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# Bioverit® I base glass/Ti particulate biocomposite: "in situ" vacuum plasma spray deposition

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**Abstract**

Bioverit®I is a bioactive glass–ceramic used for bone substitutions in several fields of human surgery. In this work, the possibility of using Bioverit®I as matrix of a biocomposite toughened by Ti particles, in order to toughen this glass–ceramic and to widen its application fields, was investigated. Bioverit®I base glass matrix/Ti particle biocomposite (B1T) coatings were prepared by vacuum plasma spray (VPS), by spraying a mixture of glass powders and 15 vol% titanium particles on Ti–6Al–4V substrates. The composite coatings were prepared starting from the base glass powders, in order to fully utilise the softening properties of this material in its amorphous state. The coatings were characterised by optical and scanning electron microscopy (SEM), energy dispersion spectroscopy (EDS) and X-ray diffraction (XRD). Vickers indentations at the interface between the substrate and the coatings and shear strength measurements were performed in order to analyse the adherence of the coatings to the substrate. The surface reactivity of the coatings was evaluated by soaking the coated samples in a simulated body fluid (SBF) having the same ion concentration as the human plasma and by analysing the Si, Ca and P ion concentration while soaking. 

*Keywords:* Bioactive materials; Coatings; Composites; Glass–ceramics; Plasma spraying; Ti

## 1. Introduction

Bioactive glasses and glass–ceramics are widely studied due to their peculiar property of directly bonding to the human tissues by interfacial reactions.[1–3] Since they have poor mechanical properties, many efforts have been addressed to toughen these materials by adding a second high-strength phase, or by using them as coatings.[4–11]

The glass–ceramic Bioverit®I is a mica- and apatite-containing machineable glass-ceramic produced by a thermal treatment of the phase-separated base glass. This glass–ceramic has been used for bone substitutions in orthopaedics, stomatology and for middle ear implants.[12–14] Due to the well known bioactive properties of this glass–ceramic, the base glass of Bioverit®I has been chosen as matrix for the preparation of bioactive composite coatings, containing 15 vol% titanium particles as toughening phase, on a Ti-6Al-4V substrate. Titanium was chosen as toughening phase because of its mechanical properties and biocompatibility.[15]

The vacuum plasma spray (VPS) is widely used to produce dense and homogenous coatings of different materials (metals, ceramics, glasses and glass–ceramics, etc.) on suitable substrates.[16] This technique was successfully used to prepare 50–300 μm thick layers of Bioverit®I glass–ceramic on titanium and Prothecast® (CoCrMo-alloy) substrates[5] and several bioactive glass–matrix/Ti particle composite coatings on Ti–6Al–4V substrates.[6–11] In this work the preparation of a composite coating by an "in situ" method is proposed: by simply mixing the base glass powder and the titanium particles and vacuum plasma spraying the mixture on Ti–6Al–4V substrates, glass–matrix composite coatings were obtained. Pure base glass coatings were also prepared for comparative purposes. A further ceramisation of the coatings can be proposed in a second step, but it is not discussed in this work.

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## 2. Experimental procedure

The chemical composition of the Bioverit®I base glass (= B1) is reported in Ref. 12. The bulk glass was ball-milled up to a suitable particle size for plasma spray deposition (50–100 μm).[6] A thermal study was performed on the glass powder and on a mixture of glass and Ti powders, by means of differential scanning calorimetry (Perkin–Elmer DSC7), differential thermal analysis (DTA, Netzsch 404 S) and hot stage microscopy (Leitz model II A), in order to determine the characteristic temperatures of the glass and the behaviour of the glass plus Ti powder mixture during heating (in Ar flow). Density measurements (Archimedean method) were performed on bulk glass specimens. Some characteristics of the B1 base glass are shown in Table 1. B1 base glass powder was mixed with Ti particles having a particle size up to 50 μm. The mixture was deposited by vacuum plasma spray on cylindrical Ti–6Al–4V substrates previously sand-blasted and ultrasonically cleaned (Bioverit®I base glass matrix/Ti particle biocomposite = B1T). The following plasma spray parameters were used: 150 × 102 Pa of Ar for the chamber pressure, 20 g/min powder flow rate, 170 mm distance between the specimens and the torch, 600 A, 40 V, 50 l/min for Ar flow, and 5 l/min for $H_2$. The pure glass coatings were prepared with the same deposition parameters. The morphology of each coating was observed by means of optical microscopy and scanning electron microscopy (SEM, Philips 525 M). Compositional (EDS, EDAX 9100) and structural (XRD, Philips PW 1710) analyses were performed in order to test if any modification occurred in the glass–matrix and titanium particles during the VPS deposition process. The interface between the substrate and the coating was mechanically tested by observing the propagation path of some cracks induced by Vickers indentations. The shear strength of the coatings was also evaluated by means of a comparative shear tests method described in a previous work[6] with a Schenck–Trabel equipment on cylindrical coated specimens glued together with Araldite AV 119 (Ciba-Geigy) and cured 40 min at 120°C. The surface reactivity of the coatings was tested by soaking them in a simulated body fluid (SBF), having the same ion concentration as the human plasma[17], up to 200 days: five samples of each coating were soaked in 50 ml of SBF, in polyethylene bottles at 37°C. The amount of Si, Ca and P ions in the solution versus time was analysed by inductive coupled plasma–atomic emission spectroscopy (ICP–AES Perkin–Elmer 5000). Morphological (SEM), compositional (EDS) and structural (XRD) analyses were performed after soaking the samples in the simulated body fluid (SBF).

Table 1
Characteristics of the base glass of Bioverit®I

| Density (g/cm$^3$) | $T_g$ (°C) | $T_{x1}$ (°C) | $T_{x2}$ (°C) | $T_m$ (°C) | $\alpha$/°C |
|---|---|---|---|---|---|
| 2.74 | 550 ± 5 | 660 ± 2 | 750 ± 2 | 1230 ± 2 | $8.9\times10^{-6}$ |

## 3. Results

B1 base glass and B1T composite coatings obtained are about 100 μm thick. The interface between the substrate and the coating was always homogeneous, the coatings are scarcely porous and their surface always showed the typical rough morphology of the VPS coatings. Fig. 1 shows the cross-section of the interface between the Ti–6Al–4V substrate and the B1T composite coating. There is no discontinuity (i.e. pores or cracks) at the interfaces, both between the substrate and the coating and between the glass matrix and the dispersed titanium particles (the few pores still present are not localised at the interfaces). The titanium particles changed their morphology from particles to platelets, likely because a partial melting occurred during the VPS process (the platelets look like filaments in their cross-section). A compositional analysis (EDS) performed on the glass coating and on the glass–matrix of the composite coating revealed that the chemical composition of the starting glass did not change remarkably during the VPS deposition (see Table 2).

The X-ray diffraction pattern of the glass coating shows an amorphous background. In the case of the B1T composite coating the Ti peaks are present on the amorphous background. The XRD patterns of B1 and B1T VPS coatings are reported in Fig. 2.

Preliminary mechanical tests were performed by means of Vickers indentation along the interface between substrate and coating. Several Vickers indentations were made on each coated sample, with different

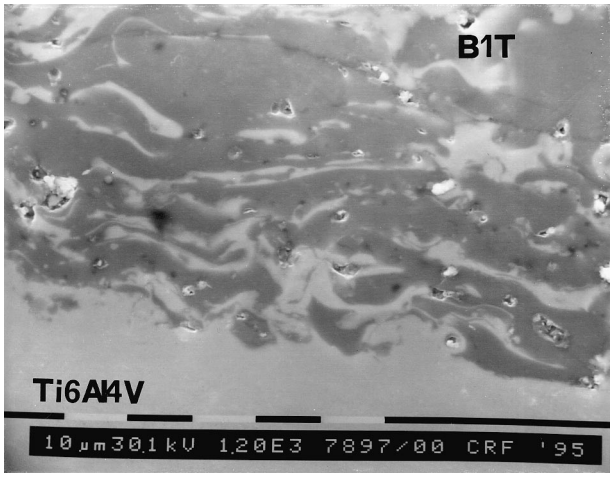



Fig. 1. Cross-section of the interface between the substrate and the B1T composite coating.

Table 2
Results of the EDS analysis performed on the B1 matrix at different steps of the process

| wt% Element | Si | Al | Mg | Ca | P | Others |
|---|---|---|---|---|---|---|
| Bioverit® I bulk | 27.6 | 13.2 | 9.10 | 22.1 | 17.1 | Balance |
| Bioverit® I VPS | 28.5 | 14.5 | 9.80 | 21.8 | 16.5 | Balance |
| B1T VPS matrix | 29.7 | 14.4 | 10.0 | 21.6 | 16.3 | Balance |

loads, up to 2.5 N. This qualitative method is useful to test comparatively both the adherence and the toughness of the coatings.[18,19] Fig. 3(a) and (b) shows-the cross sections of B1 and B1T coatings, respectively, after Vickers indentation at the interface between the substrate and the coating. The indentation induced some cracks both through the coating and at the interface of the glass coating with the substrate [Fig. 3(a)]; in the case of the composite coating [Fig. 3(b)] the cracks still propagated at the interface, but not across the composite, being partially deviated by the Ti (see arrows).

The interfacial shear strength of the glass and the composite coatings was compared by means of a shear test method. The shear strength values are in the range of 25–29 MPa for both the glass and the composite coatings. The results are reproducible and comparable with those of vacuum plasma sprayed hydroxyapatite and other glass–matrix/Ti particle composite coatings mechanically tested by the same method.[6]

The surface reactivity during the soaking in SBF, for both glass and composite coatings, was investigated by means of the ICP-AES analyses performed periodically on the simulated body fluid. In Fig. 4(a) and (b) the average values of the concentrations of Si, Ca and P ions are plotted versus time, for the B1 glass and the B1T composite coatings, respectively. Ti ions, eventually present in the SBF fluid after soaking of the coated samples were not detectable with the ICP-AES technique.[6] Both for the glass and the composite coatings, the concentration of Si, Ca and P ions reach a plateau within 30 days. The few surface dissolution was also evidenced by SEM observation, as shown in Fig. 5. After soaking in SBF the coatings were submitted to an XRD analysis, but no difference was revealed in comparison with the XRD pattern performed on the specimens before soaking.

## 4. Discussion

### 4.1. In situ plasma spray deposition

The main advantage of the vacuum plasma spray technique is the possibility of preparing coatings on a variety of substrates with materials that are difficult to be deposited by traditional methods (as firing, dipping, etc.). Three methods can be used in order to produce VPS composite coatings:[20]

1. mixing in the plasma torch particles of the two different materials (the matrix and the reinforcing phase) coming from two separated feeders.
2. mixing the two different kind of particles and then supply the mixture to the plasma torch from one feeder.
3. supplying a "composite powder" to the plasma torch (i.e. powders formed by agglomerates of the different components of the composite).

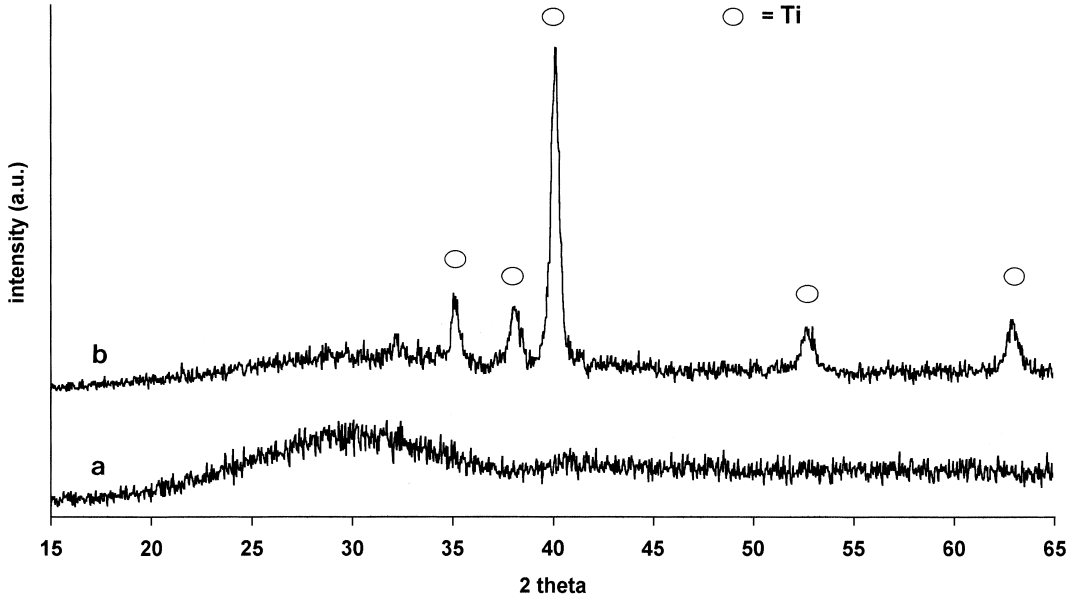
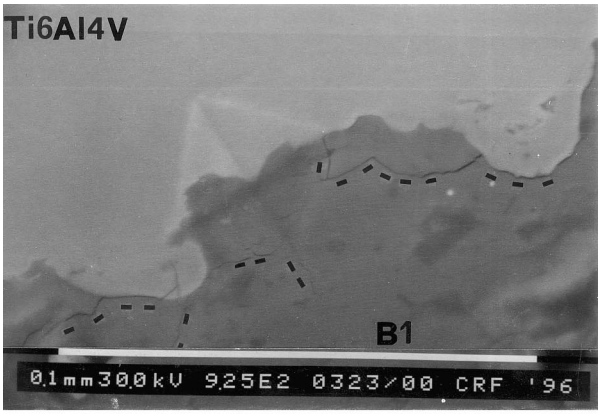
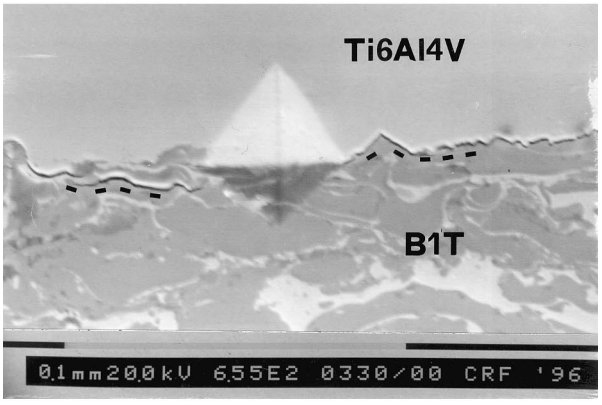



Fig. 2. X-ray diffraction pattern of (a) the glass coating and (b) of the B1T composite coating.




(a)




(b)

Fig. 3. Cross-section of (a) B1 and (b) B1T coatings, indented at the interface with the substrate.

The quality of the composite coatings usually improves from the first to the third method; in fact the first way gives not homogeneous coatings, because of the different density and different absorption of the plasma wavelength spectrum of the two separated composite components; the second way gives more homogeneous coatings, but still not satisfactory, for the same reasons mentioned above. The third way (''composite powders'' deposition) usually gives the best results.[20,21]

Several glass–matrix/Ti particle composites were successfully sprayed on Ti-6Al-4V by means of this third method and good results were obtained in terms of homogeneity, density and adherence.[6–11] A crucial step was always the preparation of the composite powders; in order to obtain homogeneous composite coatings a two step method was found to be preferable:[11] (1) sintering of the glass–matrix/Ti particle composite; (2) ball milling, sieving and vacuum plasma spraying of the powdered composite. In this way the Ti particles are covered by an amorphous layer. It was found that instead of an heterogeneous mixture of glass and titanium, a composite powder with the softening properties of the glass matrix can be sprayed. So, composite coatings with a continuous and homogeneous interface, both between the substrate and the coating and between the glass–matrix and the Ti particles, were obtained.

The B1 base glass shows very few softening properties:[22] it is very difficult to perform a pressureless viscous flow sintering process at low temperatures, and above 900°C a strong reaction with the titanium particles leads to a considerable expansion and poor results in terms of glass-to-metal interface. For that reason it was impossible to prepare a bulk composite by a viscous flow sintering process. Therefore, in this work it was necessary to operate by following the above described second method (mixing titanium particles and glass particles directly in the plasma torch from one feeder) and spray a mixture of glass plus titanium powder. By a careful optimisation of the VPS parameters, good results were obtained (as demonstrated by the cross section composite coating shown in Fig. 1). No cracks nor porosity are observable at the interface between the coatings and the substrate or, in the composite, between the glass–matrix and the Ti particle. In fact, the linear expansion coefficient of the glass ($8.9\times10^{-6}$ $K^{-1}$) and that of the titanium particles and of the substrate ($\alpha_{Ti}$ $=8.7\times10^{-6}$ $K^{-1}$; $\alpha_{Ti-6Al-4V}$ $=9.4\times10^{-6}$ $K^{-1}$, measured between 30 and 400°C) are similar. For that reason residual tensile stress at the interface between the glass and the metal, which could induce cracks propagation and poor adherence, are likely to be negligible.

### 4.2. Mechanical test

The Vickers indentation test gives a qualitative evaluation of the coatings adherence and of their toughness. It is a comparative method and only relative information could be deduced on the basis of the observation of the cracks patterns, induced by the same load, at the interface between the substrate and the coatings.[18,19] By comparison of Fig. 3(a) and (b) it is evident that, since the same load (2.5 N) induced an interfacial crack propagation in both the glass- and the composite-coating, the interfacial fracture energy of these two materials is similar. On the contrary, only the glass coating was crossed by orthogonal cracks, while no cracks were observed across the composite coating. It can be deduced that the inherent fracture energy of the composite coatings is higher than the interfacial one, while the pure base glass coatings have similar fracture energies at the interface as well as in the coating. That means that the composite coatings are likely to be tougher than the glassy ones, as expected by the addition of a dispersed phase which works as a toughening phase.

The shear strength measurements performed on cylindrical coated specimens gave results in agreement with the Vickers indentation tests; the shear strength values lie in the same range for each coated specimen (25–29 MPa), confirming that the interfacial fracture energies of the glass and the composite coatings are

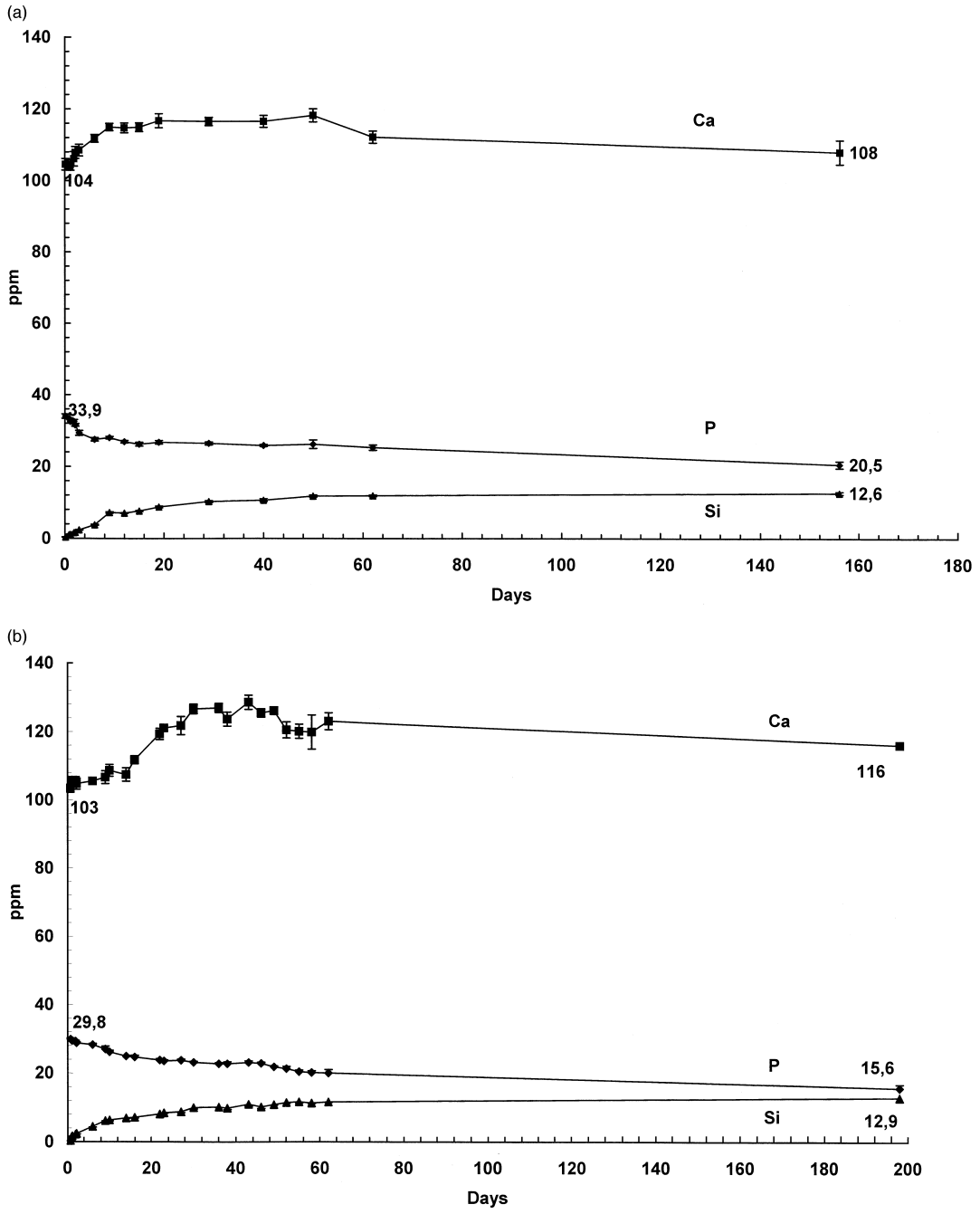



Fig. 4. Average values of the concentrations of Si, Ca and P ions versus time, for (a) the B1 glass and (b) the B1T composite coatings, during the soaking into SBF at 37 °C.

comparable, as already deduced by the indentation test. This value is higher than the shear strength between Bioverit®I glass–ceramic implants and the bone (2.3–4 MPa) by a factor of 6–10;[12] for that reason a good adherence of the coatings to the substrate even in vivo conditions could be expected.

### 4.3. Surface reactivity

As reported in literature, in vivo tests performed on Bioverit®I glass–ceramic implants revealed a very good bonding of the implant to the bone, and its well known bioactivity was demonstrated by several applications as biomaterial for bone substitutions in human surgery.[12] A certain surface reactivity was observable by soaking the glass–ceramic in different simulated body fluids (Ringer's solution, Tris-buffer-solution); in these tests an ion exchange between the glass–ceramic surface and the fluid was detected in an initial stage. But after this stage there was no further dissolution and the amount of leached ions became constant. This is a prerequisite for the long term stability of these materials. Here, a

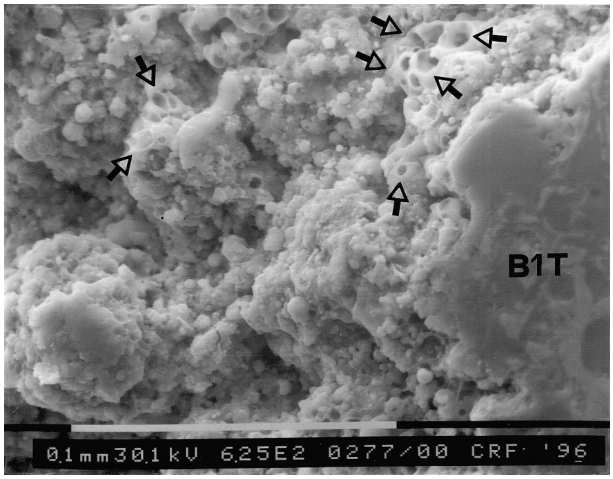



Fig. 5. Perspective view of a B1T coating, after 200 days soaking in simulated body fluid: the presence of little holes (marked by arrows) is evidence of a certain surface dissolution of the glass–matrix.

preliminary investigation was performed on the pure base glass- and on base glass–matrix composite coatings; ion leaching tests were performed using a simulated body fluid (SBF) with an ion concentration similar to that of the human plasma. A very small ion exchange between the glass and composite coatings and the SBF was observed [Fig. 4(a) and (b)].

Therefore, even if the bioactivity mechanism is complex and involves many surface modifications, the pure glass as well as the glass–matrix composite coatings prepared by vacuum plasma spray seemed to have a similar surface chemistry in comparison to the pure glass–ceramic already implanted for many clinical cases.

## 5. Conclusions

In order to widen its clinical applications, the possibility of using Bioverit®I base glass as matrix for Ti particle reinforced composite coatings was studied. The coatings were prepared by a single step vacuum plasma spray method, on Ti–6Al–4V substrates. No remarkable modifications of the chemical composition of the glass–matrix was observed after the VPS deposition. The mechanical characterisation showed a good adherence of the coatings to the substrate and the toughening effect of the dispersed Ti particles. Preliminary leaching tests demonstrated that the VPS composite coatings have a certain surface chemistry similar to that of the pure bulk glass–ceramic already implanted as biomaterial for bone substitutions.

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