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Production and characterization of plasma-sprayed TiO_2–hydroxyapatite functionally graded coatings

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Abstract

Among bioactive ceramics, hydroxyapatite (HAp) has been widely studied, especially as a coating onto metallic substrates. In clinical applications, coating delamination has been observed, close to the interface between coating and substrate. This is due to a mismatch in the thermal expansion coefficients of HAp and titanium/titanium alloy. In order to improve the adhesion, a proper bond coat may be introduced. In this work, a functionally graded coating TiO_2–HAp, in which the composition gradually changed from TiO_2 to HAp, was deposited onto Ti6Al4V substrates by atmospheric plasma spraying (APS). With the aim of defining the best spraying parameters to obtain the graded system, preliminary coatings of pure TiO_2 and pure HAp were deposited by varying systematically the typical spraying conditions, such as the torch power and H_2 flux. The preliminary coatings were characterized by means of SEM, that confirmed the strong dependence of the microstructure on the torch power, and X-ray diffraction, that showed the significant influence exerted by the hydrogen flux on the crystallinity and thermal decomposition of HAp. The results of the preliminary investigations were used to optimise the spraying conditions for the FGM deposition and, accordingly, the final graded coating was obtained and characterized. Post-deposition heat treatments were performed in order to improve further the graded coating and their effect on the mechanical properties was evaluated via Vickers micro-indentation tests. The investigation showed that, after raising the temperature, the crystallinity of HAp and the Vickers hardness increased, however, at high temperature (more than 750 °C), the stress induced by the re-crystallization promoted the propagation of cracks and weakened the interface.

Keywords: Microstructure-final; Hardness; Apatite; TiO_2; Functionally graded materials

1. Introduction

Hydroxyapatite (HAp) is widely used in biomedical applications, in both orthopaedic and dental implants, since it shows a similar chemical and mineralogical composition to living bone tissue.[1] However, HAp suffers from its brittleness and relatively poor mechanical properties, which impede its usage in long term load-bearing applications. In order to overcome this drawback, HAp is often used as a bioactive coating on metallic substrates, such as titanium and titanium alloys, which are mechanically stronger and tougher.[2]

Several techniques have already been attempted to deposit HAp coatings onto metal substrates such as, for example, sputtering, hydrothermal reaction, sol–gel or aerosol–gel methods, and electrophoretic deposition.[3] However, atmospheric plasma spraying is nowadays the most commonly used method in the industrial practice.[4] Plasma spraying is widely adopted to obtain HAp coatings onto titanium/titanium alloy implants since it is a well established and cost-effective surface treatment process,[2] nevertheless it has been asserted that the adhesiveness of HAp coatings is relatively weak and decreases in the case of thick coatings,[5] probably due to the mismatch in the coefficients of thermal expansion of HAp and titanium ($11.5 \times 10^{-6}\,K^{-1}$ and $8.9 \times 10^{-6}\,K^{-1}$, respectively).[6] In order to solve this problem, Khor et al. proposed to create a promising HAp/titanium alloy graded coating.[7] In fact, functionally graded materials (FGMs) are a new class of composite materials, whose composition and/or microstructure vary gradually in space thus allowing a better integration between dissimilar constituent phases with respect to traditional bi-material structures.[7,8]

As an alternative solution, a bioinert bond coat may be introduced. The insertion of a proper inter-layer may be advantageous

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under several respects and not only because it reduces the discrepancy between the coefficients of thermal expansion of the metal substrate and the HAp top coat. In fact, it also avoids the direct contact between HAp and metal, which is thought to promote the thermal decomposition of HAp, and decreases the steep temperature gradients during plasma spraying, which may favour the uncontrolled formation of amorphous calcium phosphates. Moreover, a specific bond coat may reduce the potential release of metal ions from the substrate and induce a cushioning effect against cyclic loading of the implant in service.[9] In particular, it has been proved that a titania bond coat may significantly increase the interfacial bond strengths and the overall performance of HAp-coated Ti–6Al–4V systems.[9]

Also TiO_2/HAp composite bond coats have shown interesting properties, since the titania hinders the crack propagation and properly modifies the coefficient of thermal expansion of pure HAp.[10]

The basic idea of the present work was to combine the benefits of a gradual change in composition typical of FGMs with the advantages of titania and titania/HAp bond coats, by depositing a titania–HAp graded coating onto Ti6Al4V substrates by plasma spraying. In the present research, in order to obtain the graded coating, titania and HAp were sprayed together, in proper proportions. However, the spraying conditions typically applied to deposit pure titania and pure HAp are quite different, as the former is thermally stable while the latter thermally decomposes, so great attention was devoted to the identification of the optimal spraying parameters to co-spray the TiO_2 and HAp powders. With this aim, several coatings of pure titania and pure HAp were produced and analysed in order to evaluate the effect of such parameters as torch power and hydrogen flux. The results of these preliminary depositions were used to define the spraying parameters for the final TiO_2/HAp graded coating, which was deposited, characterized and further optimised via proper heat treatments.

2. Materials and methods

2.1. Preliminary coatings

Commercially available HAp powder (Plasma Biotal, Captal 60-1, granulometric distribution with D50 at about 45 μm and D90 at about 83 μm) and TiO_2 powder (Sulzer METCO 102, granulometric distribution with D50 at about 30 μm and D90 at about 53 μm, Fig. 1) were used as starting materials. Commercial titanium alloy (Ti6Al4V) substrates were properly cut (about 40 mm × 40 mm × 5 mm) and employed as substrates after grit-blasting by alumina particles (Sulzer Metco Metcolite-C). All the depositions were carried out in air plasma spraying mode by using an F4-MB plasma torch installed in a Controlled Atmosphere Plasma-Spraying plant at Centro Sviluppo Materiali S.p.A. (Roma, Italy), which is co-shared with the University “La Sapienza” (Roma).

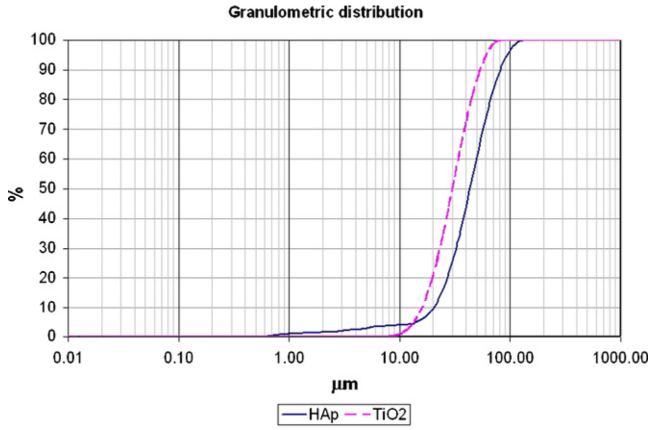


Fig. 1. Granulometric distribution of the commercial HAp and TiO_2 powders used as feedstock for the plasma spraying depositions.

Table 1
Torch power and H_2 flux values for preliminary coatings of pure HAp and pure TiO_2

Name	Power (kW)	H_2 flux (slpm)
HAp1; T1	45	15
HAp2; T2	45	5
HAp3; T3	40	15
HAp4; T4	40	5
HAp5; T5	35	15
HAp6; T6	35	5
HAp7; T7	30	15
HAp8; T8	30	5
HAp9; T9	25	15
HAp10; T10	25	5

HAp stands for pure HAp coating; T stands for pure TiO_2 coating.

In a first step, in order to analyse the effect of the spraying conditions on HAp and TiO_2, the two powders were deposited separately varying the torch power and the hydrogen flux as described in Table 1. The other parameters were kept constant as listed in Table 2. Both the pure HAp coatings (samples HAp1–HAp10) and the pure TiO_2 ones (samples T1–T10) were characterized via scanning electron microscopy, SEM, coupled with X-ray energy dispersion spectroscopy, X-EDS (ESEM Quanta 2000), in order to investigate their microstructure and evaluate their mean porosity and thickness. Moreover, all the coating surfaces underwent a X-ray diffraction test, XRD (PANalytical X’pert PRO). The diffraction patterns were collected at a scan rate of 0.017°/s with Cu Kα radiation. The

Table 2
Plasma torch operating parameters

Spraying parameters	Settings
Torch-type	F4-MB, internal diameter: 6 mm
Power	see Table 1
Spraying distance	100 mm
Number of passes	5 pre-heating + 10 spraying
Powder injection system	Carrier gas: Ar, 3 slpm; injector axial distance from torch exit: 7 mm; injector angular distance from torch exit: 90°; injector internal diameter: 1.8 mm
Plasma gas composition and flow	Ar, 50 slpm; H_2, see Table 1
Cooling system	Cooling gas: Ar; pressure 8.5 bar
Substrate temperature during deposition	About 150 °C

2θ angular range in exam was fixed to 20–60°. As regards the HAp coatings, since the plasma spraying may induce a thermal decomposition, the degree of crystallinity, DOC, after deposition was estimated by means of a relative method, comparing the intensity I_C of the main HAp peak of the coating to the intensity I_{FP} of the main HAp peak of the HAp feedstock powder[11]:

$$\mathrm{DOC}\,(\%) = \frac{I_C}{I_{FP}} \times 100 \tag{1}$$

The same relative method was also used to evaluate the content of impurity phases in the coatings[11]:

$$\mathrm{IMP}\,(\%) = \frac{I_{IMP}}{I_{FP}} \times 100 \tag{2}$$

where I_{IMP} is the intensity of the main peak of the impurity phase from the XRD pattern of the coating and, as stated before, I_{FP} is the intensity of the main HAp peak from the XRD pattern of the HAp feedstock powder. In particular, this approach was applied to estimate the content of CaO in the coatings.

The results obtained from the preliminary coatings, in terms of microstructure and HAp crystallinity and integrity, were used to define the best values of torch power and H_2 flux to deposit the final graded coating.

2.2. Functionally graded coating

The graded system was designed as a multi-layered coating, whose composition changed from pure titania (at the interface with the Ti6Al4V substrate) to pure HAp (at the outer surface). Each one of the 11 layers deposited could be considered as a traditional (i.e. not graded) composite material and, moving from the substrate to the top surface, the mean content of titania was decreased by 10 vol% from layer to layer; the mean content of HAp was increased accordingly.

In order to spray a graded coating different approaches can be experimented; usually, if the graded coating is designed as a multi-layered system, the layers can be produced by using various pre-mixed blends of powders [12–14] or coated powder particles.[15,16] In the present research, an alternative technique was preferred and the TiO_2 and HAp powders were not pre-mixed or pre-coated but separately introduced in the plasma flux by two different powder feeders.[17,18] The compositional profile was obtained by progressively modifying the feeding flow rates of the two powders. In order to achieve the desired volume fractions, the TiO_2 and HAp feeding rates for each layer were calculated on the basis of a deposition efficiency measurement. In fact the two powders were separately sprayed on substrates of known thickness under the same deposition conditions and number of passes, after that the thickness of the two coatings was measured and used to calibrate the feeding rates. The feeding parameters are reported in Table 3. Even if this approach needed a more accurate setting of the spraying process, it was chosen because it made it possible to work with two powders instead of 11 mixtures, as required by the other methods. Moreover, the use of several different mixtures or coated powders would have made it necessary to empty the feeders at the end of the deposition of each layer, while the employment of two feeders made it possible to work in a continuous way.

Table 3
Feeding parameters for the functionally graded coating

HAp % in the layer	Feeding disk speed (rpm)	
	TiO_2	HAp
0	13.0	0.0
10	11.7	2.7
20	10.4	5.3
30	9.1	8.0
40	7.8	10.7
50	6.5	13.4
60	5.2	16.0
70	3.9	18.7
80	2.6	21.4
90	1.3	24.0
100	0.0	26.7

As previously mentioned, in order to define an optimal compromise between the spraying conditions typically required for TiO_2 and HAp, the torch power and H_2 flux were suggested by the preliminary coating characterization (as discussed in the following). The other spraying parameters were the same as for the preliminary coatings, as detailed in Table 2. For both the powders, argon was used as carrier gas and its flow rate was set to 3.2 slpm for HAp and 3.0 slpm for TiO_2.

The SEM and XRD investigations were repeated on the resulting graded coating.

2.3. Heat treatments on the graded coating

Various heat treatments were performed to improve further the system: the samples were heated in air from room temperature to the maximum temperature (650 °C/750 °C/850 °C) at 10 °C/min, left at the maximum temperature for 1 h and then cooled naturally inside the kiln. Beside the microstructural and mineralogical characterization, the effect of the thermal treatments on the mechanical properties was evaluated by performing Vickers micro-indentation tests on the polished cross-section of the as-sprayed and heat-treated coatings (Wolpert Group, Micro-Vickers Hardness Tester digital auto turret, Mod. 402MVD). A maximum load of 1 N was applied for 15 s. The indentations were carried out on lines parallel to the coating–substrate interface, in order to appreciate the relation existing between local composition and mechanical properties before and after the heat treatment.

3. Results and discussion

3.1. Analysis of preliminary coatings

The air plasma spraying method is widely used to deposit TiO_2 because the plasma temperatures are high enough to melt ceramics having a high melting point (1855 °C for TiO_2).[19] On the other hand, the extreme temperatures of the plasma flame are likely to decompose the HAp.[20] As a consequence, if TiO_2 and HAp have to be co-sprayed, as it is the case of composite graded coatings, the spraying parameters should be carefully set. In particular, in the present research great attention was paid to torch power and H_2 flux, because the former controls the flame energy and the latter influences the plasma enthalpy.[21]

The effect of the spraying conditions on the microstructure could be appreciated by the SEM observation of the cross-sections, as shown in Fig. 2 (low magnification images, 100×) and Fig. 3 (high magnification images, 1000×). Based on the SEM micrographs, an image elaboration made it possible to calculate the mean porosity and mean thickness of the preliminary coatings, as reported in Table 4. The microstructure was substantially governed by the torch power, since low values of the power resulted in not-continuous coatings, in the sense that the coating was so defective that it could not completely cover the surface. In particular, if the power was less than 40 kW, the pure titania coatings became very defective and discontinuous. A decrease of the torch power induced a progressive increment in porosity and reduction in thickness of pure HAp coatings, until the HAp coatings as well became discontinuous for a torch power of 25 kW. However, as regards the pure HAp coatings, the microstructure was also influenced by the H_2 flux, since under the same torch power a low H_2 flux (5 slpm instead of 15 slpm) resulted in a thinner and more porous HAp coating (as shown in Fig. 3). Since only the TiO_2 coatings deposited at 45 kW and 40 kW were continuous, it was not possible to define unambiguously the effect

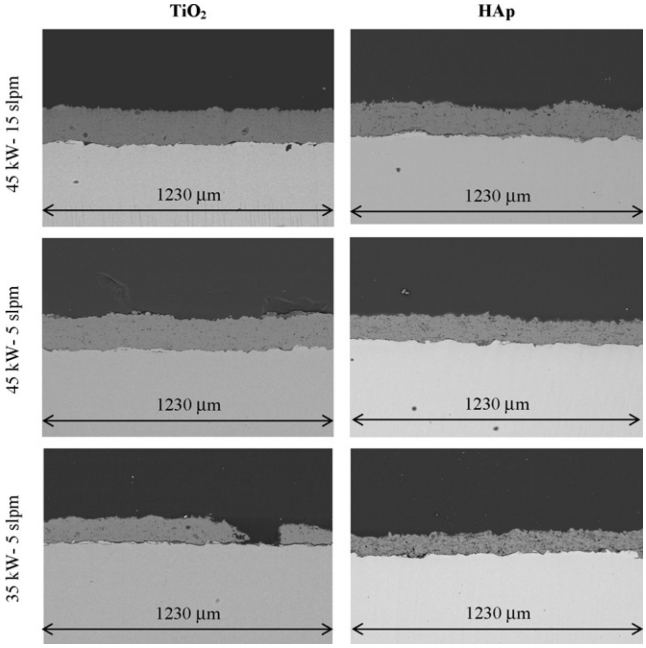


Fig. 2. Examples of preliminary coatings cross-sections (low magnification SEM images, 100×).

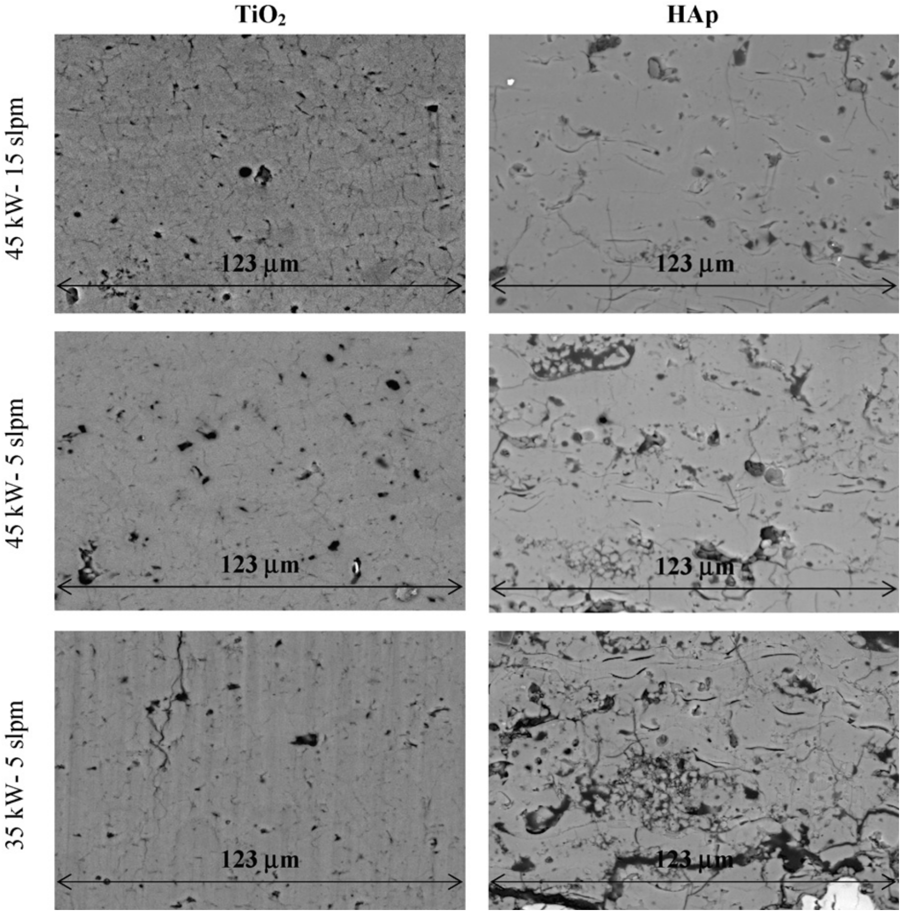


Fig. 3. High magnification (1000×) SEM images of preliminary coatings cross-sections.

Table 4
Mean porosity and thickness of preliminary coatings (pure TiO_2 and pure HAp)

	Porosity (%)	Thickness (μm)
Titania coatings		
T1	3.0 ± 0.8	153 ± 10
T2	2.5 ± 0.5	157 ± 11
T3	1.9 ± 0.1	171 ± 12
T4	4.0 ± 1.6	156 ± 10
T5	Not continuous	
T6	Not continuous	
T7	2.1 ± 0.2	152 ± 7
T8	Not continuous	
T9	Not continuous	
T10	Not continuous	
HAp coatings		
HAp1	13.9 ± 0.7	136 ± 14
HAp2	16.9 ± 2.9	107 ± 10
HAp3	16.2 ± 2.6	140 ± 18
HAp4	18.7 ± 2.4	59 ± 14
HAp5	10.7 ± 1.4	105 ± 14
HAp6	26.1 ± 2.1	68. ± 24
HAp7	14.2 ± 3.0	108 ± 14
HAp8	25.8 ± 3.5	93 ± 13
HAp9	18.7 ± 1.9	82 ± 11
HAp10	Not continuous	

of the H_2 flux on these systems. However, according to the direct SEM observation of the cross-sections, the role of the H_2 flux on the microstructural morphology, especially in TiO_2 coatings, could be considered secondary with respect to torch power.

In contrast, the effect of H_2 flux on crystallinity and the presence of impurity phases was very relevant. The XRD tests performed on the pure TiO_2 coatings showed a good crystallization, with rutile and anatase as the principal phases induced by the spraying process. Table 5 suggests that, as a general trend, the peak intensity of rutile increased at increasing power[22]; moreover the peaks of rutile were more intense for a H_2 flux of 5 slpm than 15 slpm. Table 6, instead, refers to the degree of crystallinity and content of impurity phases (CaO) of pure HAp, calculated according to Eq. (1). A direct correlation exists between the H_2 flux and the degree of crystallinity, since, with the same torch power, a low value of the flux induced a high degree of crystallinity and vice versa. Moreover, the presence of CaO, which was caused by the thermal decomposition of hydroxyapatite, was influenced by the H_2 flux too. In this case, with the same torch power, the lower the H_2 flux, the lower the CaO content and vice versa. As a general trend, the integrity of HAp was facilitated by low values of the power and, for a power of 25 kW and a H_2 flux of 5 slpm, the presence of CaO was negligible.

Table 5
Effect of spraying parameters on rutile crystallization in pure TiO_2 preliminary coatings

	Rutile peak int. (cts)
Titania coatings	
T1	406
T2	967
T3	610
T4	1126
T5	412
T6	1066
T7	388
T8	993
T9	345
T10	1179

Table 6
Effect of spraying parameters on the degree of crystallinity and content of CaO in pure HAp preliminary coatings

	DOC (%)	CaO (%)
HAp coatings		
HAp1	6.9	0.4
HAp2	8.1	0.2
HAp3	5.1	0.6
HAp4	10.1	0.1
HAp5	6.3	0.4
HAp6	9.6	0.0
HAp7	5.8	0.3
HAp8	8.2	0.1
HAp9	6.0	0.2
HAp10	8.8	0.0

3.2. Optimisation of the spraying parameters and deposition of the graded coating

Since the basic target of the present research was to deposit a high quality TiO_2–HAp graded coating, it was mandatory to work with a high torch power, not less than 40 kW, because a lower value would give place to a discontinuous TiO_2 layer at the interface with the metal substrate, thus undermining the structural strength of the coating, and it would give place to an excessively porous HAp. In particular, as regards the HAp, even if large and controlled pores are thought to promote the bone in-growth, a very high porosity would be undesirable, since it could reduce the mechanical and bonding strength of the material itself.[23,24]

However, a high power could favour the thermal decomposition of hydroxyapatite, inducing a low crystallinity and a high content of impurity phases.[11,25] As a consequence, a value of 40 kW was chosen for the graded coating production, because it was a good compromise between quality of microstructure and HAp integrity.

As regards the H_2 flux, a value of 5 slpm was adopted to deposit the graded coating, since it slightly increased the porosity (Table 4) but it was extremely beneficial to promote the crystallinity of HAp and reduce its CaO content (Table 6). In fact, it is known from the literature that plasma spraying usually induces a thermal decomposition of HAp, decreasing its crystallinity and giving place to various decomposition products.[4,20,26] As regards the HAp crystallinity, though it is usually acknowledged that a small amount of amorphous HAp may be advantageous at the coating surface, because it may promote profitable physiological activities, a high degree of crystallinity is generally preferable,[27,28] because highly crystalline HAp may create a direct bond with bone *in vivo* and show low dissolution rates. On the other hand, as regards the CaO, since its content in

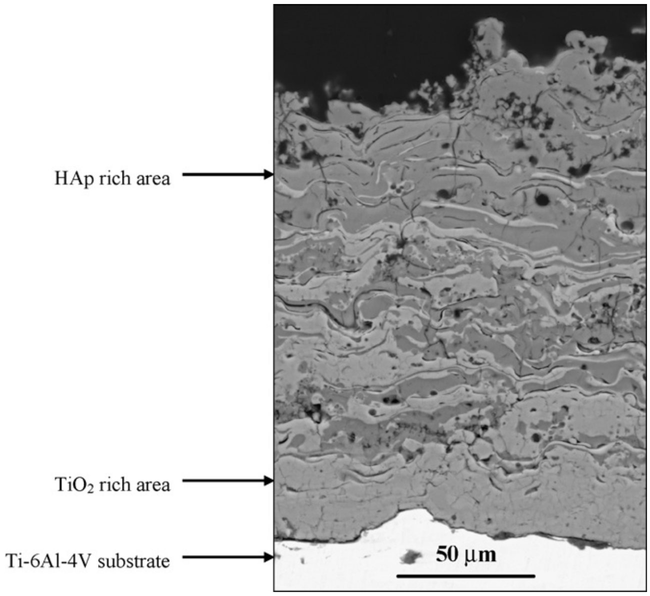


Fig. 4. Cross-section of the TiO_2–HAp graded coating.

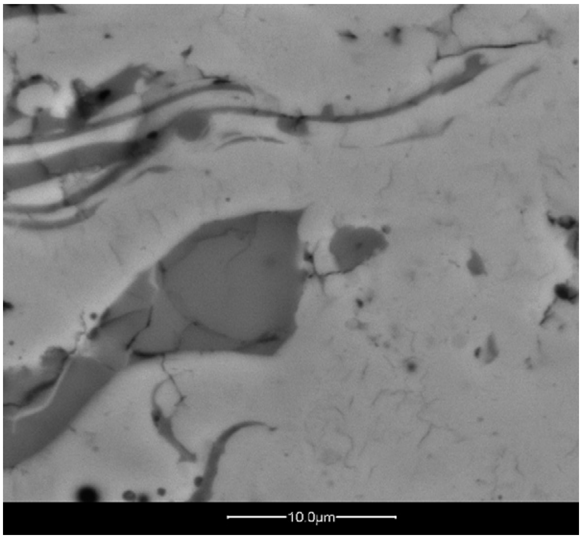


Fig. 5. Titania (dark grey) and HAp (light grey) domains in the FGM cross-section.

the feedstock HAp powder was negligible, its presence in the sprayed coatings could be considered as representative of the development of byproducts. So, the lower the CaO content, the lower the uncontrolled development of decomposition products. Moreover, the content of calcium oxide should be minimized because CaO is extremely reactive with water and undesired in biomedical implants [28] and, if its content is excessive, it cannot completely transform into HAp during post-deposition heat treatments.[26,28]

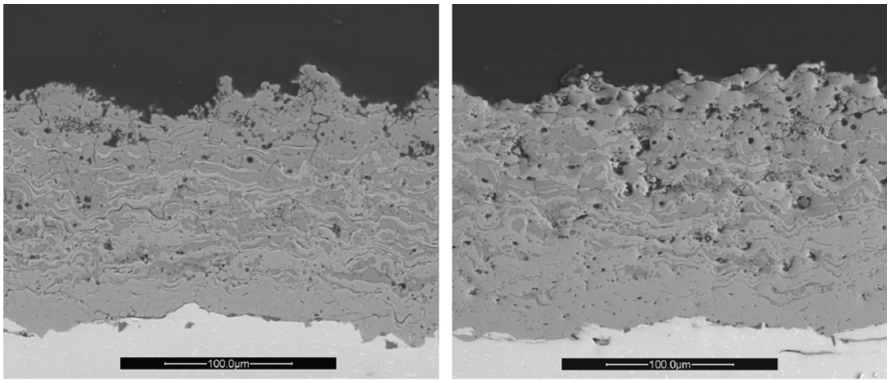
These values of torch power (40 kW) and H_2 flux (5 slpm) were used to deposit the graded coating, according to the approach previously described. The microstructure of the graded coating is presented in Fig. 4. The SEM investigation of the cross-section with back-scattered electrons revealed the typical splat-like morphology of plasma-sprayed ceramics, with the dark lamellae made of HAp and the light ones of TiO_2. The SEM inspection, coupled with X-EDS, suggested that no relevant reaction took place between the constituent phases, because the lamellae were clearly distinguishable and the interface between them quite definite (Fig. 5). It is worth noting that the 11 layers deposited to obtain the graded coating could not be distinguished, since their mean thickness was comparable with the dimension of the titania and HAp domains, and therefore the final gradient could be considered continuous and not step-wise.[8,18,29] As a matter of fact, the total thickness of the coating, 204.6 ± 26.5 μm, was reached by depositing 11 layers, that means the mean thickness of each layer was about 18 μm, that is comparable with the dimension of the titania and HAp domains in the graded coating, as displayed in Fig. 5. As shown in Fig. 5, the residual porosity (mean value: 8.8 ± 3.4 vol%) is preferentially located in the HAp-rich area, while the TiO_2-rich area close to the interface is denser and extremely compact, favouring the mechanical reliability of the coating. The XRD test performed on the surface could not detect the titania, confirming that the outer surface, in contact with the environment, was formed by HAp. The degree of crystallinity was very high and the presence of CaO limited ($51 \pm 1\%$ and $2.5 \pm 0.1\%$ respectively, according to the relative method previously described), confirming the beneficial effect of TiO_2 which impeded the direct contact between HAp and Ti alloy substrate.

3.3. *Effect of heat treatments on the graded coating*

Heat treatments are widely used to improve plasma-sprayed HAp coatings, since they can improve the HAp crystallinity and stimulate the conversion of impurity phases into HAp.[26] The temperature of annealing, however, should be carefully set, since HAp may decompose during the heat treatment. It has been reported that HAp is likely to decompose at 900 °C in air [27,30] and 950 °C in vacuum.[27,31] Moreover, the exposition to an excessive temperature may alter the Ti–6Al–4V substrate. For this reason, the temperature range 650–850 °C was considered in this study.

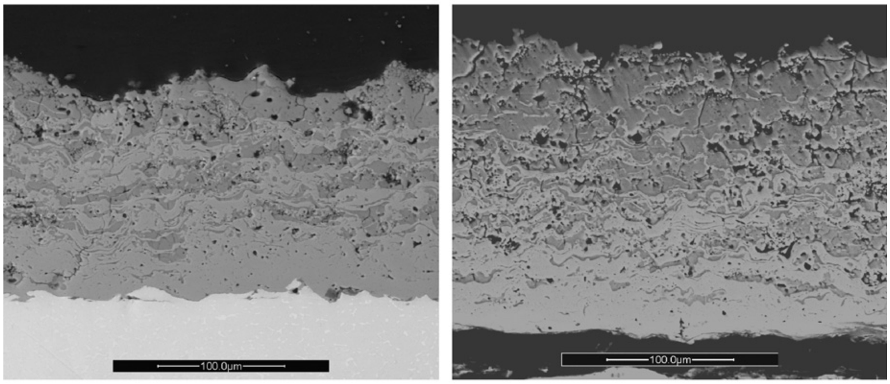
As represented in Fig. 6, the SEM investigation showed that the heat treatment did not homogenize the microstructure and the compositional gradient was preserved. However, at increasing temperature (750 °C), it was evident that the interface between the coating and the substrate became more defective and the presence of cracks increased, as shown in Fig. 7, leading to the failure of the coating at really high temperature (850 °C). Though some porosity and cracks could be tolerable and even helpful to promote the bone tissue in-growth, the mechanical properties of the coating should not be compromised by an exceeding porosity.[26]

This effect on the microstructure of heat-treated coatings may be justified by the re-crystallization of HAp proved by the XRD. In fact, as shown in Table 7, if the annealing temperature is increased, the degree of crystallinity of HAp increases and the content of impurity phases diminishes. Amorphous regions are thought to act like a binding agent, promoting the cohesion between crystalline regions.[27] After re-crystallization, this cement-like function of amorphous phases is reduced. Moreover, both re-crystallization and phase transformation cause volume



Graded coating, as sprayed

Graded coating, 650° 1h



Graded coating, 750° 1h

Graded coating, 850° 1h

Fig. 6. Effect of different heat treatments on the graded coating.

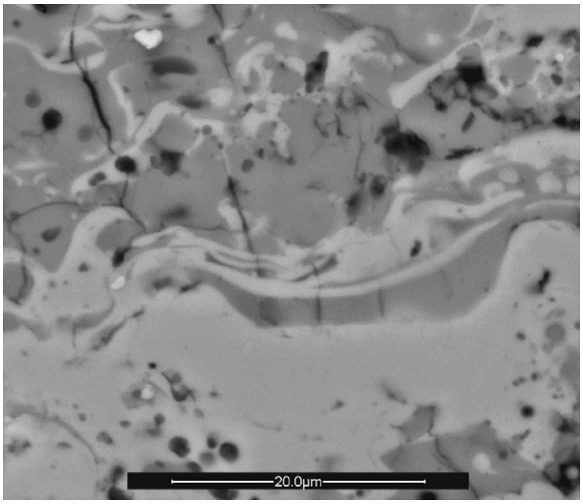


Fig. 7. Cracks induced by the HAp re-crystallization in the sample heat-treated at 750 °C for 1 h.

Table 7
Effect of thermal treatments on the degree of crystallinity (DOC) and content of CaO of the HAp in the graded coating as determined by the relative method

	DOC (%)	CaO (%)
FGM sample		
A.S.	47.7	2.0
650 °C	77.4	2.1
750 °C	80.2	2.3
850 °C	91.0	2.0

changes and hence additional stresses which superimpose on the residual stresses already present.[10,26,27] However, the presence of TiO_2, having a coefficient of thermal expansion in-between those of HAp and Ti–6Al–4V, is beneficial to decrease such residual stresses.[10]

In order to evaluate the effect of thermal treatments, the as-sprayed coating and the heat-treated ones underwent a systematic Vickers micro-indentation test. As already mentioned, since the compositional gradient is associated with a change in mechanical properties, on each cross-section the indentations were performed on two areas: close to the interface (TiO_2-rich area) and close to the upper edge (HAp-rich area). As reported in Table 8, this approach immediately proved that the hardness decreased from the TiO_2-rich area to the HAp-rich area, confirming the strengthening effect of the TiO_2. Moreover, the mechanical properties of the TiO_2 were not significantly altered

Table 8
Vickers hardness measured on TiO_2-rich and HAp-rich areas of the cross-section on samples treated at different temperatures

	$HV_{0.1}$ (Vickers)	
	TiO_2	HAp
FGM Sample		
A.S.	480.1 ± 79.8	208.3 ± 38.8
650 °C	488.8 ± 81.6	259.5 ± 51.1
750 °C	513.7 ± 113.1	302.3 ± 101.2
850 °C	363.9 ± 53.7	234.5 ± 47.2

by the heat treatment, while the re-crystallization resulted in increased hardness of the HAp. However, due to the progressive development of cracks, the samples treated at high temperature (e.g. 850 °C) achieved poorer performances. As a consequence, also on the basis of the observations regarding Fig. 7, the optimal annealing temperature was 650 °C, which promoted the HAp re-crystallization and impurity reduction without undermining the microstructural strength of the graded coating.

4. Conclusions

The present research aimed at producing a TiO_2–HAp-graded coating on a Ti–6Al–4V substrate by plasma spraying, since this system could combine the benefits of a TiO_2 bond coat with the advantages of a functionally graded material. Even if plasma spraying is a well-established technique, the deposition of a TiO_2–HAp-graded coating required a very accurate setting of the spraying parameters, since the TiO_2 and the HAp powders had to be co-sprayed. In order to investigate the effect of torch power and H_2 flux, several preliminary coatings of pure TiO_2 and pure HAp were sprayed and characterized, focusing on the microstructural integrity and potential thermal decomposition of HAp. In order to obtain a continuous and reliable coating and to minimize the content of amorphous HAp and impurity phases (CaO), a torch power of 40 kW and a H_2 flux of 5 slpm were used to produce the graded coating.

The assessment of the spraying parameters resulted in a dense coating, characterized by a small residual porosity preferentially concentrated in the HAp-rich region, a high degree of crystallinity and a very low content of CaO. Thanks to a proper selection of the annealing temperature, a subsequent heat treatment made it possible to increase further the degree of crystallinity and reduce the content of impurity phases, without altering the compositional gradient or inducing relevant crack development. The Vickers micro-indentation tests confirmed not only the functional gradient associated with the compositional change in space, but also the beneficial effect of the optimal heat-treatment on the mechanical properties.

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