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Plasma-spraying methods for applications in the production of quality biomaterials for modern medicine and dentistry♣

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Bioceramic hydroxylapatite (HA) coatings have been shown to be promising bioactive properties in load-bearing implant applications. Biocompatible heterostructure HA/TiO_2 deposits, consisting of a TiO_2 transition layer (100μm) and a HA top layer (20 and 40μm) were applied on Ti-6Al-4V (TAV) substrates, using atmospheric plasma-spraying (APS). The microstructure parameters were analysed by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The bond strength was evaluated with a tensile test for thermally sprayed coatings (ASTM C633-79). The results revealed that all deposits have a relatively dense and homogeneous, predominantly polycrystalline, microstructure. In addition, a negligible amount of an amorphous-like HA phase, formed mainly in the near-surface regions, and an insignificant amount of partially molten spherical grains are also presented. A not well pronounced crystallographic texture was detected. Compressive residual stresses in the range 7-10GPa, acting parallel to the top surface and decreasing during the growth, were registered. The HA/TiO_2 interface, about 15μm wide, was diffuse in nature and enabled a smooth transition between the two layers. The evaluated tensile bond strength was sufficiently high, and varied between 49 and 53MPa.

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Keywords: Thin films and coatings, Crystallographic structure, Interface, XRD, SEM

1. Introduction

At present, hydroxylapatite (HA, $Ca_5(PO_4)_3(OH)$) films on Ti-6Al-4V alloy (TAV) substrates are considered as very promising bioactive deposits on metallic implants for orthopaedic and dental applications. Plasma-spraying is one of the most suitable techniques for their application. In this technology, the initial powder material is injected into a gas plasma, melted and propelled towards a substrate, where a solid deposit is formed under strongly non-equilibrium conditions. The main advantages of HA/TAV implants are the relatively intense and uniform bone growth at the bone-implant interface and their chemical stability in a bodily environment, which also enable a stable mechanical fixation [1, 2]. The morphology and the parameters of the phase composition, interfaces, porosity, preferred crystallographic orientations (textures), residual stresses and bond strength are all critical properties which must be considered for biomedical purposes. However, the knowledge of these parameters and their influence on the properties of the implants is insufficient. In this paper, new information about the structures and properties of HA coatings on TAV substrates, produced by air plasma-spraying (APS), is given.

2. Experimental

2.1. Technology and samples preparation

The APS was performed on PPS-800 equipment with a PN-80E indirect current plasma torch (Plazma Ltd., Varna, Bulgaria).

Two types of heterostructure sample, consisting of a Ø36mm x 4mm TAV substrate, a TiO_2 transition layer and a HA top layer, were produced (Fig.1).

The TAV material was supplied by Synthes GmbH in the form of rods, which were sawn to prepare the circular substrates. The initial powders of AMDRY 6505 (TiO_2) and XPT-D-703 (HA), used for the deposit application,

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were supplied by Sulzer Metco Europe GmbH. The size distribution of their particles is given in Fig.2.

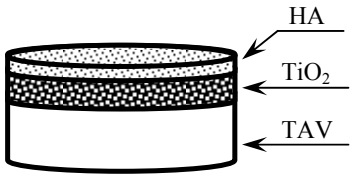

Fig. 1. Schematic illustration of a sample.

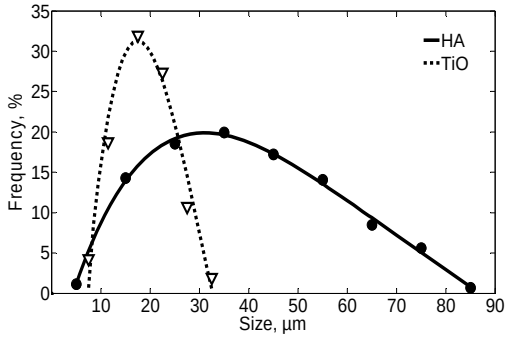

Fig. 2. Size distribution of the particles in the initial powders.

The substrate surface was grit-blasted with 450µm SiC particles, under 0.4MPa air pressure, prior to APS.

Four identical samples of each type (with thin and thick HA layer) were APS sprayed. The technological parameters are given in Table 1. An additional sample representing a TiO_2 deposit on a TAV substrate was also prepared.

Table 1. Processing parameters for APS

Current, A	500
Voltage, V	50
Power, kW	25
Ar/N_2 plasma gas flow rate, slpm	25/4
Powder feed rate, $g.min^{-1}$	15
Spraying distance, mm	120
Ar carrier gas flow, slpm	1.5
Transverse speed of the torch, $mm.s^{-1}$	10
Time of application, s	
TiO_2 transition layer	30
HA thin top layer	90
HA thick top layer	180

The characteristics of the analysed $HA/TiO_2/TAV$ samples are given in Table 2.

Table 2. Samples characteristics

Sample	Layer thickness, µm	
	TiO_2	HA
$HA(thin)/TiO_2/TAV$	100	20
$HA(thick)/TiO_2/TAV$	100	40

2.2. Experimental techniques

The structure parameters of the applied deposits were analysed by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM).

The XRD patterns were registered by a Seifert & Co diffractometer with Cu Kα radiation, in Bragg-Brentano (B-B) and Grazing Incidence Asymmetric Bragg Diffraction (GIABD) modes. A flat graphite monochromator on the diffracted beam was used.

The SEM analysis (Hitachi S-4100 FESEM, Kyoto, Japan) was performed on a cryo-fractured cross section of the sample. Topographic and density micrographs were taken at 5 and 10 kV in Secondary Electron (SE) and Back Scattered Electron (BSE) modes, respectively. Additionally, Energy Dispersive X-ray (EDX, Oxford Isis 300, UK) point analysis at 10 kV was performed along the deposit thickness. The concentrations of Ca, P and Ti at the HA/TiO_2 interface were evaluated, and a profile of their distribution analysed.

The tensile bond strength of the coatings was measured according to ASTM C633-79, using an Instron 5866 testing machine at a cross-head speed of 0.5mm/min [3]. The coated surfaces were glued with an epoxy resin adhesive (HTK Ultra Bond, Hanseatisches Technologie Kontor GmbH) to a non-coated grit-blasted stainless-steel cylindrical counter body and then heated at 150° for 80min. To improve the contact between the resin and the two surfaces, 0.7MPa compressive stress was applied during the heating. Five specimens of each kind were tested, and the average was evaluated as the bond strength of the deposit.

3. Results and discussion

The XRD patterns of all coatings, registered in the 2θ interval 10-110°, were typical of materials with polycrystalline structures. Qualitative phase analysis revealed that all diffraction peaks in the transition layer corresponded to β-TiO_2, with monoclinic symmetry. The HA top layer was polycrystalline $Ca_5(PO_4)_3(OH)$ with a hexagonal symmetry. In parts of the patterns, presented in Fig. 3a, the HA peaks are marked by the Miller indexes. The observed halo-like part in the 2θ interval 25-35°, with relatively low intensity, shows that besides the predominately polycrystalline structure, a much smaller amount of a disordered amorphous-like phase has been formed, which is in agreement with previous data [4]. The intensity of the halo is higher in the GIABD pattern (Fig. 3b). This indicates that the amorphous-like phase is formed mainly near the top surface of the HA coatings.

In Fig. 4a, a SEM picture of the polycrystalline lamellar structure of the interface HA/TiO_2 is shown. Because of the optimally selected technological conditions, the amount of spherical grains, formed from partially molten particles in the plasma jet, is negligible.

The interface (about 15μm wide) is dense and diffuse in nature, which enables a smooth transition between the TiO_2 and HA layers.

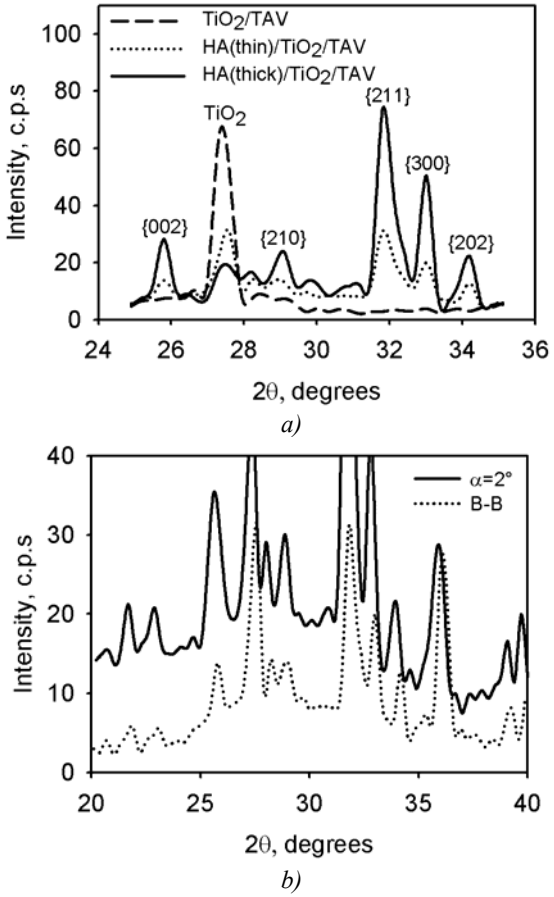

Fig. 3. Experimental XRD patterns registered in B-B mode (a) and a halo-like part registered in B-B and GIABD modes at an incident angle α=2° (b).

The crystallographic texture was characterised via the pole density $P_{\{hkl\}}$, which is proportional to the probability that a particular family of crystallographic planes {hkl} is parallel to the sample surface:

$$P_{\{hkl\}} = \frac{I^{f}_{\{hkl\}} / I^{st}_{\{hkl\}}}{(1/n)\sum_{n}(I^{f}_{\{hkl\}} / I^{st}_{\{hkl\}})} \qquad (1)$$

where $I^{f}_{\{hkl\}}$ and $I^{st}_{\{hkl\}}$ are the intensities of the {hkl} XRD peaks of the HA films and a textureless HA powder standard, registered in B-B mode, and n is the number of the analysed peaks.

From Fig. 5, it is obvious that neither in the thin nor in the thick HA layer was a pronounced crystallographic texture formed.

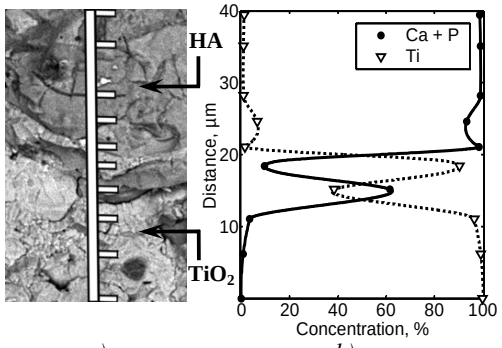

Fig. 4. SEM-BSE fractured cross section picture of the HA/TiO_2 interface (thick deposit), together with the EDX points of measurement (a) and element distribution of Ca, P and Ti along the interface (b).

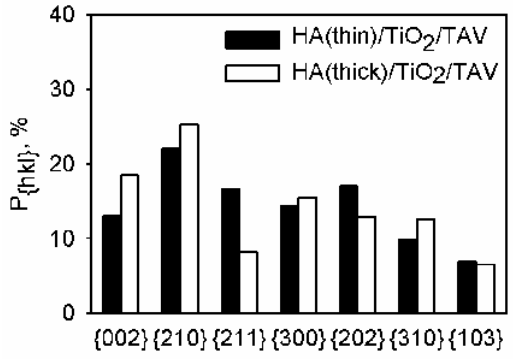

Fig. 5. Histograms representing the share of HA crystallites with {hkl} planes parallel to the top surface.

The residual stresses, acting parallel to the top surface, were analysed via the XRD "$\sin^2\psi$" method [5]. For this purpose, the interplanar spacings of a particular family of {hkl} planes, making different ψ angles with the surface, were evaluated, and the linear dependencies presented in Fig. 6 were plotted. The $d_{\{211\}}$ values were obtained from the Bragg equation, and the centroids 2θ of the {211} XRD peaks were registered in a GIABD mode at different incident α angles (ψ=θ-α). Then, the residual stresses σ were calculated as follows [5]:

$$\sigma = \frac{E}{1+\nu} \cdot \frac{1}{d_0} \cdot \left(\frac{\partial d_\psi}{\partial \sin^2 \psi} \right) \qquad (2)$$

where E and ν the Young's modulus and Poisson's ratio for HA; d_0 and $\frac{\partial d_\psi}{\partial \sin^2 \psi}$ are the intercept on the y-axis and the gradient of the linear plots, respectively.

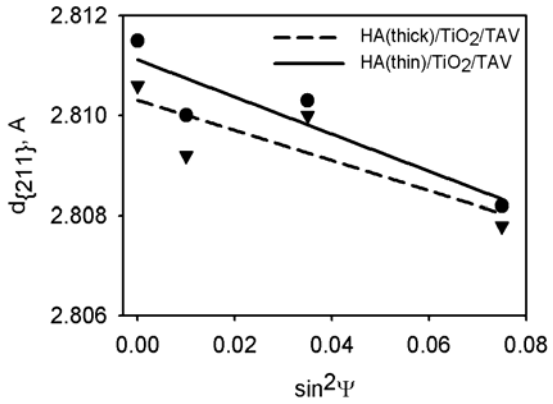

Fig. 6. Linear dependencies $d_{\{211\}}$ versus $\sin^2 \psi$ for both types of sample.

The negative gradients indicate the existence of compressive residual stresses, acting parallel to the surface. Their values in the thin and the thick HA layers are 10 and 7GPa, respectively. These results agree with those observed in similar HA coatings produced by flame spraying [6].

Relatively high, comparable with data [3, 4] values of the tensile bond strength were obtained as follows: 53±10.1MPa for the HA(thin)/TiO_2/TAV and 49±8.3MPa for the HA(thick)/TiO_2/TAV samples.

4. Conclusions

The selected optimal combination of the APS technological conditions allows an efficient and fast application of HA/TiO_2 deposits with a dense and a homogeneous, predominantly polycrystalline, microstructure, without a well pronounced crystallographic texture.

The formed compressive residual stresses in the sprayed HA layers do not cause cracking or depletion of the deposit.

The interface between the HA surface and the underlying TiO_2 layer is dense and smooth. The discussed microstructure parameters of the deposits and interfaces enable a high bond strength between the coating and substrate.

Potentially good properties and sufficient mechanical stability of the HA/TAV implants in the human body are expected.

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