



## Plasma spraying of bioactive glass-ceramics containing bovine bone

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### Abstract

*Natural bone derived glass-ceramics are promising biomaterials for implants. However, due to their price and weak mechanical properties they are preferably applied as coatings on load bearing implants. This paper describes result obtained by plasma spraying of bioactive glass-ceramics containing natural bone onto selected implant materials, such as stainless steel, alumina, and titanium alloy. Adhesion of plasma sprayed coating was tested by computed X-ray tomography and SEM of cross sections. The results showed defect free interface between the coating and substrate, without cracks or gaps. Dissolution rate of the coating in simulated body fluid (SBF) was readily controlled by the bone additives (phase composition), as well as microstructure. The SBF treatment of the plasma sprayed coating did not influence the boundary between the coating and substrate.*

**Keywords:** *bioceramics, natural bone, plasma spraying, bioactive, glass-ceramic implants*

### I. Introduction

During the last fifty years another revolution has occurred in the use of ceramics to improve the quality of life of humans, as well as in the application of previously unforeseen raw materials, e.g. natural bone derived calcium phosphates [1,2]. This revolution is clearly expressed by the development of specially engineered and manufactured bioceramics and bioglass-ceramics for the repair and reconstruction of bones [3].

The term “bioceramics” refers to biocompatible ceramic materials, applicable for biomedical or clinical uses. Bioceramics can be produced in crystalline and amorphous forms. The most clinically used ceramics of the calcium phosphates group are hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ , further on referred as HA) and  $\beta$ -tricalcium phosphate ( $\beta\text{-Ca}_3(\text{PO}_4)_2$ , further on referred as  $\beta\text{-TCP}$ ), as they are analogous to the inorganic constituents of hard tissues of vertebrates. The glasses and partially crystallized glasses, which are also very important for clinical application, belong to  $\text{SiO}_2\text{-P}_2\text{O}_5\text{-CaO-Na}_2\text{O}$  system. They are classified as bioactive glasses (Bioglass<sup>®</sup>) and can bond to living bone without forming fibrous tissue around them [4]. These are known as, and are expected to be useful as bone substitutes in various applications. Some of the examples are Ceravital<sup>®</sup> containing apatite crys-

talline phase in  $\text{Na}_2\text{O-K}_2\text{O-MgO-CaO-SiO}_2\text{-P}_2\text{O}_5$  glasses [5], glass-ceramics containing apatite and wollastonite (A-W) in  $\text{MgO-CaO-SiO}_2\text{-P}_2\text{O}_5$  glasses, Bioverit<sup>®</sup> containing apatite and phlogopite in  $\text{Na}_2\text{O-MgO-CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-P}_2\text{O}_5\text{-F}$  glasses [6], Imaplant<sup>®</sup> will crystallize apatite and wollastonite in  $\text{Na}_2\text{O-K}_2\text{O-MgO-CaO-SiO}_2\text{-P}_2\text{O}_5\text{-CaF}_2$  glasses [7], and some glass-ceramics segregate canasite in  $\text{Na}_2\text{O-K}_2\text{O-CaO-CaF}_2\text{-P}_2\text{O}_5\text{-SiO}_2$  glasses [8]. Among these glass-ceramic A-W has been the most widely used clinically.

Hydroxyapatite is biocompatible and osteoconductive, allowing the growth of bone cells on its surface. As a result of its favourable biological properties it has been used successfully for many applications in restorative dentistry and orthopaedics. One such application is a coating applied to hip implants, where it provides implant fixation [9]. Coating of implants with biomaterials is gaining more and more popularity for many reasons. The coating reacts with the body fluids producing a new bone surface. Instead of having a mechanical fixing only, this way a strong biochemical bond is formed between the implant surface and the bones [10,11]. The application of plasma sprayed hydroxyapatite coatings on metallic substrates for biomedical application has been proven to be successful, since the bone tissue can grow into the layer, in this way forming a tight adhesion between implants and bone tissues [12]. The plasma sprayed wollastonite coatings *in vitro* showed excellent

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bioconductivity and good mechanical properties, indicating that a wollastonite coating may be suitable for the repair and replacement of living bone, especially for load-bearing situations [13].

The stability of the coating is the most critical factor to ensure the success of this type of implant. Several techniques have been used to create HA coating on metallic and other implant substrate surfaces, such as plasma spraying, thermal spraying, sputtering, pulsed laser ablation, dynamic mixing, dip coating, sol-gel, electrophoretic deposition, biomimetic coating, ion-beam-assisted-deposition and hot isostatic pressing. Plasma spraying process involves melting of ceramics or metal powders using the heat of an ionized inert gas (plasma). The molten powder particles (droplets) are then sprayed onto the surface to be coated, forming a protective layer which provides a barrier against corrosion, wear, and high temperatures. This technique offers advantages such as relative low cost and rapid deposition rate [14].

The lifetime of the hydroxyapatite coating on metal substrate is limited by its in-service susceptibility to various types of failures such as cracking of the coating, delamination of the coating layer/substrate interface, corrosion of metal substrate, etc. Therefore, sufficient mechanical performance is required for the HA coating. The adhesion of implants is believed to be achieved through two processes: one is ingrowths of the bone into the hydroxyapatite coating resulting in a mechanical fixation, and the other is a reciprocal dissolution/precipitation reaction between the bone with the coating, which is determined by the concentrations of ionic species such as  $\text{Ca}^{2+}$ ,  $\text{OH}^-$ , and  $\text{PO}_4^{3-}$ , in body fluids. The complete adhesion will be achieved when the last deposited ions completely bond the coating to the bone (bioactive fixation). These processes will strongly influence the mechanical performance of HA and other phosphate-based coating in implants [12].

The stability of HA coating has been shown to be largely affected by its crystallinity and purity. Highly amorphous coatings (having higher internal energy) dissolve more quickly leading to the rapid weakening and disintegration of the coating. Coatings with high degree of crystallinity have lower dissolution rates and are thus more stable *in vivo*. The production of HA coatings by plasma spraying leads to some extent to the decomposition of HA at high temperatures resulting in the formation of less stable calcium phosphate phases, such as  $\alpha$ -tricalcium phosphate ( $\alpha$ -TCP),  $\beta$ -tricalcium phosphate ( $\beta$ -TCP), tetracalcium phosphate (TTCP), as well as amorphous calcium phosphate (ACP) and calcium oxide [9].

To achieve long term stability of a coating, the dissolution behaviour of the coating is a critical factor. Two primary factors that control the dissolution characteristics of a coating are: a) inherent material properties such as chemical composition, presence of secondary phases, crystallinity, particle size, surface morphology, surface

roughness, and b) environmental factors such as media composition and pH. In HA coated implants, the presence of ACP increases the dissolution of coatings [15].

In addition, early biological responses to HA coatings are influenced by the surface roughness of the coating which affects osteoblast cell attachment and thus bone growth on the coating once it is implanted into the body. Whereas fibroblasts and epithelial cells prefer smoother surfaces, osteoblasts attach and proliferate better on rough surfaces. Thus, it is clear that in order to improve implant life, the tailoring of the properties of HA coatings is of utmost importance [9].

This paper summarizes the results obtained with plasma sprayed coatings of glass-ceramics containing natural bones on stainless steel, alumina, and titanium alloy substrates.

## II. Materials and methods

### 2.1. Materials

A basic frit raw mixture was prepared from high purity chemicals (analytical grade silica,  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{P}_2\text{O}_5$  and  $\text{MgO}$ ) as listed in Table 1. The mixture was melted at  $1300^\circ\text{C}$  in an alumina crucible and the melt was quenched by pouring into cold water. The obtained frit was ground in a porcelain ball mill and then in an agate mortar to a grain size of  $<63\ \mu\text{m}$ .

**Table 1. Composition of base glass raw mixture**

Raw materials	Composition [wt.%]
$\text{SiO}_2$	35.0
$\text{CaCO}_3$	42.0
$\text{MgO}$	2.0
$\text{Na}_2\text{CO}_3$	7.0
$\text{K}_2\text{CO}_3$	1.0
$\text{P}_2\text{O}_5$	13.0

Glass-ceramics raw mixtures were prepared from the basic frit and two different natural calcium phosphate additives: pre-treated (protein free) bovine bone of 63 to  $100\ \mu\text{m}$  grain size (PTB) and protein free bovine bone sintered at  $965^\circ\text{C}$  and ground to 63 to  $100\ \mu\text{m}$  grain size (SBB). In this way two different mixtures were obtained (75 wt.% frit + 25 wt.% PTB; 75 wt.% frit + 25 wt.% SBB). The mixtures were homogenized in a ball mill, then ground to a grain size of  $<63\ \mu\text{m}$  in a Netzsch rotary mill. Both mixtures were heat treated at  $1000^\circ\text{C}$  for 2 hours resulting in glass-ceramic samples GC-PTB and GC-SBB [2].

The heat treated samples were again ground in a Netzsch rotary mill to  $<63\ \mu\text{m}$ . In order to provide free flowing properties necessary for the plasma coater, the powder was pelleted using a water solution containing a binder (Optapix PAF 35 manufactured by Zschimmer and Schwarz GmbH) and a detergent (Dispex AA4040, manufactured by BASF). The suspension of about 51/49 solid/liquid mass-ratio was sprayed into liquid nitrogen and the frozen pellets were dried for one day. The prod-

uct was separated on a 220  $\mu\text{m}$  sieve and calcined at 1000  $^{\circ}\text{C}$  for one hour.

The plasma sprayer using a Metco 9MB gun with a 70 mm gun-to-surface distance operated with a 10 g/min feed rate for the powder, and carrier gas (argon) flow rate was 15 l/min. Before the spraying the substrates were heated to 200  $^{\circ}\text{C}$ . The plasma was obtained using Ar (42 l/min) and  $\text{H}_2$  (3 l/min) at current of 280 A and voltage of 80 V.

A simulated body fluid (SBF) as described by Kokubo and Takadama [16] was used to test bioactivity as well as body fluid induced surface changes of bioglass-ceramics.

## 2.2. Structural characterization

Phase composition of the prepared samples was analysed using Philips PW3710 X-ray diffractometer (PANalytical X'Pert Data Collector, X'Pert High Score Plus). The quantitative phase composition was determined by addition of 10 wt.% ZnO using Rietveld analysis. Microstructure and porosity of the samples were tested by a PHILIPS/FEI XL30 environmental scanning electron microscope (SEM), and the coating thickness was measured in a NIKON XT 225 HS X-ray tomograph. SEM samples were sputter coated by a 15 nm thick Au layer. Molar ratio of calcium to phosphor was measured by energy dispersive X-ray spectroscopy of uncoated samples by an EDAX EDS spectrometer.

## 2.3. Dissolution in SBF

Bioactivity of the plasma sprayed coatings was tested by treating the samples in simulated body fluid (SBF) as described above. The samples were kept in the simulated body fluid for 21 days at 36.5  $^{\circ}\text{C}$ . After this treatment the change of the calcium to phosphor ratio of the SBF was measured by a PANalytical MiniPal 4 energy dispersive X-ray fluorescence spectrometer. Morphology of the dried surface of SBF-treated samples was again tested by scanning electron microscopy. Changes of the amounts of calcium and phosphor of the surface were measured with SEM by energy dispersive X-ray spectroscopy and compared to the values obtained on the original (untreated) samples.

## 2.4. Testing and etching of the interface

Cross sections of the coatings plasma sprayed onto the three different substrates were embedded into a slow setting resin and were ground and polished finally with a 1  $\mu\text{m}$  diamond grit. The interconnection of the coating and substrate was tested on these polished cross sections by scanning electron microscopy. Further on after the

first SEM testing the cross sections were again treated by SBF for 7 and 21 days to determine the effect of simulated body fluid onto the morphology and binding at the coating to substrate interface.

## III. Results and discussion

Bioactive glass-ceramics coatings were plasma sprayed onto the surfaces of three different commonly used substrates (stainless steel, alumina and titanium alloy (Ti6Al4V)). The characteristic properties of these substrates are listed in Table 2.

The phase composition, porosity, coating thickness, as well as the interface between the support and plasma sprayed coating were tested on all samples. However, phase composition by X-ray diffractometry was not tested on the plasma sprayed titanium alloy samples, since the substrate (actually a titanium alloy rod) has cylindrical surface. Bioactivity was characterized by treating the samples in simulated body fluid (SBF). Surface of coatings was tested after 21 days of SBF treatment, and polished cross sections were submerged into SBF for 7 and 21 days.

### 3.1. Structure of prepared coatings

Overview of the phase compositions of the basic glass-ceramics containing bovine bone (Fig. 1) and the plasma sprayed coatings (Fig. 2) leads to the following conclusions:

- The basic glass-ceramic samples (GC-PTB, GC-SBB) contain various amounts of  $\beta$ -whitlockite, wollastonite, cristobalite and quartz crystalline phases. The amorphous (glassy) content of GC-PTB and GC-SBB is 44.4% and 31.8%, respectively.
- Due to the high-temperature processing, the plasma sprayed glass-ceramic coatings, besides of  $\beta$ -whitlockite and wollastonite, contain large amounts

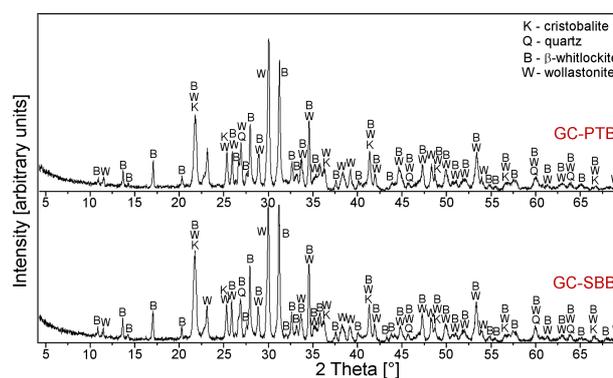


Figure 1. X-ray diffraction patterns of glass-ceramics containing PTB and SBB

Table 2. Characteristic properties of substrates [17]

Substrate	Costs	Density [ $\text{g}/\text{cm}^3$ ]	Compressive strength [MPa]	Biocompatibility	Manufacture
stainless steel	low	7.8–8.2	1000–4000	high	easy
alumina	low	3.85–3.99	3000–5000	medium	moderately easy
titanium alloy (Ti6Al4V)	high	4.4	450–1850	high	complicated

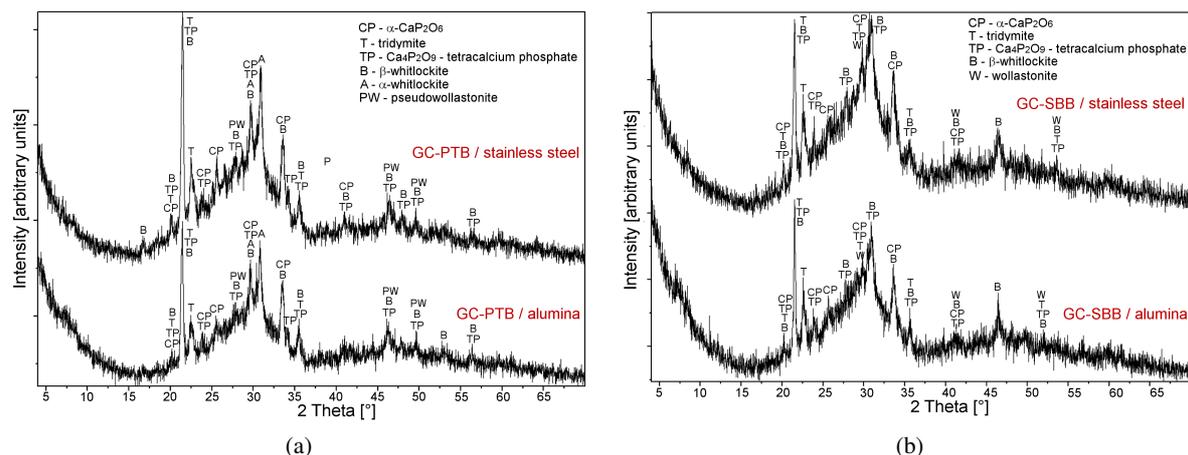


Figure 2. X-ray diffraction pattern of glass-ceramics coating containing: a) PTB and b) SBB

Table 3. Porosity of coatings

Sample	Porosity (V/V%)
GC-PTB Stainless steel	2.16
GC-SBB Stainless steel	3.21
GC-PTB Alumina	3.7
GC-SBB Alumina	6.25

Table 4. Vickers microhardness and compressive strength of bulk materials

Sample	Microhardness [MPa]	Compressive strength [MPa]
GC-PTB	2280	155.22
GC-SBB	1623	101.36

of glassy/amorphous phase, tridymite, tetracalcium phosphate ( $\text{Ca}_4\text{O}_9\text{P}_2$ ),  $\alpha\text{-CaP}_2\text{O}_6$ ,  $\alpha$ -whitlockite and pseudowollastonite crystalline phases.

- Along the  $\beta$ -whitlockite, additional crystalline phases such as tridymite,  $\text{Ca}_4\text{O}_9\text{P}_2$ ,  $\alpha\text{-CaP}_2\text{O}_6$ ,  $\alpha$ -whitlockite, and pseudowollastonite were also found in the plasma sprayed samples prepared with pre-treated protein free bovine bone (PTB).
- The plasma sprayed samples with sintered protein free bovine bone (SBB) contain  $\beta$ -whitlockite and wollastonite, accompanied by other crystalline phases, such as tridymite,  $\text{Ca}_4\text{O}_9\text{P}_2$  and  $\alpha\text{-CaP}_2\text{O}_6$ .
- Due to these high-temperature phosphate phases the dissolution rates in SBF might increase for both samples with SBF and PTB additives.

The surface of all substrates is fully covered by these plasma sprayed coatings, as seen in SEM micrographs in Figs. 3 and 4. Although the coatings do not seem fully dense, they perfectly cover the substrates and have low porosity. The pre-treated protein free bovine bone containing coatings (GC-PTB) has lower porosity, higher Vickers microhardness in bulk, and higher compressive strength (Tables 3 and 4). Such microstructure will easily dissipate mechanical stresses and will not deteriorate even after the subsequent SBF-treatment (during the formation of a new Ca-phosphate layer), neither will they crack nor scale.

The coatings have relatively high specific surface area and therefore it will provide a better contact with the body fluid which in turn promotes the formation of a new layer and enhances the binding of implants. The

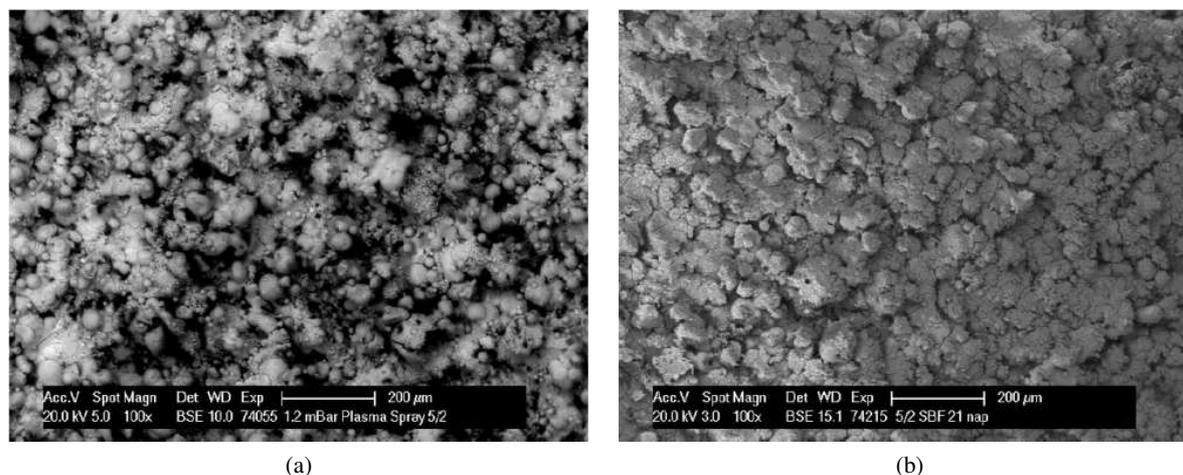


Figure 3. SEM micrographs of PTB containing coating on alumina substrate: a) before and b) after SBF treatment

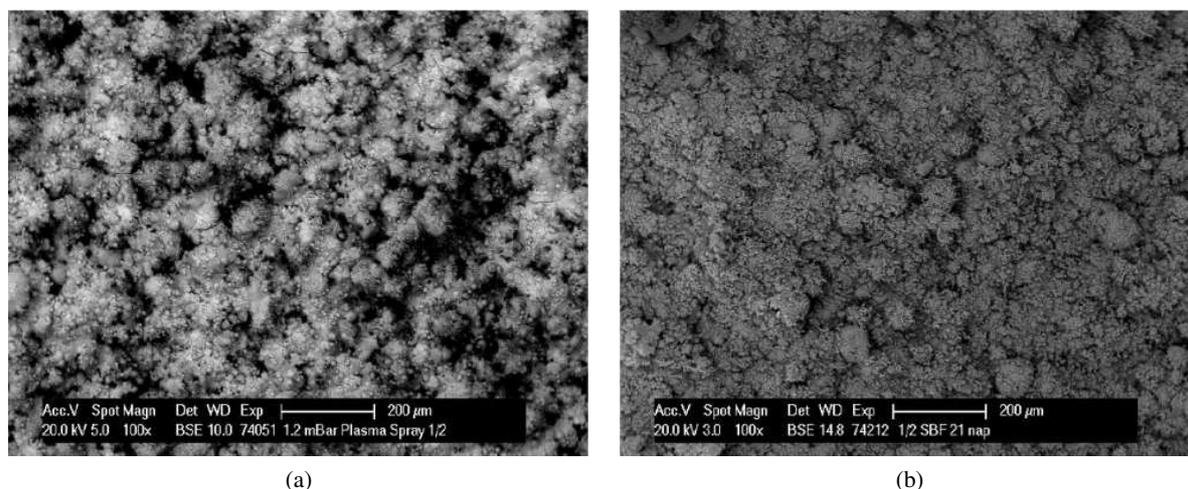


Figure 4. SEM micrographs of SBB containing coating on alumina substrate : a) before and b) after SBF treatment

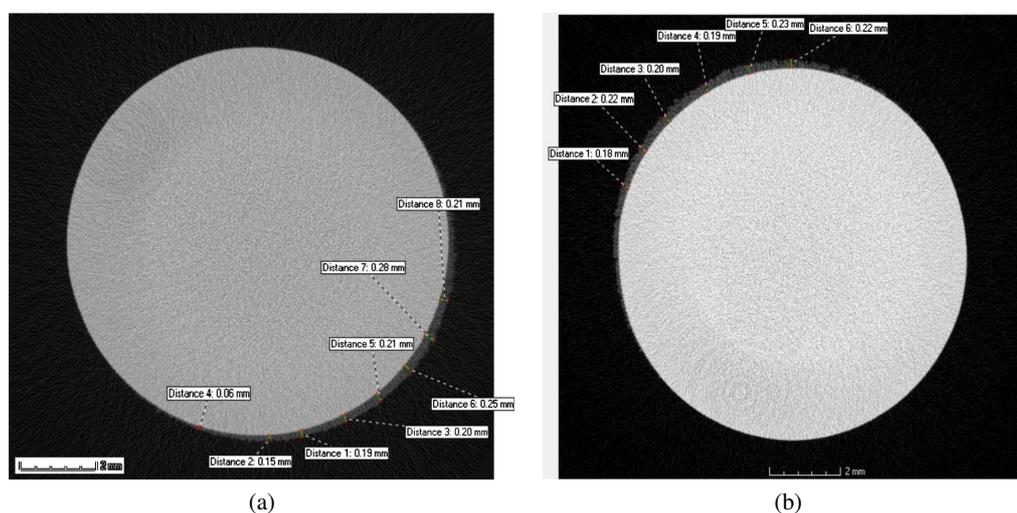


Figure 5. Computed X-ray tomography image of PTB (a) and SBB (b) coating on titanium alloy substrate

Table 5. Ca and P contents in coatings and SBF (before and after 21-days of SBF treatment)

Sample	Dissolution time [days]	On coating surface		In SBF	
		Ca [wt.%]	P [wt.%]	Ca [mg/l]	P [mg/l]
GC-PTB	-	36.89	12.61	-	-
	21	45.46	20.46	407.667	54.352
GC-SBB	-	35.90	13.06	-	-
	21	35.90	15.66	252.211	46.382
GC-PTB stainless steel	-	34.68	9.20	-	-
	21	46.84	15.68	234.010	42.151
GC-SBB stainless steel	-	37.63	10.00	-	-
	21	40.40	12.52	230.097	39.499
GC-PTB alumina	-	34.80	9.12	-	-
	21	48.59	16.03	178.895	35.696
GC-SBB alumina	-	37.44	9.40	-	-
	21	44.67	15.70	253.202	40.291
GC-PTB titanium	-	32.15	8.46	-	-
	21	32.68	14.43	349.505	62.933
GC-SBB titanium	-	31.73	9.31	-	-
	21	42.00	15.44	210.490	37.746

coating thickness measured by computed X-ray tomography is about 0.2 to 0.3 mm (Fig. 5). It should be noted here that the coating thickness strongly correlates to the process conditions of plasma spraying, and shall be further optimized.

### 3.2. Solubility in SBF (21 days)

Solubility in simulated body fluid (SBF) of the plasma sprayed coatings was tested as described for the bulk bioglass-ceramics in a previous publication [2]. After 21-days treatment the dissolved amount of calcium and phosphor was measured by X-ray fluorescence spectroscopy (Fig. 6). Dissolution rate of the protein free bovine bone containing plasma sprayed coatings (GC-PTB) is slower as compared to the original pressed bulk glass-ceramics, while the coatings containing sintered bovine bone (GC-SBB) have a dissolution rate similar to the bulk. Although the coatings prepared with PTB with lower porosity produce much lower amount of dissolved calcium, the dissolution rate is higher, since at the same time the amount of calcium on the surface is increasing faster, as compared to the coatings containing SBB. The  $\alpha$ -whitlockite phase observed in PTB containing samples is influencing the dissolution rate more effectively, in contrast to the SBB containing samples with better crystallized calcium phosphates having more stable structure resulting in a lower dissolution rate.

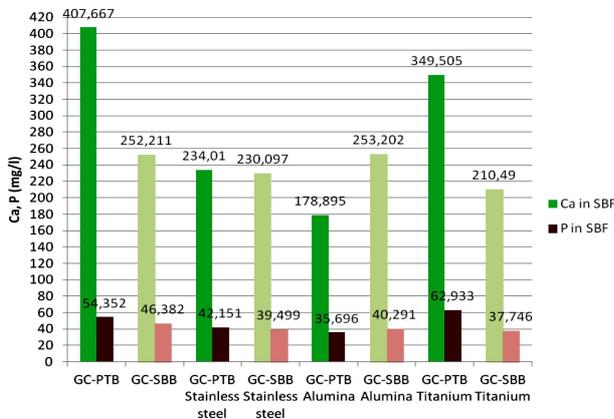


Figure 6. Ca and P contents in SBF after 21 days

During the treatment in SBF the amount of calcium and phosphor was increasing on the surface of all samples as revealed by energy dispersive X-ray spectroscopy (Table 5). This observation is further confirmed by the appearance of spherical calcium phosphate crystals (see SEM micrographs in Figs. 3 and 4). The strongest dissolution was observed for the GC-PTB coating plasma sprayed onto the titanium alloy substrate. In accordance to this observation the calcium phosphate layer is even less visible on the surface (see SEM micrographs in Fig. 3). In contrast to all other samples the increase of the amount of calcium and phosphor on the surface was significantly lower. These observations are also confirmed by the SEM micrographs of cross sections (see Section 3.3).

### 3.3. Testing and dissolution of interfaces

Interface of substrate and coating was tested on polished cross sections in order to investigate the effect of SBF treatment on the substrate/coating interface. As seen in the micrographs showing dissolution of the interface between the coating and the substrate as well as changes of morphology of plasma sprayed coatings (Figs. 7–9), the interface is free of generic cracks or gaps on all substrates (stainless steel, alumina and titanium alloy). This strong bonding does not deteriorate even after 21 days of SBF treatment. However, grain boundaries of plasma sprayed coating are more expressed, and to more or less extent a calcium phosphate layer starts to crystallize on the surface of all samples. The reaction of coating and SBF leads to the migration of calcium ions to the surface and formation of a new calcium phosphate layer. As the reaction proceeds, more and more ions migrate towards the surface and will induce mechanical stress in the layer resulting in microcracks. These cracks (Fig. 9) are therefore results of simultaneous diffusion

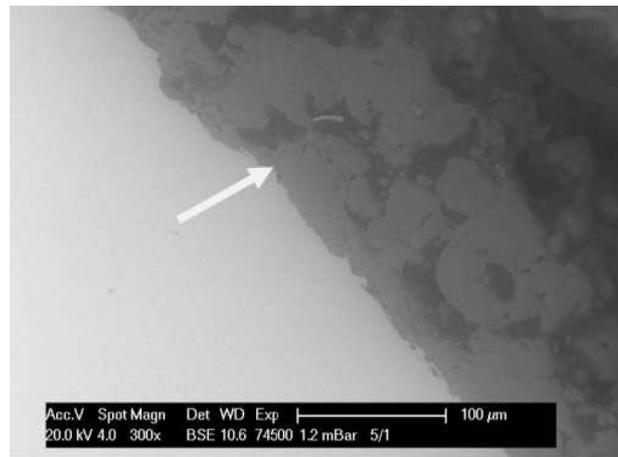


Figure 7. SEM micrograph of cross section of coating prepared with PTB on stainless steel substrate (arrow indicates the substrate to coating boundary)

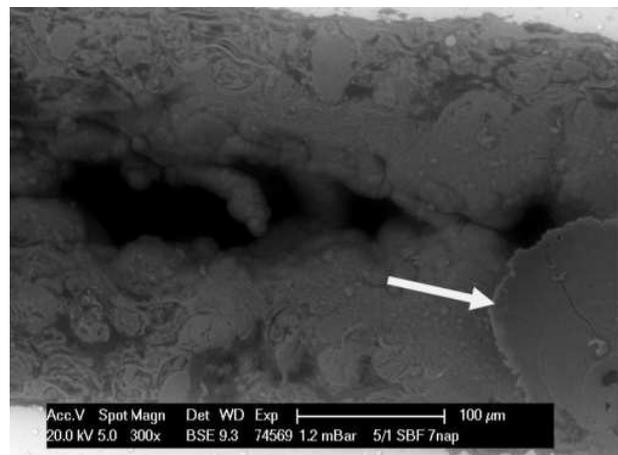
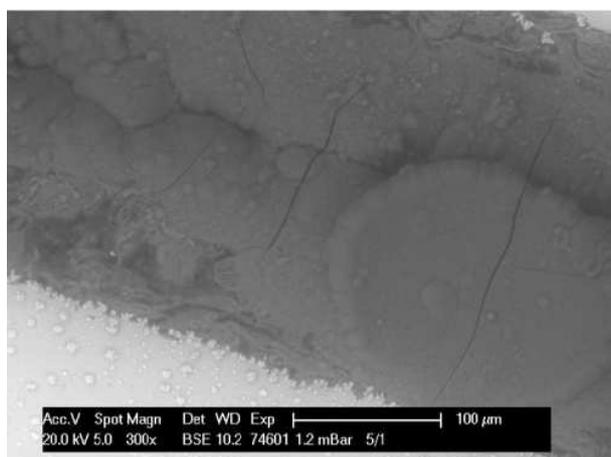


Figure 8. SEM micrograph of cross section of coating prepared with PTB on stainless steel substrate after 7 days of SBF treatment (arrow indicates the newly formed calcium phosphate/apatite phase)



**Figure 9. SEM micrograph of cross section of coating prepared with PTB on stainless steel substrate after 21-days of SBF treatment (the surface is fully covered by the newly formed calcium phosphate/apatite phase)**

and interaction between the biologically active coating and the SBF [10].

#### IV. Conclusions

Bioactive glass-ceramics containing natural bone were plasma spray coated onto selected implant materials, such as stainless steel, alumina and titanium alloy. Glass-ceramics containing the protein free and the sintered protein free bovine bone were obtained as crack-free, nearly dense, low porosity coatings. The plasma spraying modifies the phase composition, and new calcium phosphate phases e.g.  $\alpha$ -whitlockite, tetracalcium phosphate, etc. are formed at the high temperature of the plasma. Adherence of the coating is excellent, and the process itself is beneficial to the dissolution properties, because the dissolution rate is slower as compared to the bulk material. The plasma spraying of glass-ceramics containing different natural calcium phosphates provides a method of controlling the incorporation, hence the ossification. Moreover, the improvement of dissolution rate/ossification is easily controlled by the appropriate selection of animal bone additives' phase composition, which correlates to the pre-treatment of bones.

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