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Structural analysis of hydroxyapatite/bioactive glass composite coatings obtained by plasma spray processing

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Abstract

Bioactive materials such as hydroxyapatite (HA) are used as coatings on metallic implants, producing a conjugate with better performance. The coatings are in general obtained by a plasma spray process. In this work the structural properties of composite coatings hydroxyapatite/bioactive glass (HA/BG) as well as coatings of the pure materials are measured. The coatings were obtained by plasma spraying mixtures of the powders Bioglass® and HA, in different proportions. The process parameters, arc current and primary/secondary gas ratios, were also varied. X-ray diffraction (XRD), infrared spectroscopy and scanning electron microscopy (SEM) measurements were made of the coatings. The in vitro bioactivity of the different coatings was also evaluated. The results showed that Bioglass® addition to the coating powders increased the dissolution rates and rate of formation of a HA film on the surface of the coatings, thus increasing its in vitro bioactivity compared to pure HA coatings.

1. Introduction

The coating of metallic implants with bioactive materials is of interest in the biomedical area [1]. In this case, the bone bonding ability of the bioactive surface is associated with the mechanical properties of the metallic substrate. The advantage of the bonding ability of a bioactive material is mainly the stabilization of an implant in the short term and the fixation of the prosthesis without the use of cements in the long-term [2,3].

Hydroxyapatite (HA) coatings produced by plasma spray processing have been the most accepted and studied material [1–5]. Ideally, a bioactive material should have a controlled reactivity that leads to the establishment of a bonding with the surrounding tissue in a suitable time. The solubility of a coating must not lead to a fast resorption nor should a low reactivity increase the time for bonding to occur. Several studies show that glasses of the system Na_2O–CaO–P_2O_5–SiO_2 have greater bioactivity than HA [6]. Therefore, bioactive glass coatings or composite coatings glass/HA have a potential for an increase in bioactivity [7].

Here we attempt to increase the bioactivity of coatings through the production of hydroxypatite/bioactive glass (HA/BG) composite coatings on titanium alloy, Ti6Al4V, by plasma spraying mixtures of the pure powders, in different pro-

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portions. The structural properties of composite coatings BG/HA, as well as BG and HA coatings, were measured. The in vitro bioactivity of the coatings was also measured.

2. Experimental procedures

The substrate used for the coatings was the titanium alloy Ti6Al4V. Rectangular samples ($22 \times 22 \times 1.5$ mm) were grit blasted and cleaned.

The powders used to produce the coatings were HA crystalline powder (Calcitek) with particle size in the range 4–150 μm ($P_{50} = 90$ μm) and Bioglass® powder (US Biomaterials), with composition 45% SiO_2–25% Na_2O–24% CaO–6% P_2O_5 and particle size in the range 4–80 μm ($P_{50} = 43$ μm). Coatings with four different compositions shown in Table 1 were obtained.

Two coating conditions were used in the plasma spray apparatus (Metco 3MBII) which were arc currents 300 and 400 A and primary/secondary gas ratios of argon/nitrogen 100/10 and 100/5 standard cubic foot per hour (SCFH). The torch–substrate distance was 200 mm.

The structure of the coatings was determined by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) using the diffuse reflection method. Phase and porosity analysis were carried out using an image analysis software (Quantikov) [8].

The bioactivity of the coatings was measured by reacting the coated samples in a tris buffer solution, pH 7.25, at 37°C for different times [9]. The solutions were analyzed by inductive coupled plasma (ICP) atomic emission spectroscopy and the FTIR spectra of reacted surfaces were measured.

Table 1
Proportion of Bioglass® (BG) and Hydroxyapatite (HA) used in coating powders

Samples	wt%	
	BG	HA
HA	0	100
10BG90HA	10	90
50BG50HA	50	50
BG	100	0

3. Results

Fig. 1 shows the XRD spectra of several coatings. In the case of pure Bioglass® (BG) coatings no diffraction lines are observed. The peaks observed in the other spectra are indexed as HA. Similar results were obtained for the two coating conditions used.

FTIR spectra of the coatings are presented in Fig. 2. Two bands of the HA phase at 598 and 566 cm^{-1}, assigned as P–O bending vibrations [10], are present in the coatings containing HA. Their amplitudes are smaller in the sample 50BG50HA than in the sample 10BG90HA. The band at 482 cm^{-1}, corresponding to the Si–O–Si bending vibration [11], indicates the presence of a silicate glass phase in the three coatings containing BG. Its amplitude increased as the amount of glass increased. The three bands observed in the 480–630 cm^{-1} region of the heat treated HA coating spectra indicate a better crystalline coating than that obtained with HA coating [1].

Fig. 3 shows SEM micrographs of the transverse sections of the composite coatings, BG/HA, showing two different phases. EDS analysis of

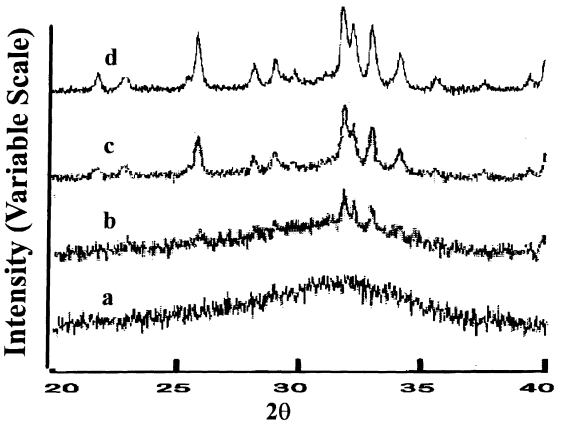

Fig. 1. X-ray diffraction spectra of various coatings: (a) BG; (b) 50BG50HA; (c) 10BG90HA; (d) HA.

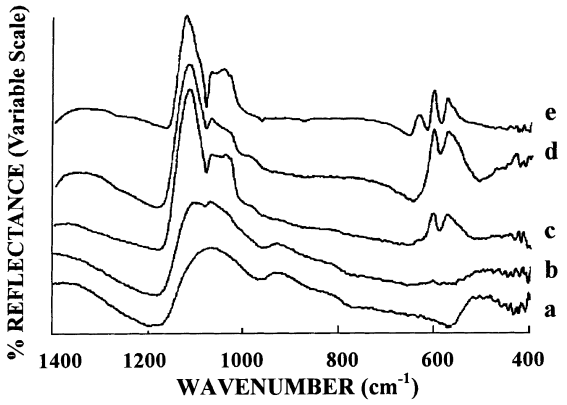

Fig. 2. FTIR reflection spectra of various coatings: (a) BG; (b) 50BG50HA; (c) 10BG90HA; (d) HA; (e) HA heat treated.

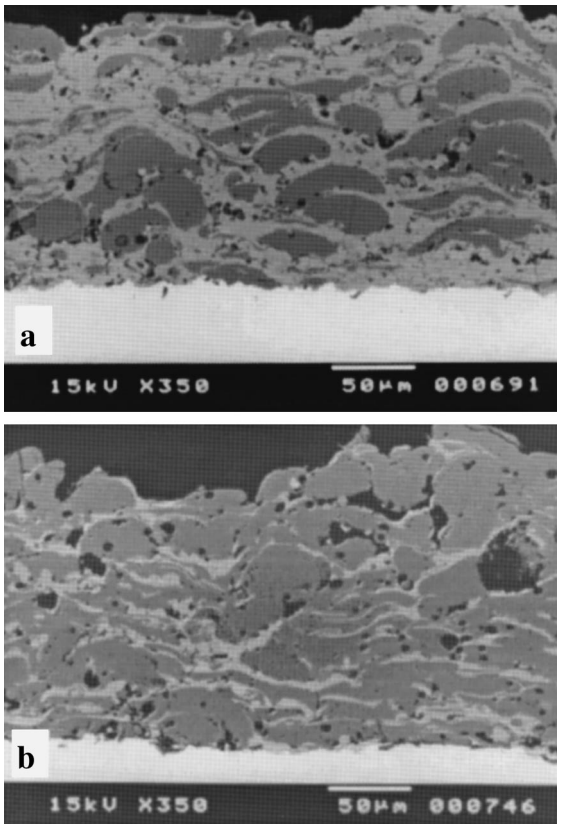

Fig. 3. Scanning electron micrographs showing morphology of coatings: (a) 10BG90HA; (b) 50BG50HA.

each phase detected calcium and phosphorus in the light phase (lighter regions in both micrographs), indicating that these regions correspond to the original HA particles. In the dark phase (darker regions in both micrographs) silicon and sodium were detected, in addition to calcium and phosphorus, indicating that these regions were the original glass particles. The phase analysis results obtained with the image analyzer are shown in Table 2. For comparison, the volume fraction of each material in the starting coating powder, which was calculated based on the density of HA (3.2 g/cm^3) and Bioglass® (2.6 g/cm^3), is shown. The numbers in parenthesis are the measured volume fraction of each phase in the coating not considering the pores. We note also that the porosity increases as the BG content in the coating powder increases.

The bioactivity of the coatings was measured by reacting the coated samples in Tris buffer solution at 37°C. The surface reactions as a function of immersion time were analyzed by FTIR and the results are shown in Figs. 4 and 5. The spectrum of the pure BG coatings shows the bands of the HA phase at 598 and 566 cm^{-1} [10] and the silicate band at 482 cm^{-1} [11], after immersion in Tris buffer for 14 h (Fig. 4(a)). After 24 h reaction the silicate band is not apparent anymore (Fig. 4(b)). The spectra of all other coatings show HA bands after immersion in Tris buffer for 14 and 24 h. The spectra of all the samples after immersion for 3 and 7 days are similar to the spectra shown for 14 and 24 h reaction.

The calcium ion concentration as a function of immersion time in Tris buffer is shown in Fig. 6. We observe that the Ca concentration increases with immersion time and is larger the larger the Bioglass® content in the coating.

4. Discussion

The XRD results showed that only an amorphous phase was observed in the pure BG coating. HA peaks were observed in all other coatings. However the crystallinity of the coatings containing HA is imperfect and decreases as the amount of HA in the starting powder decreases.

Table 2
Volume fraction of phases in starting powder and in coatings

Sample	% volume phases in starting powder (calculated)		% volume phases in coating (measured)		
	BG	HA	Dark phase (glass) (±5)	Light phase (HA) (±5)	Pores (±1)
HA	0	100	–	95	5
10BG90HA	12	88	50 (53) [a]	45 (48)	5
50BG50HA	55	45	76 (83)	16 (17)	9
BG	100	0	91	–	9

[a] Volume fractions in parenthesis were measured not considering the pores.

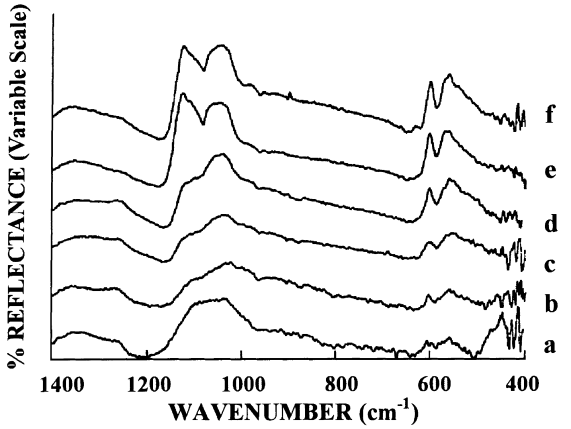

Fig. 4. FTIR reflection spectra of various coatings after reaction in Tris Buffer for 14 h and 1 day: (a,b) BG; (c,d) 50BG50HA; (e,f) 10BG90HA.

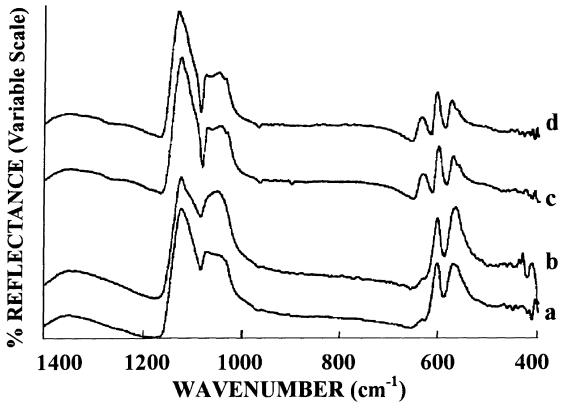

Fig. 5. FTIR reflection spectra of coatings after reaction in Tris buffer for 14 h and 1 day: (a,b) HA as coated; (c,d) HA heat treated.

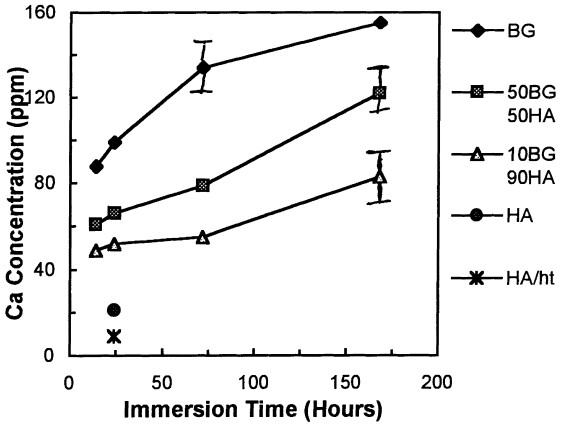

Fig. 6. Calcium concentration as a function of immersion time for various coatings. Lines were drawn as guides for the eye (HA/ht = heat treated HA coating).

The temperature of the plasma and the cooling rates can promote the formation of amorphous phases, as has been observed in the case of hydroxyapatite coatings [12]. The crystallinity index calculated for the pure HA coating according to a procedure described elsewhere [13] was 40%. A heat treatment at 600°C for 20 min increased the crystallinity of the coating to 99%. The results obtained by XRD are confirmed by FTIR analysis.

The identification of two distinct phases in the composite coatings BG/HA, with compositions similar to the BG and HA starting powders, indicates that the melted particles deposited on the titanium alloy substrate as separate phases. We observed an increase in the volume fraction of the region attributed to the glass phase, compared to

the amount of BG in the starting powder. Bioglass® particles are smaller and have a smaller density than HA particles, therefore causing a greater deposition efficiency than HA particles.

The bioactivity tests showed that after 14 h, a HA film was formed on the reacted surface of BG coating. After 24 h reaction the spectra do not show the band at 482 cm^{-1} (see Fig. 2(a)) corresponding to the silicate glass coating, indicating that the HA film thickness had increased. These results are typical of the reaction of Bioglass® [1] and show that the BG coating is bioactive as was the original glass.

The spectra of the composite coating 50BG50HA (Fig. 4(c) and (d)) show that after 14 h reaction only the HA bands are observed and the silicate glass band is not present in the reacted spectra as it is on the unreacted sample (Fig. 2(b)). These results indicate the formation of an HA film on the surface of the composite coating 50BG50HA after 14 h reaction. It is not possible to determine if this film forms only on the surface of the glass regions or on the whole surface of the coating. We note that the measured volume fraction of glass in this coating is 83% (Table 2).

With respect to the other coating compositions, 10BG90HA or pure HA (as coated or heat treated), the FTIR spectra of unreacted (Fig. 2) and reacted (Figs. 4 and 5) are very similar. Therefore, no changes in the coating surface could be detected by this technique. However, both coatings had some dissolution as shown by the ICP results (Fig. 6). We observed that the 10BG90HA coating had a greater dissolution rate compared to pure HA coatings. It should be remembered that the actual measured volume fraction of glass regions in the coating is 52% (Table 2), which would account for the larger dissolution rate observed. Fig. 5 also shows a decrease in the dissolution rate of the crystalline HA coating (HA/heat treated) compared to the as coated condition, as observed by other authors [4].

The FTIR and solution analysis results show that the Bioglass® addition to the coating powders increase the dissolution rates and rate of formation of an HA film on the surfaces of the coatings, thus increasing its in vitro bioactivity.

5. Conclusions

The Bioglass coatings obtained were completely amorphous and the HA coatings had a crystallinity of 40%, which increased with heat treatment to 99%. In the BG/HA composite coatings glass regions and HA regions were detected. The volume fraction of the glass phase in the coating was larger than the volume fraction of Bioglass in the starting powder. The difference observed is due to the greater deposition efficiency of glass particles. The porosity of the coatings increased as the Bioglass content in the coating powder increased. The FTIR and solution analysis results showed that the Bioglass® addition to the coating powders increased the dissolution rates and rate of formation of a HA film on the surfaces of the coatings, thus increasing its in vitro bioactivity.

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