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Bond-coating in plasma-sprayed calcium-phosphate coatings

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Abstract The influence of bond–coating on the mechanical properties of plasma-spray coatings of hydroxyatite on Ti was investigated. Plasma-spray powder was produced from human teeth enamel and dentine. Before processing the main apatite coating, a very thin layer of Al_2O_3/TiO_2 was applied on super clean and roughened, by Al_2O_3 blasting, Ti surface as bond-coating. The experimental results showed that bond-coating caused significant increase of the mechanical properties of the coating layer: In the case of the enamel powder from 6.66 MPa of the simple coating to 9.71 MPa for the bond-coating and in the case of the dentine powder from 6.27 MPa to 7.84 MPa, respectively. Both tooth derived powders feature high thermal stability likely due to their relatively high content of fluorine. Therefore, F-rich apatites, such those investigated in this study, emerge themselves as superior candidate materials for calcium phosphate coatings of producing medical devices. The methods of apatite powder production and shaping optimization of powder particles are both key factors of a successful coating. The methods used in this study can be adopted as handy, inexpensive and reliable ways to produce high quality of powders for plasma spray purposes.

1 Introduction

Calcium phosphate ceramics (CPCs) are the most popular bioceramics because of their ability to accelerate bone growth around the implant. Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, is one of the crystalline phases of CPCs. Biological apatites belong to the big family of apatites, where several substitutions at the Ca^{2+}, PO_4^{3-} and OH^- sites of HA can occur [1], causing modifications of HA lattice parameters. They contain several trace elements [2], such as fluorine [3–6], and sometimes form heterogeneously [7]. Tooth enamel mainly comprises HA (92 wt.% [8]), while bones comprise up to 60 wt.% HA [2]. In teeth, trace elements are probably involved in nucleation of apatites and prevent tooth caries. Okazaki et al. have studied the role of fluorine on heterogeneous synthesis of apatite [6].

The poor mechanical properties of bulk HA ceramics does not indicate them for large bony defect replacements,

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especially for load-bearing applications. HA coatings on metallic substrates, such as Ti-based implant devices, improve fixation and promote osseointegration of cementless restorations [9]. There is still poor documentation on clinical experience of HA-coatings with regard to their long-term performance.

However, several earlier experimental studies have demonstrated that plasma-sprayed HA exhibits osteoconductive characteristics. Although the mechanism of this reaction is not completely understood yet, the research of the last decade points out that dissolution of calcium phosphate coating surface results in re-precipitation of crystals and ion-exchange with the surrounding tissue, leading to the formation of carbonated calcium phosphate layer of micro- and macro-crystals, along with incorporation of collagen matrix. A physicochemical precipitation mechanism, whereby mineralization on HA coatings appears to be acellular, has been suggested [10].

Nevertheless, the very high temperatures held in plasma-spraying, usually far beyond HA melting point (1550 °C; note that HA transforms at lower temperatures), inevitably causes decomposition of HA and changes of crystalline phases [11]. Furthermore, rapid cooling from molten state to room temperature causes formation of amorphous calcium phosphate on the coating. Therefore, the resulting HA-layer after plasma-spray may be subjected to biodegradation and bioresorption over prolonged implantation periods, probably accelerated by micromotions of the implant, resulting in loosening of mechanical fixation and delamination of the coating [12]. These phenomena certainly affect the long-term stability of plasma-sprayed HA coatings [13].

Recently, fluorapatite (FA) coatings were introduced in biomedicine. FA generally features better chemical stability than HA at high temperatures, which is seemingly important since plasma-spray takes place at elevated temperatures. With regards to clinical applications, in comparison with HA, FA is less soluble [14], especially at environment of low pH-values created by bacteria caries in mouth, enhances re-mineralization and retards demineralization of teeth [15]. Unloaded studies in transcortical models have also shown that bone ingrowth was better in the case of FA-coated implants. In particular, accelerated mineral apposition rate and an increase of bone mass were observed in oral treatments with sodium fluoride in patients having osteoporosis [10]. Nevertheless, the question still remains if FA-coatings fit well to the clinically relevant intra-articular weight loaded model or if they have adverse effects on bone remodeling, in comparison with HA.

Materials' properties and processing greatly determine the clinical performance of coating implants. Coating thickness, chemical composition, crystallinity and purity of the materials used, cohesive and adhesive strengths and resorption resistance are factors of particular interest for the quality of the produced coating [16].

The matching of chemical, mechanical and thermal properties between coating and substrate crucially determine the stability of the coating/substrate interface and largely anticipates the structural integrity of coatings upon fatigue during functional time, with regards to chipping, delamination and peeling off effects. From the clinical perspective, the demand of strong interfacial stability has been also indicated. For instance, to suppress undesirable leaching of fluoride ions in body liquids, cell culture studies have concluded that the plasma-sprayed FA-coatings should feature high mechanical and chemical stability [17]. To achieve better matching of the thermal expansion coefficients between the coating and the substrate and thus to suppress the development of detrimental residual stresses at the interface, bond-coating has been proposed, whereby an intermediate thin layer of a third phase is introduced between them [18]. The fine bond-coating layer fits in the grooves of the metal and improves the surface finishing of the initial metal surface for receiving better the coating.

There are only few studies on bond-coating in biomedical applications. Kurzweg et al. had used dicalcium silicate (C_2S, 10–50 μm thick) to maximize the adhesion strength and to suppress cracking, sheering off and chipping of HA coatings on AISI 316L stainless steel [19]. Silva and Monteiro have applied Mo before spraying Al_2O_3 on total hip prostheses of stainless steel 316L [20]. Recently, Teoreanu and Ioncea prepared coatings of HA on Hastelloy X (a Ni-base alloy) using a mixture of Ni-Al metallic powder with Al_2O_3 powder as bond-coating [21]. However, the biocompatibility of Ni is an issue which needs further discussion.

Beyond matching of thermal expansion coefficients of coating and substrate, several other reasons have been also proposed for using bond-coatings. For instance, direct contact of Ti with HA is not demanded because it is supposed that it catalyzes thermal transformation of HA to tri- or tetra-calcium phosphate or even to non bio-tolerant CaO. Bond-coating layer can act as barrier to reduce release of metal ions from substrate to living tissue. This phenomenon has been found that can induce extensive hepatic degeneration in mice and impair development of human osteoblasts. Bond-coating can also reduce the thermal gradient at the substrate/coating interface caused by rapid quenching of molten particle splats. High thermal gradient can result in deposition of amorphous apatite with concurrent reduction of resorption resistance and decrease of *in vivo* performance (i.e. life-time of implants) [19].

Bond-coating certainly features high potential for biomedical applications. However, in the light of the current technology state, there is still need for further development, which will assure biocompatible and safe high-quality coated-devices for endoprostheses [16]. This study addresses itself to this aim. Apatite, obtained from human tooth enamel (EFA) and dentine (DFA), was coated on Ti substrates, using a mixture of Al_2O_3/TiO_2 (60/40 in wt.%) as bond-coating agent. Crystallography and micro-structure analyses together with tensile strength measurements aimed at evaluating the durability of the produced coatings.

2 Materials and experimental procedure

Enamel and dentin were obtained from freshly-extracted human teeth. The teeth were irrigated with tap-water and soaked overnight in antiseptic solution (1 vol.% SAVLON; Savlon Concentrated Antiseptic Liquid, Novartis, UK) to prevent bad odor and contamination from various infectious diseases. Then the teeth were re-irrigated and deproteinized in alkali solution (1 vol.% sodium hypochloride) and then were re-irrigated with tap-water. After calcination at 850 °C for 3 hours (heating and cooling rates 5 K/min), dentine was easily separated from enamel (60% and 40% of teeth mass, respectively) [3]. Enamel and dentine matter were carefully grounded (blade grinder, K Janke & Kunkel GmBH Co., Germany) which is very important for powder flowability in plasma-spraying. The powders were sieved (Endocotts Octagon 200 test sieve shaker, UK; 9th level of shaking amplitude, 20 min). The fractions between 75 and 250 μm were pooled. To remove debris, stuck on the surface of big particles, the powders were ultrasonically agitated in pure acetone for 5 minutes and after drying, they were sieved using a 50 micron sieve. Particle size distribution was determined by light scattering method (Coulter LS 230, UK; Fraunhofer optical model).

Standard HA-powder, applied in biomedical coatings with the trade name AMDRY® 6021 (Sulzer Plasma Technic Inc., MI, USA), was used as reference material [22].

The flowability of ceramic powders was measured according to the ASTM B213-90 with a Hall flow-meter, fabricated in our laboratory similarly to the study of Kweh et al. [23].

Cylindrical bulk samples (Ø 25 mm, facing area 1 in^2) of annealed pure titanium (IMI Titanium Limited, USA), which satisfied the ASTM F67-89 GR2, were used as substrates. The surfaces of the samples were sandblasted with Al_2O_3 powder (Aladur Treibacher Schleifmittel Corp., NY, USA) in a close chamber and then cleaned with compressed air. The samples were ultrasonically agitated in acetone bath to eliminate grease of the compressed air-stream and to remove any entrapped Al_2O_3 particles from metal surface. The samples were immediately plasma-sprayed to suppress, as much as possible, the effect of oxidation of Ti. The samples were not touched with bare fingers during this process since finger grease can tremendously influence interfacial adhesion.

An Al_2O_3/TiO_2 powder mixture (already prepared in a 60/40 wt.% ratio, Spritzpulver 4031.0, Abler Producte, Germany, Din Nr. 3252; average particle size 25 ± 5 μm) was used as bond-coating agent.

Table 1 Parameters of the plasma-spraying processing [11]

Parameter	Standard setting
Injector nozzle diameter	1.5 mm
Injector distance	6 mm
Injector angle	90°
Plasma spraying distance	75 mm
Speed of rotation of substrate surface	15.5–19.0 m/s
Speed of torch movement	0 m/s
Current	500 A
Voltage	70 V
Primary gas	Ar
Primary flow	80 W
Flow rate	15.5 l/min
Secondary gas	N_2
Secondary flow	40 W
Flow rate	12 l/min
Carrier gas	Ar
Flow rate	4.5 l/min

Plasma-spray was realized by using a 3 MB Metco plasma flame spray gun with Metco type 4MP Perkin Elmer powder feed unit, following the standard parameters suggested by the manufacturer (Table 1). The bond-coating of Al_2O_3/TiO_2 was coated first (the process lasted 1–2 minutes). The thickness of this layer was measured by a coating thickness gauge (Elcometer 345 FN, UK). The apatite main coating was then plasma-sprayed, whose thickness was also measured. The surface roughness of the coatings was measured by a profilometer (Taylor/Hobson Surtronic 25, UK; diameter tip 10 μm, resolution 0.01 μm (Simple coatings (hereafter denoting the coatings with no bond-coating) were also produced.

X-ray diffraction analysis (XRD, Rigaku Geigerflex D/Mac, C Series, Cu K_a radiation, Japan) was employed to determine the crystalline state of materials before and after coating processing. Microstructure observations were carried out with a scanning electron microscope (SEM, Hitachi S-4100, Japan, 25 kV acceleration voltage). Coating/Ti interfaces were cross-sectioned and then polished until mirror finishing.

The adhesion and cohesion strength of the plasma-spray coatings were measured according the proper ASTM C-633-01 [24], using a very handy tensile bond strength testing device developed by Kemper and Klian [25] in a universal testing device (Instron, U.K.), according to the ASTM C 633-79 (cross-head speed 1.0 mm/min, 25 °C, 33% humidity). Bisphenol A-Epichlorhidrinharze (Germany; molecular weight $\leq$700; after 20 hours 20 N/mm^2; it lasts up to 120 °C) was used as glue-material, according to the ASTM C-633-01. The areas of the occurrence adhesive and cohesive failures at the coat/Ti interfaces, as defined by Yang et al. [26], were carefully projected on millimetric paper and measured. The

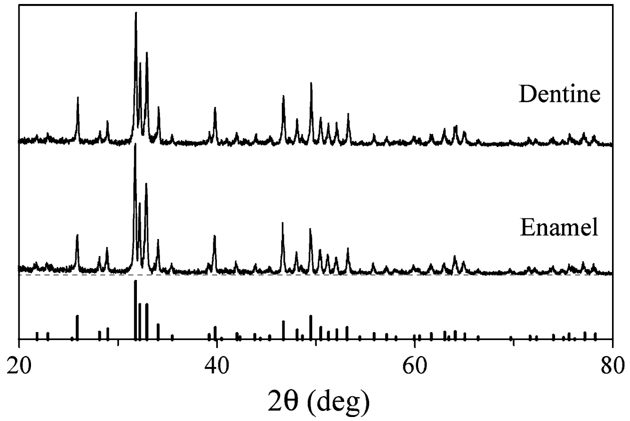

Fig. 1 X-ray diffractograms of enamel and dentine powders. (The patterns of the HA JCPDS card 9-432 are plotted at the bottom side of the diagram; the intensities have not been normalised; full scale of the intensity axis: 2600 cps)

results were statistically analyzed. Using the non-parametric Mann-Whitney U tests, cross comparison analyses were conducted through the general statistical software Kwikstat 4 (Texasoft, 1995), whereby statistical significance is put into consideration if $p < 0.05$ or equivalently if $z > 1.96$.

3 Results

The powders of enamel and dentine featured high crystallinity, being apatites the predominant crystalline phases, as expected (Fig. 1). It is, however, difficult to securely distinguish HA from FA at X-ray diffractograms since the peaks of the two phases differ for a very small shift. The coexistence of these two phases in solid solution has been proposed in the case of naturally derived apatite from bone, which contains ∼0.03 wt.% F [27].

Table 2 presents the particle size distribution of the powders of enamel and dentine after sieving. The morphology of the particles of the pooled fractions between 75 and 250 μm is shown in Fig. 2. There is obviously large amount of debris, either free or stuck on the surface of big particles. Ultrasonic cleaning in acetone and sieving afterwards efficiently removed this debris, better in the case of enamel, as shown in Figs. 3a–d. It is also noticeable that this cleaning process evidently rounded the edges of the particles. These images must be compared with the morphology of particles of the standard plasma-spray powder AMDRY 6021, shown in Figs. 3e–f. Round-cornered particles and absence of debris characterized the particles of AMDRY 6021. According to manufacturer specifications, the particles of this powder are sized between 80-160 μm [28]. Nevertheless, Fig. 3e shows also many bigger particles (∼300 μm). Similar images have been also reported in earlier studies [28, 29]. Consequently, the particles of the produced powders of enamel and dentin after washing (especially enamel) resemble fairly well the morphology of the particles of the standard plasma-spray powder.

The washing process also improved the flowability of the produced powders of enamel and dentine, being even better than the standard AMDRY 6021 powder (Table 3). Therefore, the washed enamel and dentine powders were selected for plasma-spray. The particle size distribution of the powders used for plasma-spray is plotted in Fig. 4. Evidently, the powders of enamel and dentine are similar and have slightly bigger mean particle size than AMDRY 6021.

Low crystallinity characterized the ceramic coatings made by plasma-spraying (Fig. 5), slightly poorer, however, in the case of the coatings made with dentine powder than enamel. The peaks fit fairly well to HA, but as mentioned earlier, FA can not be excluded. It is worthy noting that this analysis, using low incidence X-ray beam, verified that the surface of

Fig. 2 Enamel (a, b) and dentine (c, d) unwashed particles of the pooled fraction 75–250 m after sieving, according to Table 2

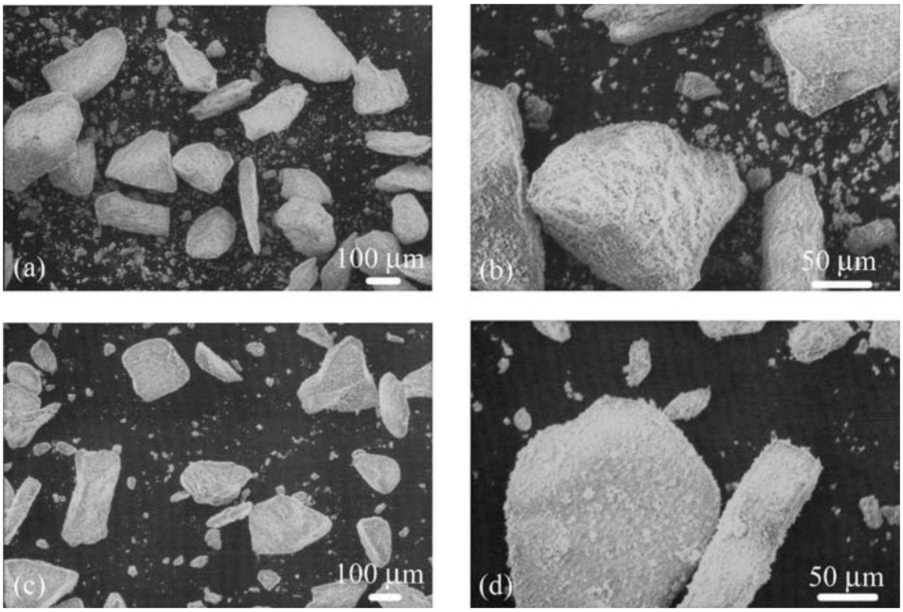

Table 2 Particle size distribution (in wt. %) of enamel and dentine powders produced from human teeth

Particle diameter (μm)	Enamel	Dentine
>355	3.60	0.77
355–250	24.87	16.14
250–212	15.71	15.46
212–150	21.93	22.80
150–125	9.29	16.78
125–100	6.69	11.45
100–75	4.08	4.04
75–45	10.27	7.88
<45	3.55	4.68

Note. After completing sieving, a bulky layer of agglomerated HA, whose formation can be likely attributed to the processing method, was remained stuck on all the sieves. With respect to the total amount of the powders sieved, this amount was 14.44% in the enamel and 10.55% of the dentin powder. The above values correspond to the rest part of the powders.

ceramic coatings was contaminated by neither Ti, diffused from the substrate, nor the bond-coating agents, Al_2O_3 and TiO_2.

Characteristic SEM images at cross-sections of interfaces between Ti and coatings made from the enamel and the AMDRY 6021 powders after simple and bond-coating plasma-spray are shown in Fig. 6. Similar microstructures were observed in the case of coatings made with the dentine powder. In general, there is no perceptible evidence of any influence of the type of the powder used (i.e. enamel or AMDRY 6021) on the microstructure of the Ti/coating interface. With regard to the quality of the coating layer, bond-coating evidently resulted in a layer free of microcracks and voids (Fig. 6b and d). Although the Al_2O_3/TiO_2 bond-coating layer is observable between Ti and the main coating layer, it was seemingly merged optimally in the coating layer since no interface can be observed between the two ceramic layers. There is also no evidence of formation of reaction zones due to reduction reactions of oxides or apatite from Ti.

Table 4 summarizes the characteristics of the produced coatings, which were obtained by image-analysis of several

Table 3 Flowability measurements (in s)

Enamel		Dentine		
No-wash	Washed	No-wash	Wash	AMDRY 6021
5.00	4.00	4.50–4.48	4.36	5.00–5.20

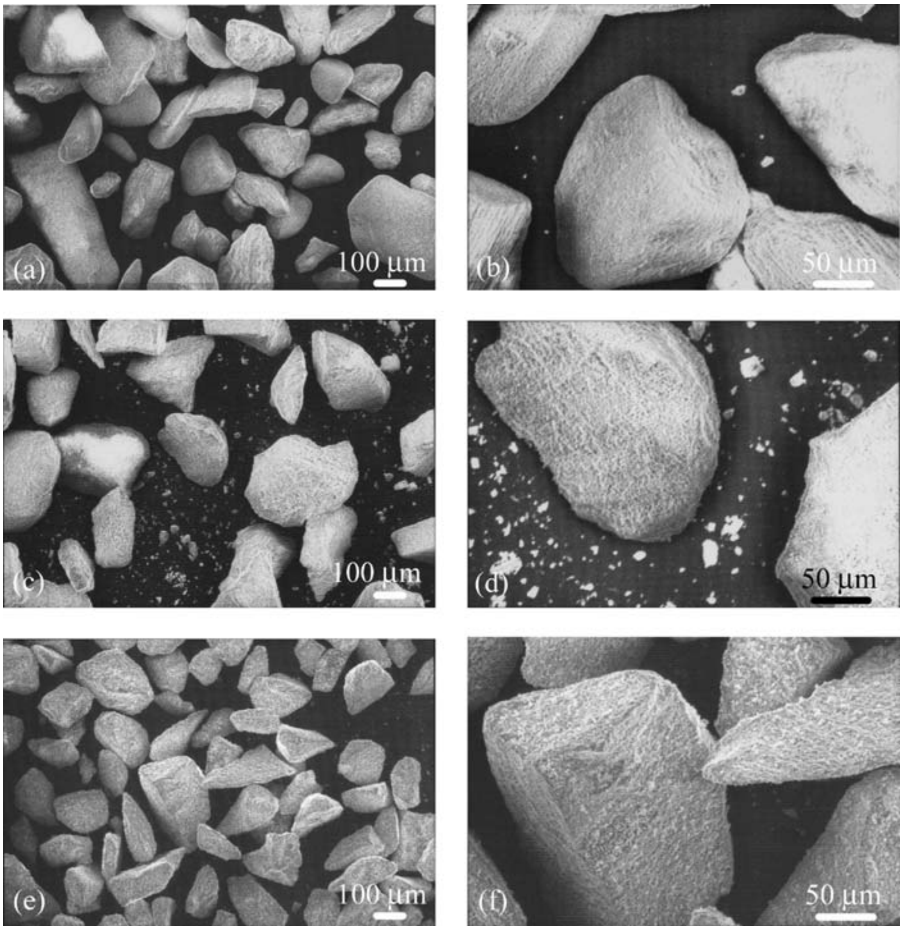

Fig. 3 The effect of ultrasonic cleaning on the particles of enamel (a, b) and dentine powder (c, d) that shown in Fig. 2 and comparison with the particles of the commercial powder AMDRY 6021 (e, f)

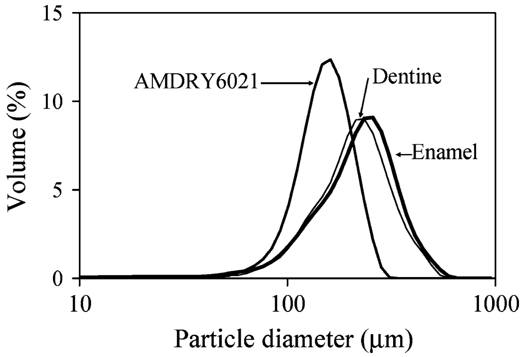

Fig. 4 Particle size distribution of the investigated powders used for plasma-spray

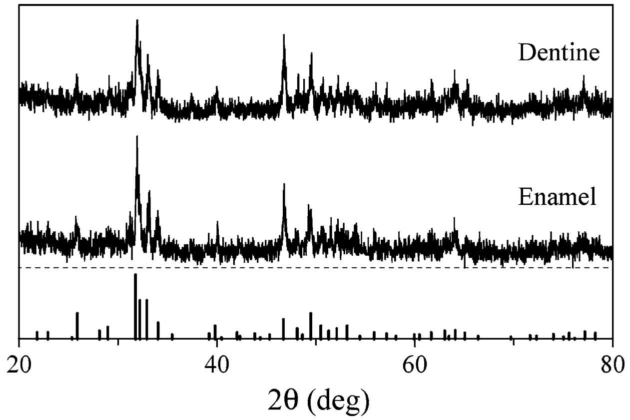

Fig. 5 X-ray diffractograms under low incidence beam mode at the surface of enamel and dentine plasma-spray coatings on Ti made using bond-coating technique. (The patterns of HA JCPDS card 9-432 are plotted at the bottom side of the diagram; the intensities have not been normalised; full scale of the intensity axis: 470 cps)

similar (to Fig. 6) SEM images at cross-sectioned interfaces. The significant reduction of microvoids in the bulk of coating layer is certainly the most sound effect of bond-coating plasma-spray.

Figure 7 shows the surface morphology (top-view) of plasma-spray coatings produced by simple coating of enamel and dentine powders. Bond-coating resulted in similar aspects, which agrees fairly well with the slight effect on the surface roughness of plasma-sprayed coatings, shown in Table 5.

The results of tensile strength tests are summarized in the Tables 6–8. The statistical analysis, summarized in Table 7, indicates that the comparison of the enamel simple is statistically insignificant except in the case of the enamel bond-coating ($p = 0.037$ or $z = 2.089$). Dentine bond-coating does not show statistical significance but similarities when compared with both enamel bond-coating and dentine simple. Comparison between enamel bond-coating and dentine simple is meaningful and statistically significant.

In general, bond-coating has improved tensile strength of coatings made with enamel and dentine powder, likely more pronouncedly in the case of enamel, but the values were still lower than those obtained at the coatings made with the standard AMDRY 6021 powder (Table 6). The application of bond-coating seemingly made the behavior of the three types of the produced coatings similar since in all cases the adhesion failure areas ranged between 80% and 85% of the total fraction area (Table 8), whereas no firm conclusion can be drawn out from the results of the simple coatings with regard to the influence of the type of the used powder on the ratio between adhesion and cohesion failure areas.

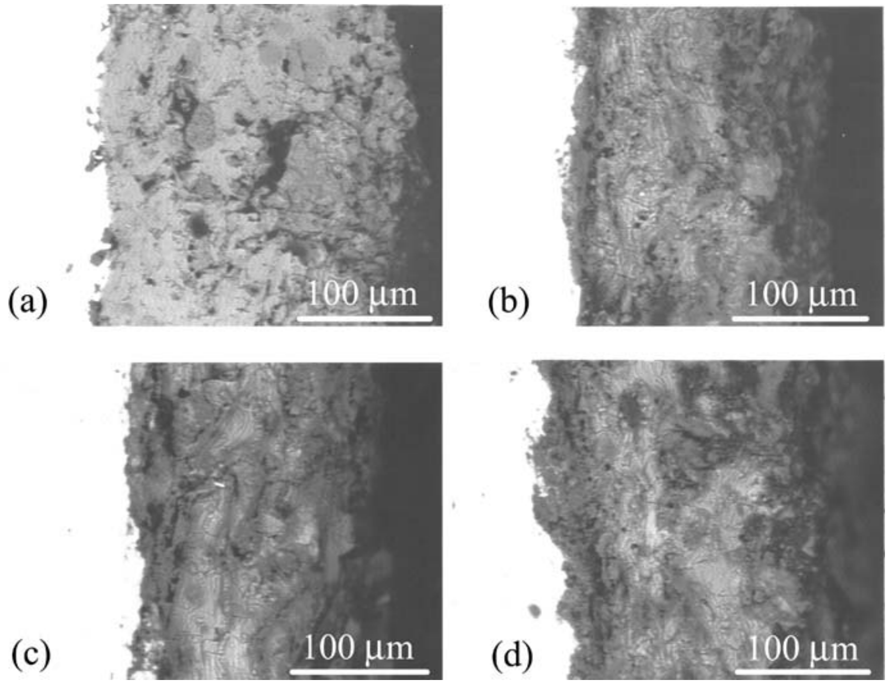

Fig. 6 Microstructure of interfaces produced by plasma-spray between Ti and enamel (a, b) and AMDRY 6021 (c, d), in the case of simple (a, c) and bond-coating (b, d). (From the left to the right: Ti is the white phase. Then the ceramic coating layer is seen. The dark part is the bakelite used to embed the samples)

Table 4 Characteristics of simple and bond-coating plasma-sprayed samples

	Enamel		Dentine		AMDRY 6021	
	Simple	Bond	Simple	Bond	Simple	Bond
Bond-coating thickness (μm)	–	25–50	–	25–45	–	25–30
Coat thickness (μm)	135–170	110–120	115–135	130–150	125–135	100–110
Microvoids (%)	2.83	0.17	1.19	0.19	1.11	0.29
Microvoids at metal coat border (%)	0.27	0	0.14	0	0.36	0
Microvoids at bond-coat layer (%)	–	0	–	0	–	0.29

Table 5 Roughness (R_a) of the outer surface of the Al_2O_3-blasted Ti surfaces (before coating) and of the coatings produced by simple and bond-coating plasma-spray (in μm)

	Enamel		Dentine		AMDRY 6021	
Ti	Simple	Bond	Simple	Bond	Simple	Bond
19.0	20.3	20.0	17.6	17.5	13.8	13.3

4 Discussion

Comparison of Figs. 1 and 5 indicates that plasma-spray caused significant lowering of crystallinity of ceramics, evidently due to high temperatures applied to the particles of the powders during the process. However, there was no evidence of formation of derivative phases of hydroxyapatite due to thermal transformation, such as tricalcium phosphate (TCP whitlockite), which would enhance the *in vivo* dissolution and lead to mechanical failure of coating after implantation [30], or dehydroxylation, such as tetracalcium phosphate, oxyhydroxyapatite, and amorphous calcium phosphate [31, 32].

Under this perspective, FA-coatings are seemingly promising alternatives of HA-coatings used in orthopedic implants [33, 34]. Indeed, push-out tests have shown that after 25 weeks of implantation in dogs, the push-out strength was 6.3±1.8 MPa for HA-coatings and 6.1 ± 1.1 MPa for FA ones [10]. In femur of goats (implant dimensions Ø5 mm and height 7 mm), after 12 weeks, the push-out strength was 13.3 ± 2.1 MPa for HA-coatings and 15.3 ± 2.7 MPa for FA ones, and after 25 weeks 17.3 ± 6.1 for HA and 16.8 ± 5.5 MPa for FA [35].

Small amount of fluorine ions enhances the stability of apatite lattice [34], increase crystallinity and decrease solubility of apatite. Fluorine is involved in the prevention or local treatment against caries at the enamel surface and the fluoridation of water [36]. Among the two types of apatite occurring in the body, FA in teeth (that was the case of the present study) and HA in bones, the former one is more thermally stable. Therefore, the high temperatures of plasma-spray should have less compositional and structural influence on FA than HA [34]. Accordingly, although X-ray analysis did not distinguish HA from FA (Figs. 1 and 5), it is reasonable to suggest that in this study the produced coatings were primarily made of FA.

In vivo studies have demonstrated that FA-coatings feature similar degree of bone apposition to HA-coatings but less dissolution after the first 3 months of implantation, provided that no other phases from apatite decomposition, mentioned earlier, have contaminated the coating [14, 37].

With regard to interfacial stability between the Ti substrate and the apatite coating layer, after 24 weeks of implantation, the tensile strength of coatings (implant dimensions Ø5 mm and height 3 mm) was 0.90 MPa for FA-coatings and 1.17 MPa for HA-coatings [38]. Similar tests in *in vitro* conditions after 25 weeks resulted in 76.3 MPa for HA-coatings and 79.6 MPa for FA ones (in that case, however, the joint was glued with Araldite AV 118, which was strengthedned by heating the glue) [39]. Therefore, the incorporation of fluorine ions in apatite lattice does not alter the adhesive properties of coatings. Moreover, FA is generally accepted as technically easier material for plasma-sprayed coatings than HA [1, 39].

FA and HA have been combined in bi-layered coating implants, whereas the inner layer was FA and the outer

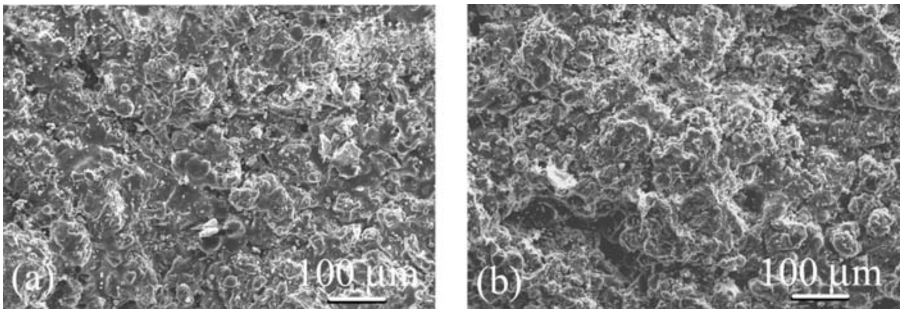

Fig. 7 Microstructure (top view) of single plasma-spray coatings of (a) enamel and (b) dentine powders on Ti

Table 6 Tensile strength and standard deviation (ASTM C-633-01) of simple and bond plasma-spray coatings on Ti prepared with the investigated powders and comparison with the results of similar earlier studies, where different type of naturally derived apatites were used [45, 46]; the particle size ranges of the powders are also presented (see also Tables 7 and 8)

		Tensile test (MPa)	
Coating material	Particle size range (μm)	Simple	Bond
Enamel	75–250	6.66 ± 1.82	9.71 ± 1.43
Dentine	75–250	6.27 ± 1.25	7.84 ± 1.60
AMDRY 6021	45–160	11.49 ± 0.21	12.05 ± 0.52
Human bone [45]	60–99	6.91 ± 1.65	13.20 ± 1.70
Bovine bone [46]	150–200	9.34 ± 1.45	10.20 ± 2.13

Table 7 Statistical analysis of tensile strength measurements (see also Table 6)

Enamel simple	–			
Enamel bond-coating	$z = 2.089$ $p = 0.037$	–		
Dentine simple	$z = 0.209$ $p = 0.834$	$z = 2.298$ $p = 0.022$	–	
Dentine bond-coating	$z = 0.627$ $p = 0.531$	$z = 1.671$ $p = 0.095$	$z = 1.462$ $p = 0.144$	–
	Enamel simple	Enamel bond-coating	Dentine simple	Dentine bond-coating
Failure	6.7 ± 1.8 26.87%	9.7 ± 1.4 14.43%	6.3 ± 1.3 20.63%	7.8 ± 1.6 20.51%

Notes: (a) The % has been calculated by dividing the SD by the mean value (e.g. 1.8/6.7 = 26.87%).
(b) The condition for acceptance is <30%.

one was HA. Clinical tests showed that the implant to bone contact was lost due to failure of the HA-outer and the FA-inner layers [40]. However, further investigation in this system is necessary.

To match the difference of thermal and chemical properties between the materials of the substrate and the coating, bond-coating has been adopted in many industrial plasma-spray applications. Metals, such as Al, Ni, and Mo, have resulted in strengthening of interfacial adherence [41]. In the case of Ni and Al, it has been proposed that exothermal reaction between these two metals occurs during plasma spraying [42], but these phenomena need further documentation [43]. Several studies have demonstrated that bond-coating results in stronger interfaces than simple coating (according to ASTM C-633). For instance, AISI 1020 carbon steel and AISI 304 stainless steel with Al_2O_3 Metco 101, ZrO_2 Metco 201, Ni-Cr-Al Metco 443 [41, 43].

In biomedicine, few studies have been carried out on bond-coating, as it has been already outlined in the introduction section [20, 21]. Heinemann et al. have used several compounds as bond-coatings, such as calcium zirconate (2–5 μm thick), CaO stabilized zirconate (10–15 μm), eutectic mixture of non-stabilized zirconia with titania (10–15 μm), and they found that titania bond-coatings increased the resistance to peel off effect up to 50% or even 100%. They have also stated that zirconia-titania bond-coating functional layers can be also considered as biocapacitors since they can store electrical charges close to the interface, which can stimulate bone ingrowth and reduce the time required for endosteal callus remodeling [16].

Table 8 Ratio of adhesive/cohesive failure areas (in %) of the tested simple and bond plasma-spray coatings

Material	Simple coating	Bond-coating
Enamel	4.27/95.73	85.24/14.76
Dentine	57.49/42.50	81.39/18.61
AMDRY 6021	96.99/3.01	82.92/17.06

The effect of bond-coating was obvious in the quality of the three Ti/apatite interfaces investigated in this study (Fig. 6, Table 4). It is clear that coating layers made with simple coating (Fig. 6a and c) suffer from microcracks, which probably occurred due to the difference of the thermal properties between Ti and apatite. The use of the Al_2O_3/TiO_2 bond-coating layer seemingly closed the gap of properties between the two phases and thus there are no microcracks, whereas the homogeneity of the coating layer is seemingly higher. The presence of TiO_2 probably assisted the matching of the metallic nature of Ti and the ionocovalent ceramic, while Al_2O_3 provided durability to the joint. However, these phenomena need further investigation and confirmation. The absence of formation of reaction zone between Ti and the bond-coating oxides, even at the places where the bond-coating agent was deeply penetrated into the narrow grooves of surface asperities of Ti, and the interdiffusion between this layer and apatite further confirm the good quality of the produced coatings. The good effect of bond-coating has been also stated by Oktar, who had applied Al_2O_3 bond-coating in Ti/HA implants and he found significant reduction of the volume of microvoids in the coating layer (form 6–8% in simple-coatings to 1–2% in bond-coatings). The use of TiO_2 in the present study further improved those values obtained in the case of using merely Al_2O_3 [44].

The improvement of the quality of the interface and of the coating bulk due to bond-coating had evident impact in tensile strength. The measured values significantly increased (Table 6) and the ratio of adherence over cohesive failure areas was similar for all the investigated coatings (Table 8). There are few studies on tensile strength measurements of such bond-coatings using the ASTM C 633-01 (note that this standard was obtained in 2001, derived from earlier ones starting from the C-633-69). Comparison of the results of the present work with results obtained from similar earlier studies using different types of naturally derived apatites (i.e. human [45] and bovine [46]) indicate that bond-coating with Al_2O_3/TiO_2 increases the tensile strength of the Ti/coating interface (Table 6). In the light of the domination of adhesion failure areas over cohesive ones in the fracture areas (Table 8), the images of Fig. 6 indicate that the Ti/ceramic adhesion is mainly due to mechanical interlocking of ceramic into the asperities of Ti surface (created by the blasting of Ti surfaces with Al_2O_3 powder prior to plasma-spray, see Table 5) rather than chemical or diffusion bonding. This means that the interfacial adherence should be much lower in the case of coating smooth Ti surfaces.

The results of this study also indicate that the tensile strength of the coatings made with enamel and dentine powders was lower than that of bone derived or the standard HA AMDRY 6021 (Table 6). The present results can not indicate which parameters are responsible for this difference. Flowability of initial powders is a very important factor. The size and the shape of the particles usually depend on powder preparation method. In the case of metals, the size of particles from plasma atomization processing is about 40 μm, 65 μm for from rapid solidification 65 μm, 80 from gas atomization 80 μm, from rapid spinning cup method 25 μm, and from the rotating-electrode process 150 μm [47]. Ceramic powders for plasma spraying are usually prepared with sol-gel method [28], but other conventional methods are also possible.

Owing to the fact that the apatite investigated in this study was not synthetic but was derived form natural source (thus we could not apply any of the aforementioned techniques), we can say that the simple and low cost preparation method that we used resulted in powders with very good morphology (i.e. high purity from debris, suitable size and rounded corners of particles), similar to the regularly used plasma-spray powders [29], especially in the case of the enamel powder (Fig. 3), while flowability was also excellent (Table 3). It should be mentioned, however, that there is no standard test for measuring flowability of ceramic powders but only of polymers and metals ones. In this work we used the flowability test for polymers [23].

Several studies have focused at obtaining ceramic powders suitable for plasma spray, with regards to particles morphology and flowability. Powder of typically rounded HA particles has been produced by spray-dry, using a polymeric binder, which has, however, to be removed afterwards [23]. Freely flowable powders ensure good control and constancy of feed rate to plasma spray gun resulting in high quality coatings. To obtain such characteristics, the powder is mixed with polymeric binder (polyvinyl alcohol) in a paste form, dried and particulated (50–300 μm) [48, 49]. Various agglomeration methods, such as spray-dry, have been employed to turn normally non-flowing small diameter particles to freely flowing powders. Nevertheless, organic compounds can decrease the apparent density of powder and cause blockage (fouling) of plasma gun due to vaporization of organic material [50, 51], or affect the quality of another similar technique of flame spray. In some US patents, the agglomerates are pre-sintered to remove the binder [50, 52]. In the work of Khor and Li, plasma-spheroidized powder was sprayed directly into water, collected and sieved [53]. Gitzhofer et al. started from a gel of HA-precipitate following by drying, calcination, sintering, crushing and screening [54]. However, all these methods need extra energy, effort and time.

5 Conclusions

Powder flowability is a crucial parameter of successful plasma-spray, which depends on the particle size distribution, the purity of powder from debris and the shape of the powder particles. Until now, little attention has been paid to this important issue in the literature. The proposed production method of apatite powders from teeth enamel and dentine is very simple and economic, comparing to the time-consuming and delicate methods proposed earlier, resulting in high quality powders for plasma-spray applications, with regard to flowability.

The enhanced thermal stability of the investigated powders, most probably due to the relatively high content of fluorine of both enamel and dentine tooth derived powders, indicate them as superior candidate materials for calcium phosphate coatings of producing medical devices.

Bond-coating made of Al_2O_3/TiO_2 seemingly closed the gap of properties between the contacting phases of Ti and apatite in plasma-spray coatings of both teeth derived powders on super clean and roughened, by Al_2O_3 blasting, Ti surface. This resulted in a significant increasing of mechanical properties of the produced coatings. The microstructure at the ceramic/metal interface featured no microcracks, whereas the homogeneity of the coating layer was higher than in the case of simple coatings. The presence of TiO_2 should assist the matching of the metallic nature of Ti and the ionocovalent ceramic, while Al_2O_3 provided durability to the joint. The absence of formation of reaction zone between Ti and the bond-coating oxides, even at the places where the bond-coating agent was deeply penetrated into the narrow grooves of surface asperities of Ti, and the excellent interdiffusion between this layer and apatite further confirm the good quality of the produced coatings.

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