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Sintering and Plasma Spray Deposition of Bioactive Glass-Matrix Composites for Medical Applications

E. Verné,[a] M. Ferraris,[a] A. Ventrella,[a] L. Paracchini,[b] A. Krajewski[c] and A. Ravaglioli[c]

[a]Materials Science and Chemical Engineering Department, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino, Italy
[b]Joint Research Centre of the European Community, Ispra (Va) Italy
[c]IRTEC/CNR, Via Granarolo, 64 - 48018, Faenza, Italy

Abstract

Three different bioactive glass-matrix composites were obtained by a viscous flow sintering process: the green samples were prepared by uniaxial cold pressing of powdered glasses (labelled as AP40, TAP and RKKP in this paper), mixed with 15% (volume) of titanium particles. The viscous flow sintering process was optimised by thermal analysis (DTA) and by heating microscopy to obtain high density bulk composites. The glasses and the sintered composites were also powdered and deposited by Vacuum Plasma Spray (VPS) on a Ti-6Al-4V alloy, to obtain bioactive glass and composite coatings. Each coating was characterised by means of optical and electron microscopy, X-ray diffraction (XRD), energy dispersion spectroscopy (EDS), Vickers indentations and shear tests. The bioactivity of the coatings was tested by soaking the coated samples into a simulated body fluid (SBF) at 37°C: the growth of a Ca and P rich silica-gel layer was observed on their surface after 30 days. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analyses were performed on the SBF in order to observe the Si, Ca and P leaching versus the time. Each coating showed a good adherence to the metallic substrate, comparable with that of the VPS hydroxyapatite coatings and a remarkable bioactivity. Moreover the intrinsic toughness of the composite coatings was found to be higher than that of the pure glass coatings. © 1998 Published by Elsevier Science Limited.

1 Introduction

Pure titanium and titanium alloys, e.g. Ti-6Al-4V, are suitable materials for load-bearing prostheses in orthopaedics, due to their good and reliable mechanical properties. From a biochemical point of view, they are considered nearly inert materials (as well as some ceramics), because they do not chemically or biologically bond with the tissues when implanted, but they are simply surrounded by them. Actually, they are not totally inert materials, because, even if the implant does not induce a specific biological response from the living tissues, a non-adherent fibrous capsule progressively forms around it, leading in some cases to interfacial displacements and clinical failure. Moreover, a certain chemical degradation of metallic materials may occur, giving detrimental effects for the patient.[1]

Several bioactive materials (bioactive glasses and glass-ceramics) have been recently studied: their peculiar characteristic is the surfacial reactivity when they are put in contact with body fluids. The mechanisms involves several complex reactions such as: ion leaching, partial dissolution of the glass and precipitation of an apatite layer from the solution to the glass surface: the apatite layer provides a strong bond of the implant with the surrounding tissues.[1]

Bioactive glasses and glass-ceramics have been developed and increasingly studied in order to give an alternative to the conventional metallic implants, especially in the field of small defects reconstruction, ear surgery, dentistry, or as coatings of inert materials for load-bearing applications:[1-4] for example, a tough and reliable material like a metal, could be coated with a bioactive glass, obtaining a coated implant which offers two main advantages: the protection of the metallic substrate from the corrosion and from the chemical degradation due to body fluids, and the strong interfacial bonding of the coated implant with the tissues.[1,5]

The bioactive glasses, which are intrinsically brittle, could also be toughened by the addition of a certain amount of biocompatible metallic inclusions; in this way, a bioactive composite could be prepared, with the further advantage of tailoring and predicting its mechanical properties; the bioactive composite can be used as bulk or as coating material.

An effective way to deposit glasses and composites on metals is the vacuum plasma spray technique (VPS), which provides adherent, dense and homogeneous coatings, with a controlled thickness and tailorable morphology, structure and properties, according to the plasma deposition parameters.[5–8]

In this work, three kinds of bioactive glass-matrix composites, reinforced with Ti particles (labelled as APT, TAPT, RKKPT in the paper), were prepared and vacuum plasma sprayed on Ti-6Al-4V substrates, with the aim of obtaining bioactive glass-matrix composites and coatings suitable for load-bearing applications.

2 Experimental Procedure

The composition (wt%) of the three bioactive glasses used in this work are reported in Table 1: AP40 is a bioactive glass-ceramic developed by Berger *et al.*[9] used in its amorphous state in this work; TAP glass differs from AP40 by the addition of 5·0 wt% of titanium oxide; RKKP was developed at CNR-IRTEC (Faenza, Italy) by modifying the AP40 composition with the addition of small amounts of Ta and La oxides.[10,11] The glasses were prepared by melting the starting products in platinum crucibles at 1450°C (AP40 and RKKP) and 1650°C (TAP) for 60 to 120 min. After melting, the glasses were quenched into cold water, or poured on a stainless steel sheet, in order to produce bars. The bars were successively annealed, cut and polished up to a 1 μm finishing, up to a final size of $50 \times 7 \times 3$ mm^3. Young modulus (Grindosonic Lemmens-Electronic), density (Archimedean method) and linear expansion coefficient measurements (Netzsch dilatometer) were performed on the bars. In order to prepare the composites, the quenched glasses were pulverised in a ball mill and sieved up to 100 μm, and the glass powder was mixed with 15 vol% of Ti particles (Plasma Technik 99·99% pur-

ity) having the same granulometry. The composites, named APT, TAPT and RKKPT, were prepared by a viscous flow sintering process, optimised by a thermal simulation of the process, in order to obtain sintered samples with the best compromise between high density and low crystallinity: as described in a previous work,[12] a thermal study on glasses and glass plus Ti powders was performed, in Ar flow, by means of Differential Thermal Analysis (DTA, Netzsch Mod. 404 S); an isothermal treatment (30 min) on the powders of each glass was carried out in the range of temperature between the glass transition temperature (T_g) and the first crystallisation temperature (heating rate 10°C min^{-1}, Ar flow, in platinum crucibles). After this isothermal treatment each sample was directly submitted to a scan between 600 to 1000°C in order to investigate if, during the isotherm, any crystallisation of the glass occurred; the higher temperature after which the isothermally treated samples still shows T_g and the main crystallisation peaks was chosen as the suitable temperature for a viscous phase sintering of the glass-matrix composites.

The linear shrinkage of glasses and composites greens were measured by means of heating microscopy (Leitz Mod. II A) on small green cubes of $3 \times 3 \times 3$ mm^3 size, at heating rate of 10°C min^{-1}, in Ar flow. Greens of the composites (glass plus Ti powders), obtained by uniaxial cold-pressing using a pressure of 4–6 tons cm^{-2}, were pressureless sintered for 30 min, in Ar flow, at the temperatures chosen on the basis of the previously described thermal studies. As a blank, greens of pure glasses were sintered at the same conditions. The sintered samples were characterised by means of XRD (Philips PW1830), SEM (Philips 525 M), EDS (Philips—EDAX 9100), density measurements (Archimedean method), and mechanical tests (Young modulus, induced crack propagation by Vickers indentations).

The bulk glasses and the sintered composites were then ball milled up to 50–100 μm and deposited by Vacuum Plasma Spray (VPS, Plasma Technik AG-JRC Ispra(Va)Italy) on cylindrical Ti-6Al-4V substrates (10 mm diameter, 50 mm high) previously sand blasted and ultrasonically cleaned, using deposition parameters already optimised for glass-matrix composite powders (170×10^2 Pa of Ar for the chamber pressure, 17 g min^{-1} powder flow rate,

Table 1. Compositions of the bioactive glasses (wt%)

Glass	SiO$_2$	Ca$_3$(PO$_4$)$_2$	CaO	Na$_2$O	K$_2$O	MgO	CaF$_2$	TiO$_2$	Ta$_2$O$_5$	La$_2$O$_3$
AP40	44·30	24·50	18·60	4·60	0·20	2·80	5·0	—	—	—
TAP	42·08	23·27	17·67	4·38	0·19	2·66	4·75	5·0	—	—
RKKP	43·82	24·23	18·40	4·55	0·19	2·79	4·94	—	0·9	0·09

220 mm distance between the specimens and the torch, 600 A, 50 V, 45–50 litres min^{-1} for Ar flow, and 2–8 litres min^{-1} for H$_2$).[5]

A morphological (optical and scanning electron microscopy), structural (XRD) and mechanical characterisation (Vickers indentations at the interface between the substrate and the coating and shear tests by means of a Schenck-Trabel equipment) was performed on each coated samples, as described in previous works.[5–8,11] The comparative shear tests were performed on cylindrical specimens, glued together with Araldite AV 119 (Ciba-Geigy) and cured 40 min at 120°C, as reported in Ref 5.

Both glasses and composites coated specimens were soaked into a simulated body fluid (SBF) having the same ion composition of the human plasma[13,14] in order to test *in vitro* their bioactivity: five samples of each one were soaked in 50 ml of SBF, into polyethylene bottles, at 37°C, up to 30 days; the Si, Ca and P ions amount in the solution was periodically analysed by ICP–AES. The samples were then removed from the solution, dried at room temperature and analysed by SEM, EDS and XRD.

3 Results

3.1 Optimisation of the sintering process

Table 2 reports some characteristics of the glasses used in this work. The softening temperatures were measured by dilatometry: they ranged between 680 and 700°C for each glass. The linear expansion coefficients were measured between 100 and 600°C. The linear shrinkage of glass and composite greens was observed by measuring their size variations versus the time during a temperature scan into the heating microscope (the linear shrinkage of the pure glasses was measured as reference). Figure 1 reports the shrinkage curves for AP40 and APT greens (glass and composite respectively; the characteristic temperatures of the glass matrix are also indicated by arrows). In the case of the glass a certain shrinkage ($\cong 15\%$) occurs between 600 and 900°C, and the crystallisation takes place without any volume expansion. On the contrary, in the case of the composite, the shrinkage stops at a lower temperature in respect to the glass, and at about 900°C the sample begins to expand. A similar
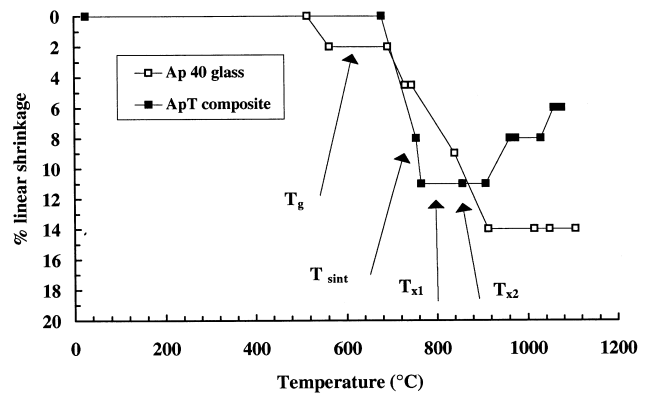

Fig. 1. Linear shrinkage curves of the AP40 glass and the APT composite.

behaviour was observed for the other glasses, according to their compositional similarity.

Figure 2 shows the DTA curves of AP40 powders (measured as reference), isothermally treated (30 min) at the labelled temperature (± 10°C) and successively scanned between 600 and 1000°C. An important difference appears after the isothermal treatment at 740°C: it is evident that this glass begins to crystallise after 30 min at 740°C and the subsequent scan shows the disappearing of the first crystallisation peak. However, the glass remains mainly in the amorphous state after 30 min at 720°C. The same behaviour was found for TAP and RKKP glasses, as well as for the composite powders, with slight temperature differences.

On the basis of the DTA results and those of the linear shrinkage of glasses and composites, the following temperature ranges were chosen, in order to perform a viscous phase sintering process: AP40
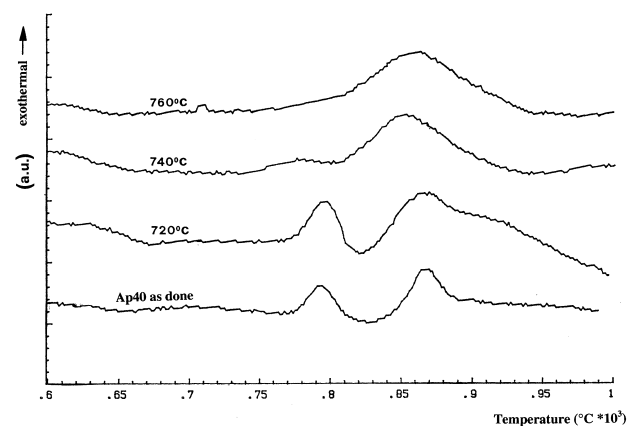

Fig. 2. DTA curves of AP40 powders isothermally treated at the labelled temperatures (30 min) and successively scanned (heating rate 10°C min^{-1}).

Table 2. Characteristics of the glass-matrices (* = dilatometric). All the temperatures are expressed in °C

Glass	d (g cm^{-3})	T_g	T_{soft}*	T_{x1}	T_{x2}	T_{x3}	T_{melt}	α(K^{-1})
AP40	2·84	640	680–700	725 ± 5	800 ± 2	860 ± 2	>1200	11×10^{-6}
TAP	2·86	675	680–700	725 ± 5	888 ± 2	918 ± 2	>1200	13×10^{-6}
RKKP	2·85	640	680–700	725 ± 5	820 ± 2	895 ± 2	>1200	12×10^{-6}

and APT: 720–730°C; TAP and TAPT: 790–800°C; RKKP and RKKPT: 750–760°C.

3.2 Characterisation of the sintered samples

All the sintered samples showed a density close to the theoretical one. They appeared almost completely amorphous (no crystalline phases were detectable by optical and scanning microscopy); the XRD on powders of sintered composites showed Ti peaks and the presence of an amorphous background, with only some of the peaks of apatite.

The interface between Ti particles and the glass-matrices in composites was always homogeneous and continuous; no cracks or pores were observed nearby the metallic particles. As shown in Fig. 3 (APT composite) the interface Ti/matrix shows a certain diffusion of the metal into the glass-matrix (the shadow surrounding the titanium particle). This feature, still present in the case of RKKPT composite, was completely absent in the case of TAPT composite.

The Young moduli (*E*) were measured on bulk glasses, and on sintered samples (glasses and composites) having comparable densities (the Young moduli of the pure glasses was measured as reference). The measured values are in good agreement with the theoretical ones, calculated by the law of mixtures[12] ($E_{Ti} = 110\,GPa$): the Young modulus values ranged between 63 to 80 GPa for the sintered glasses and were higher for the corresponding sintered composites, ranging between 78 to 87 GPa; bulk glasses showed Young moduli higher than those of the sintered glasses of the same composition, but lower than those of the corresponding composites.

The sintered composites were ball milled and sieved up to 50–100 μm, in order to obtain 'composite powders' to be vacuum plasma sprayed on Ti-6Al-4V substrates: Fig. 4(a) and (b) show a pure titanium particle and a particle of powdered RKKPT composite; as confirmed by the EDS
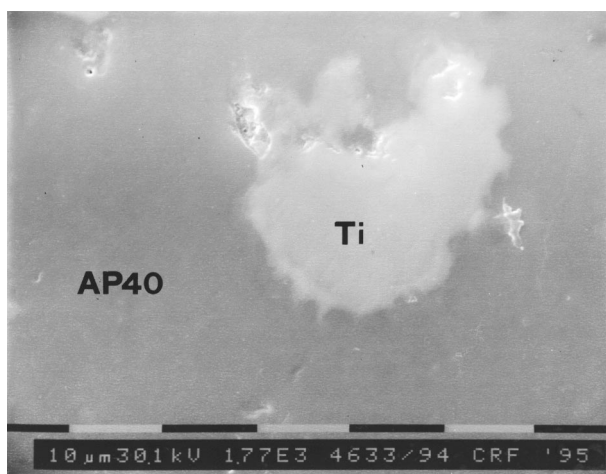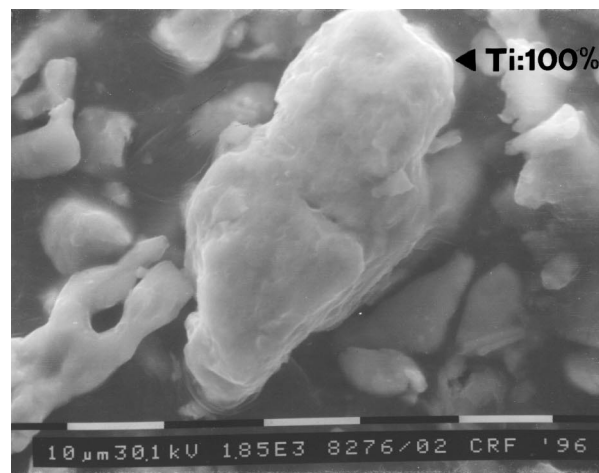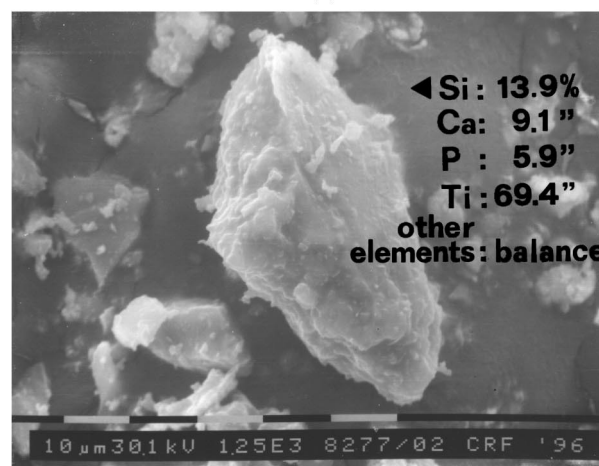

Fig. 3. Scanning electron micrograph of a Ti particle in the sintered APT composite.

(a)

(b)

Fig. 4. Scanning electron micrographs of (a) a Ti particle and (b) of a particle of powdered RKKPT composite. EDS results are reported on each micrograph (wt%).

results reported on each micrograph, the Ti particle in Fig. 4(b) is covered by RKKP glass, that means that after grinding the sintered composite, a 'composite powder', and not only a mixture of Ti and glass powders, was obtained. The same features were observed by comparing Ti particles with APT and TAPT composite powders.

3.3 VPS deposition of the bioactive coatings on Ti-6Al-4V

Figure 5 shows the cross-sections of the TAPT composite coating on the Ti-6Al-4V substrate. The interface between the substrate and the coating is continuous. The coating (150 μm thick) is scarcely porous. The morphology of the Ti particles changes from particles to platelets during the VPS process but they are still well embedded into the glass matrix (platelets look like filaments in the cross-section). The same morphology and thickness were observed for each composite coating.

The compositional analysis (EDS) was performed on the glass-matrix during each step of the composite coatings preparation: bulk glass, glass-
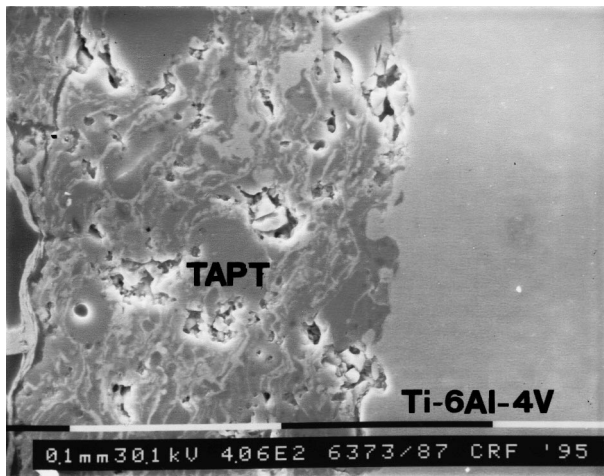
Fig. 5. Scanning electron micrograph of a cross-section of a TAPT composite coated sample.

matrix of the sintered composite and glass-matrix of the VPS composite coating (these results are summarised in Table 3). By comparing the theoretical values for the composition of the three bulk glasses with the values detected on the glass-matrices of the three composites (sintered and coating), it is evident that all the glass-matrices retained their starting composition both during the sintering process and the vacuum plasma spray deposition (it is reported here only the Si, Ca and P wt%, i.e. the three most abundant elements in all glasses). The XRD analysis on the coatings, mechanically detached from the substrate, only showed an amorphous background, with the Ti peaks in the case of the composites.

Table 3. EDS results of the analyses performed on the glass matrices at different steps of the process. (wt% of the elements; Th. values = theoretical values). [The experimental phosphorus content is always overestimated because its EDS peak and those of gold (used as coating layer for SEM observation) are at the same KeV values.]

| Wt% element	Si	Ca	P	Others
Th. values (AP40)	36·8	45·0	8·7	Balance
Bulk AP40	34·51	47·33	13·2	Balance
Sintered APT glass-matrix	35·56	47·46	14·37	Balance
VPS APT glass-matrix	31·77	49·05	13·24	Balance
Th. values (TAP)	34·09	41·7	8·05	Balance
Bulk TAP	34·31	45·15	13·25	Balance
Sintered TAPT glass-matrix	34·78	44·67	13·22	Balance
VPS TAPT glass-matrix	30·25	41·15	14·57	Balance
Th. values (RKKP)	36·2	44·4	8·6	Balance
Bulk RKKP	33·1	44·9	14·9	Balance
Sintered RKKPT glass-matrix	31·8	46·3	14·0	Balance
VPS RKKPT glass-matrix	34·5	48·1	9·2	Balance

3.4 Mechanical tests

At least five Vickers indentations on each coated sample were made along the interface substrate/coating, with loads progressively higher, up to 2,5 N, in order to induce a crack propagation and to qualitatively test both the adherence and the intrinsical toughness of the coatings. Two examples of the typical behaviour are shown in Fig. 6(a) and (b), where the indented cross-section of RKKP and RKKPT coatings are reported (load = 2,5 N). In the case of the RKKP glass coating [Fig. 6(a)] the indentation contemporaneously induced some cracks both parallel and orthogonal to the interface with the substrate, while in the case of the RKKPT composite coating [Fig. 6(b)] the cracks due to the same load ran only parallel and not orthogonal to the interface.

The shear strength of the substrate/coating interface was evaluated by means of shear tests described in a previous paper.[5] It was found that the interfacial shear strength of both the glass and the composite coatings lies in the same range
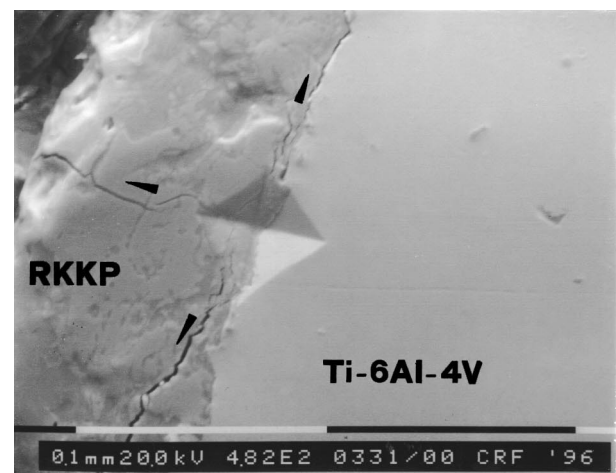
(a)
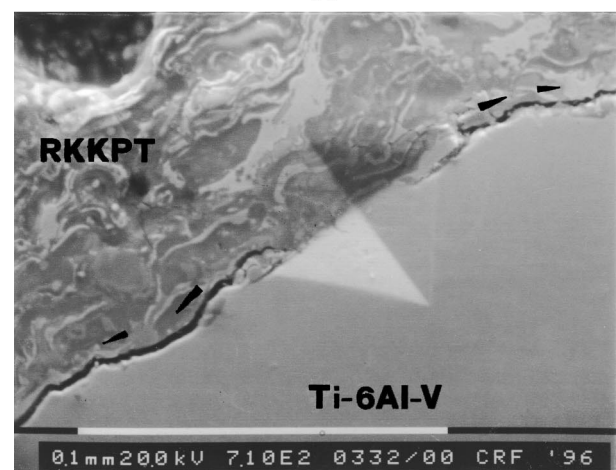
(b)

Fig. 6. Scanning electron micrographs of (a) the cross-section of an RKKP glass coated sample and (b) of an RKKPT composite coated sample after Vickers indentation at the interface substrate/coating.

$(\tau = 21\text{--}22 \pm 1\cdot5\,\mathrm{MPa})$ The results are similar for all the samples and they are comparable with those of VPS hydroxyapatite coatings mechanically tested in the same conditions.[5]

3.5 Bioactivity tests

Figure 7(a) shows a back-scattered electron image of a RKKP coated sample, after 30 days soaking in a simulated body fluid: the glass coating is covered by a 30–40 μm thick 'gel-like' layer, which shows some bright dishomogeneities. The average EDS analysis on this layer revealed the presence of Si, Ca and P ions, with a Ca/P weight ratio close 2·15 (i.e. the theoretical value for apatite). A similar gel-like layer was observed on the RKKPT composite coating even if thinner [a perspective view is shown in Fig. 7(b)] and the EDS analysis performed on it gave the same results in terms of Ca/P ratio. The same behaviour was observed also in the case of the other two glasses and composites coatings.

After soaking in SBF, the coatings were submitted to XRD analysis. Figure 8 shows (a) the XRD
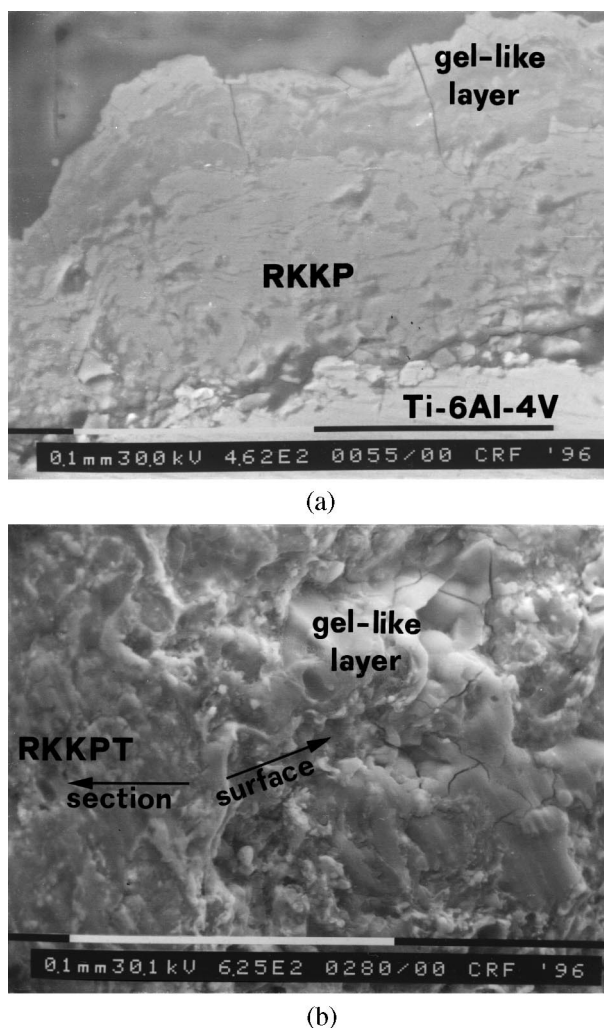

(a)

(b)

Fig. 7. (a) Back-scattered electron image of a RKKP glass coated sample (cross-section) after 30 days in simulated body fluid. (b) Scanning electron micrograph of a RKKPT composite coated sample (perspective view) after 30 days in simulated body fluid.

patterns of a VPS RKKPT coating, (b) the same after 30 days in SBF, and (c) for comparison, the XRD pattern of a VPS hydroxyapatite. In the pattern (b), beyond the Ti signals, some of the stronger signals of hydroxyapatite are detectable.

The bioactivity of both glasses and composites coatings was also investigated by the ICP–AES analyses performed periodically on the simulated body fluid during the specimens immersion. In Fig. 9(a)–(d), the average values of the concentrations of Si, Ca and P ions are plotted versus time, for the AP40 glass, the APT composite, the RKKP glass and the RKKPT composite coatings. (The titanium ions leaching was not detectable because this ICP–AES analysis method is not sensitive to small amounts of this element into a ion sovrasaturated solution like SBF). In each case, an increase of silicon and calcium, and a decrease of phosphorous ions was observed. These variations are very rapid in the first days of soaking, and gradually reach a plateau within five days. This phenomenon is less quick in the case of Ca ions. The first part of the ion leaching curves are slightly slower for the composite coatings, in comparison with the pure glass ones. The leaching curves of the TAP glass and the TAPT composite coatings are similar to those already reported and they are not shown here.

4 Discussion

4.1 Optimisation of the sintering process

Several surgical applications are known for AP40 as bioactive glass-ceramic.[9] In this work we propose the use of AP40 and of two other glasses, obtained by modifying the starting AP40 chemical composition, as glass-matrices for Ti particle reinforced bioactive composites. Titanium was chosen as toughening phase for the composites because of its acceptable biocompatibility.

The modification of AP40 (glass TAP) with 5 wt% of TiO_2, (one oxide of the metal used as substrate and as toughening phase in the composite), was chosen in order to control the interfacial reactivity between the glass and the metal.[5–7,15,16] The modified glass is still bioactive: it was also found by in-vitro cell culture tests[15] that other glasses containing up to 5 wt% of TiO_2 are very well tolerated over a long time. The evident interfacial reactivity between AP40 and Ti particles during the sintering process (Fig. 3) is due to a diffusion of titanium through the glass and it is limited at the interface between the glass-matrix and the Ti particles: the addition of small amounts of TiO_2 in the TAP glass composition made the interface in TAPT composite more stable.
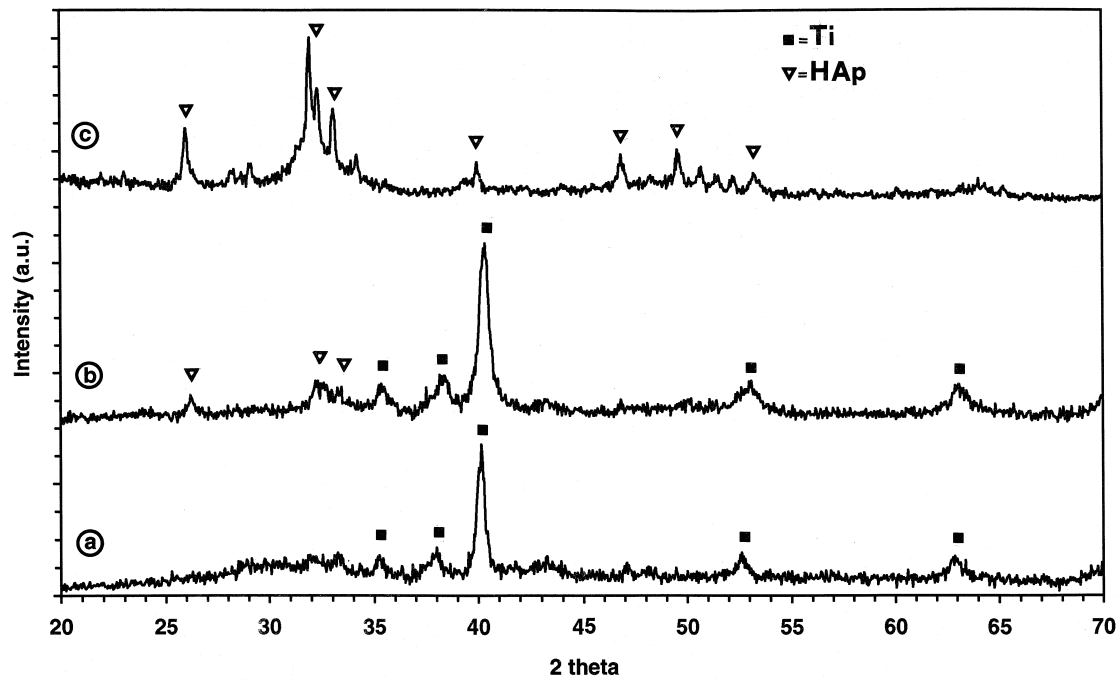
Fig. 8. (a) XRD patterns of a VPS RKKPT coating as done and (b) after 30 days in simulated body fluid, compared with (c) the XRD pattern of hydroxyapatite deposed by vacuum plasma spray on the same substrate.
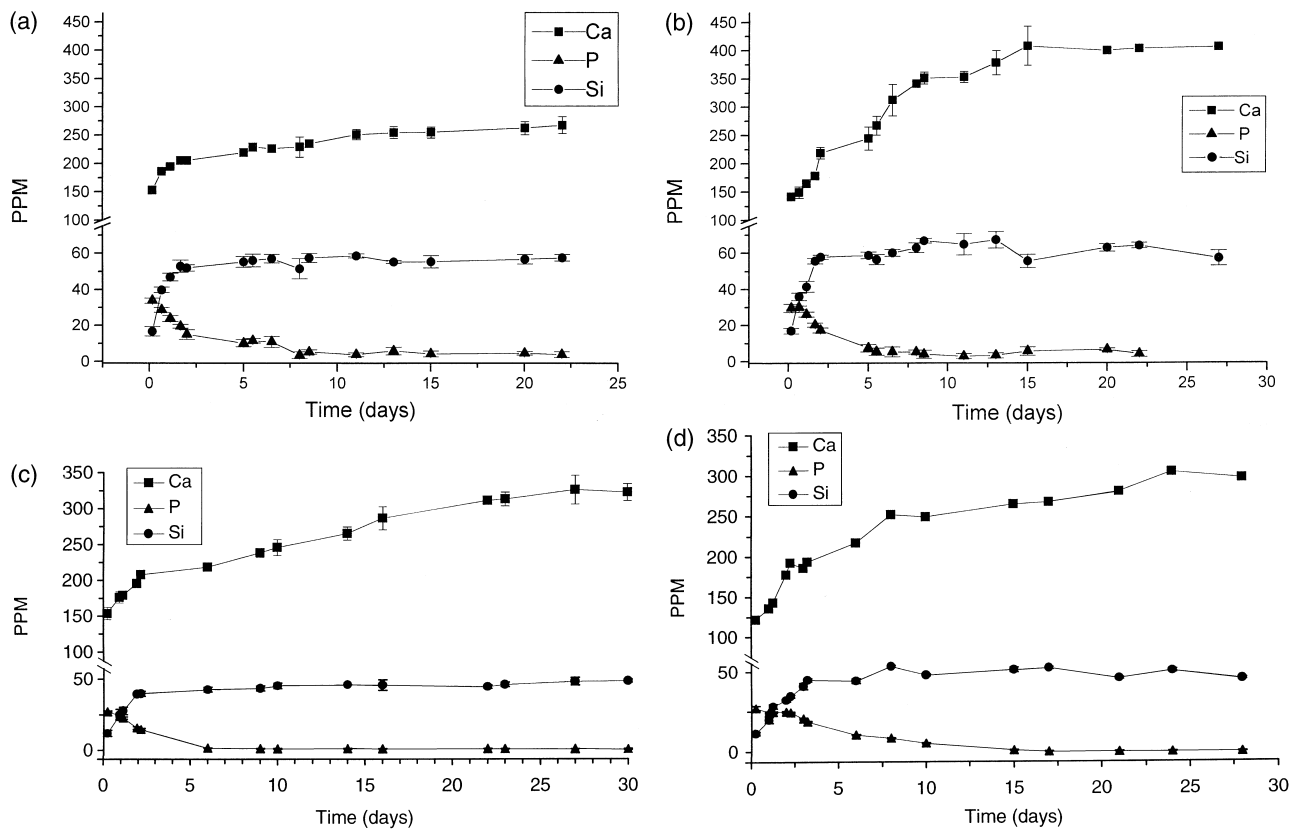

Fig. 9. Concentrations of Si, Ca and P ions versus time in the simulated body fluid, during (a) the soaking of AP40 glass, (b) APT composite, (c) RKKP glass and (d) RKKPT coated samples.

By means of the differential thermal analysis simulation of the sintering process, each composite green was sintered at a temperature high enough to minimise the viscosity but not high enough to give a complete crystallisation of the glass-matrix, which could affect the pressureless densification of the green. Moreover the presence of a certain amount of amorphous phase is essential to induce the growth of the apatite layer[17] and it was found that a glass is more bioactive than the derived glass-ceramic.[18] In this case the choice of the sintering temperature was also limited by the Tiα–Tiβ

transformation (from hcp to bcc), which occurs at $882 \pm 5°C.$[19] From this temperature on, it was observed an expansion of the composite greens (see Fig. 1, heating microscopy) probably due to a different crystallisation induced by the Ti particles phase transformation or by the high reactivity of titanium and glass at this temperature.

Taking into account all these features, the composites were sintered using an easy, low cost, pressureless viscous flow process; they retained an amorphous matrix, with small amounts of apatite, which can effectively partially crystallise at the sintering temperatures chosen for these glass-matrix composites.[9] The interfaces between Ti particles and the glass-matrices were always continuous, as demonstrated by the morphological observation and as confirmed by the increased Young moduli of the composites in comparison with those of the bulk glasses. Moreover, in the case of the TAPT composite, the modification of the glass composition with 5 wt% of TiO_2 was found to be useful to control the interfacial reactivity between the glass and the Ti particles, without affecting the bioactivity of the glass and of the composite coatings.

The sintering process is a crucial step for the composite preparation, also when they have to be powdered and plasma sprayed. In fact, the VPS deposition of mixtures of different powders (e.g. a mixture of glass and titanium powders) gives poor results in terms of particle distribution and homogeneity of the coatings.[20] The best results are obtained by spraying 'composite powders', i.e. powders formed by glassy coated Ti particles. By milling the sintered composites, it was effectively possible to spray powders formed by Ti particles covered by a layer of glass [see Fig. 4(b)], and therefore the softening properties of the glass-matrices were fully utilised also during the plasma spray process, to obtain an acceptable stability of the interface between the glass, the particles and the Ti-6Al-4V substrate.

4.2 VPS deposition of the bioactive coatings on Ti-6Al-4V

All the VPS coatings did not change their starting compositions and resulted to be completely amorphous. Metallic Ti particles are still present after the VPS process, with a platelet-like morphology, due to a partial melting followed by the rapid cooling typical of this process. The platelets are oriented parallel to the interface composite/substrate: this orientation could be favourable in case of stresses of the coating in that direction.[21]

The linear expansion coefficients of the three glasses are higher than that of the substrate and of the Ti particle one (Table 2): $\alpha_{Ti} = 8 \cdot 7 \times 10^{-6}$; $\alpha_{Ti-6Al-4V} = 9 \cdot 4 \times 10^{-6}$ (between 30 and 400°C).[22]

This should cause a residual tensile stress at the interface between the glass and the metal which could induce cracks propagation and poor adherence. In spite of this difference all the coatings resulted to be well bonded to the substrate and the interface between the glass matrix and the Ti particles appeared to be continuous both before and after the deposition. Moreover, the possibility of tailoring the thermal expansion coefficient in the case of the composites, minimises the α mismatch between the substrate and the coatings. In the case of the three composites prepared in this work, it can be estimated, on the basis of the mixtures rule, that their α values could range between $11 \cdot 3$ and $11 \cdot 6$ $^{10-6}$ K^{-1}.

4.3 Mechanical tests

The Vickers induced crack propagation gives a qualitative valuation of the fracture energy of the coatings and of the interface substrate/coatings.[23] By comparing Fig. 6(a) and (b) it is clear that the interfacial fracture energies of glass and composite coatings are comparable, while the intrinsical toughness of the composite coatings is higher than that of the glass: in both cases the induced cracks run along the interface, but only in the glass-coated sample a crack propagates across the coating, orthogonal to the interface. These results are in good agreement with the shear tests results: even if, on the basis of the indentation test, the composites coatings appear to be tougher than the glassy ones, the interfaces with the substrate show a similar mechanical behaviour ($\tau = 21$–22 MPa).

Any difference of adhesion between the glass and the metal particles or the substrate were observed by comparing APT and TAPT composite coatings.

4.4 Bioactivity tests

The in-vitro tests proved that both the glass and the composite coatings are still bioactive. The bioactivity of the bulk glass-ceramic AP40 is well known;[9,10] the addition of Ti particles in the composites, and of Ti, La and Ta oxides in the two modified matrices, did not affect significatively its bioactivity in terms of the formation of a self-grown silica gel layer, rich in Ca and P ions, which represents the first step of a more complicated process that leads, after a first surfacial dissolution of the bioactive glass, to the growth of an apatite layer.[1]

The presence of this layer after 30 days of soaking into the simulated body fluid was proved by the morphological observations [Fig. 7(a) and (b)], the EDS and XRD results, and by the periodic chemical analyses of the SBF solution. The dishomogeneity of the gel-like coating observed in Fig. 7(a), is probably due to its compositional

variation, typical of the early stages of the apatite growth process. The presence of the silica-gel layer containing a partially crystallised apatite phase was confirmed by EDS analyses (Si, Ca and P were detected) and XRD (some of the stronger peaks of apatite were observed). The decrease of phosphorous concentration and the contemporaneous increase of the silicon and calcium concentrations into the simulated body fluid, during the soaking of the coated specimens, is a clear evidence of the apatite growth mechanism.

The compositional modification of AP40 to prepare RKKP was suggested on the basis of in-vitro studies performed into biological media, already reported in Ref. 10, with the aim of increasing its bioactivity; it was found in the present work that RKKP is suitable as glass-matrix for titanium particle composites and both RKKP and RKKPT coatings are bioactive, but no difference was observed in terms of gel-like layer growth between the modified glass (RKKP) and the starting one (AP40).

5 Conclusions

Bioactive glass-matrix composites were prepared by a viscous flow sintering process. A continuous interface between the glass-matrix and the Ti particles was obtained in all the sintered composites, and a further optimisation of this interface was performed by adding small amounts of TiO_2 to the AP40 chemical composition.

Glasses (AP40, TAP, RKKP) and composites (APT, TAPT, RKKPT) were successfully deposited by vacuum plasma spray (VPS) on Ti-6Al-4V substrates. Adherent, dense and homogeneous coatings were obtained, without any significant modification of the starting glass-matrices compositions. The interfacial fracture energies of both the glass and the composite coatings are similar, but a qualitative indentation test method demonstrated a higher intrinsical toughness of the composites coatings in comparison to the glasses. Their bioactivity was demonstrated by in-vitro tests; the addition of Ti, La or Ta oxides into the glass matrix neither affected nor enhanced the bioactivity in terms of growth of a Ca and P rich silica-gel layer (the first step towards the formation of apatite).

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References

1. Hench, L. L. and Wilson, J. In *An Introduction to Bioceramics*, Vol.1. World Scientific Publications, 1993.
2. Hench, L. L., Bioceramics: from concept to clinic. *J. Am. Ceram. Soc.*, 1991, **74**(7), 1487–1510.
3. Biomaterials, 1991, *Mater. Res. Soc. Bull.*, **9**, (XVI).
4. Kokubo, T., Kushitai, H., Ohtsuki, C., Sakka, S. and Yamamuro, T., Chemical reaction of bioactive glass and glass-ceramics with a simulated body fluid. *J. Mater. Sci.:Mat. Med.*, 19912, 3, 79–83.
5. Ferraris, M., Rabajoli, P., Brossa, F. and Paracchini, L., Vacuum plasma spray deposition of titanium particle/ glass-ceramic matrix biocomposites. *J. Am. Ceram. Soc.*, 1996, **79**(6), 1515–1520.
6. Verne', E., Ferraris, M., Ventrella, A., Krajewski, A. and Ravaglioli, A. Bioactive glass-matrix composite coatings on titanium alloy. In *Ceramic in Oral Surgery*, ed. A. Ravaglioli and A. Krajewski. Gruppo Editoriale Feanza Editrice, 1995.
7. Verne', E. and Ferraris, M. Characterisation of vacuum plasma sprayed biocomposites. In *Bioceramics*, ed. A. Ravaglioli. Vol. 8, 1995, p.147.
8. Ferraris, M., Rabajoli, P., Verne', E., Paracchini, L., Chiesa, R. and Brossa, F., Plasma sprayed biocomposites for clinical applications. In *Materials in Clinical Applications—Advances Science and Technology*, Vol. 12, ed. P. Vincenzini. Techna Srl., 1995, p.281.
9. Berger, G. and Gildenhaar, R., *Long-Term Stable Bioactive Glass Ceramic as Implant Material—Ten Years of Clinical Experience*. Fourth World Biomaterials Congress April 24–28, Berlin, 1992, p.33.
10. Krajewski, A., Malavolti, R. and Piancastelli, A., Albumin adhesion on some biological and non-biological glasses and connection with their Z-potentials. *Biomaterials*, 1996, **17**, 53–60.
11. Verné, E., Terzuolo, A., Mousty, F., Pigozzi, G., Ravaglioli, A., Krajewsky, A. and Piancastelli, A., Glass-matrix biocomposite coatings on a Ti-6Al-4V alloy. 3rd Meeting and Seminar on Ceramic, Cells and Tissues—*Bioceramics Coatings for Guided Bone Growth*, ed. A. Ravaglioli and A. Krajewski. Gruppo Editoriale Faenza Editrice S.p.A, Faenza, 1997, p.37–42.
12. Ferraris, M. and Verné, E., Viscous phase sintering of particle-reinforced glass matrix composites. *J. Eur. Ceram. Soc.*, 1996, **16**, 421–427.
13. Kokubo, T., Kushitoni, H., Ohtsuki, C., Sakka, S. and Yamamuro, T., Chemical reaction of bioactive glass and glass-ceramics with a simulated body fluid. *J. Mater Sci. Mat. Med.*, 1992, **3**, 79–83.
14. Ohura, K., Nakamura, T., Yamamuro, T., Ebisawa, Y., Kokubo, T., Kotoura, Y. and Oka, M., Bioactivity of $CaO-SiO_2$ glasses added with various ions. *J. Mater. Sci. Mat. Med.*, 1992, **3**, 95–100.
15. Vrouwenvelder, W. C. A., Groot, C. G. and de Groot, K., Better histology and biochemistry for osteoblast cultured on titanium-doped bioactive glass: Bioglass 45S5 compared with Iron-, Titanium-, Fluorine- and Boron-containing bioactive glasses. *Biomaterials*, 1994, **15**(2), 97–107.
16. Ferraris, M., Badini, C. and Couzinet, B., Interfacial equilibria in titanium particle/glass ceramic composites. *Composites*, 1994, **25**(7), 494–498.
17. Li, P., Yang, Q., Zhang, F. and Kokubo, T., The effect of residual glassy phase in a bioactive glass-ceramic on the formation of its surface apatite layer in vitro. *J. Mater. Sci.: Mat. Med.*, 1992, **3**, 452–456.

18. Ferraris, M., Verné, E., Moisescu, C., Ravaglioli, A. and Krajewski, A., Bioactive coatings on Al_2O_3 and ZrO_2. 3rd Meeting and Seminar on Ceramic, Cells and Tissues—*Bioceramics Coatings for Guided Bone Growth*, ed. A. Ravaglioli and A. Krajewski. Gruppo Editoriale Faenza Editrice S.p.A, Faenza, 1997, p. 31–36

19. *Encyclopedia of Materials Science and Engineering*, Vol. 7, ed. M. B. Bever. Pergamon Press Ltd., Oxford, 1986.

20. Gruner, H., Dense oxide coatings. Technical Report, Plasma Technik, Switzerland.

21. Cheang, P. and Khor, K. A., Addressing processing problems associated with plasma spraying of hydroxyapatite coatings. *Biomaterials*, 1996, **17**, 537–544.

22. Maruno, S., Ban, S., Wan, Y., Iwata, H. and Itoh, H., Properties of functionally gradient composite consisting of hydroxyapatite containing glass coated titanium and characters for bioactive implant. *J. Ceram. Soc. Jap. Int. Ed.*, 1992, **100**, 372–377.

23. Sbaizero, O. and Lucchini, E., Influence of residual stresses on the mechanical properties of a layered ceramic composite. *J. Eur. Ceram. Soc.*, 1996, **16**, 813–818.