 °C. The FTIR analyzes showed that the coatings and the bulk glasses had similar compositions. The surface morphology of the amorphous films, which was originally characterized by a droplet structure, changed following immersion in SBF. After 7 days in SBF, a newly formed phase covered the surface of the coatings, as revealed by the SEM analysis. PLD proved to be an appropriate method for the successful preparation of glass multistructures.

Acknowledgments

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References

- [1] P. González, J. Serra, S. Liste, S. Chiussi, B. León, M. Pérez-Amor: *Vacuum* Vol. 67 (2002), p. 647
- [2] L.L. Hench and Ö. Anderson, in: *An Introduction to Bioceramics*, edited by L.L. Hench, J. Wilson (World Scientific, Singapore, 1993).
- [3] J. Serra, P. González, S. Liste, C. Serra, S. Chiussi, B. León, M. Pérez-Amor, H.O. Ylänen and M. Hupa: *J. Non-Cryst. Solids* Vol. 332 (2003), p. 20
- [4] S. Lopez-Esteban, E. Saiz, S. Fujino, T. Oku, K. Suganuma and A.P. Tomsia: *J. Eur. Ceram. Soc.* Vol. 23 (2003), p. 2921
- [5] S. Foppiano, S.J. Marshall, E. Saiz, A.P. Tomsia and G.W. Marshall: *Acta Biomater* Vol. 2 (2006), p. 133
- [6] S. Liste, J. Serra, P. González, J.P. Borrajo, S. Chiussi, B. León and M. Pérez-Amor: *Thin Solid Films* Vol. 453–454 (2004), p. 224
- [7] C.X. Wang, Z.Q. Chen and M. Wang: *J. Mater. Sci. - Mater. Med.* Vol. 13 (2002), p. 247
- [8] J.H. Chern Lin, K.S. Chen and C.P. Ju: *Mater. Chem. Phys.* Vol. 41 (1995), p. 2820
- [9] A. Pazo, E. Saiz and A.P. Tomsia: *Acta mater.* Vol. 46 (1998), p. 2551
- [10] D. Stojanovic, B. Jokic, Dj. Veljovic, R. Petrovic, P.S. Uskokovic and Dj. Janackovic: *J. Eur. Ceram. Soc.* Vol. 27 (2007), p. 1595
- [11] E. Gyorgy, S. Grigorescu, G. Socol, I.N. Mihailescu, A. Figueras, C. Ducu, Dj. Janackovic, A. Dindune, Z. Kanepe, E. Palcevskis, E.L. Zdrentu and S.M. Petrescu: *Appl Surf Sci* (2007) doi:10.1016/j.apsusc.2007.02.146.
- [12] D. Tanaskovic, B. Jokic, G. Socol, A. Popescu, I.N. Mihailescu, R. Petrovic and Dj. Janackovic: submitted to *Applied Surface Science* (2007)
- [13] S. Liste, P. González, J. Serra, J.P. Borrajo, S. Chiussi, B. León, M. Pérez-Amor, J. García López, F.J. Ferrer, Y. Morilla and M.A. Respaliza: *Thin Solid Films* Vol. 453–454 (2004), p. 219
- [14] Q. Bao, C. Chena, D. Wang, T. Lei, and J. Liu: *Mater. Sci. Eng., A* Vol. 429 (2006), p. 25
- [15] V. Nelea, C. Morosanu, M. Iliescu and I.N. Mihailescu: *Appl. Surf. Sci.* Vol. 228 (2004), p. 346
- [16] S. Lopez-Esteban, E. Saiz, S. Fujino, T. Oku, K. Suganuma and A.P. Tomsia: *J. Eur. Ceram. Soc.* Vol. 23 (2003), p. 2921