

Hydroxyapatite coatings: a comparative study between plasma-spray and pulsed laser deposition techniques

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A comparative study between hydroxyapatite coatings produced by two different techniques, plasma spray (PS) and pulsed-laser deposition (PLD) was carried out. Plasma spray is currently commercially used for coating dental and orthopaedic implant devices, and pulsed-laser deposition (or laser-ablation deposition) gave good results in the field of high critical temperature superconductive thin films, and is being applied to produce calcium phosphate coatings for biomedical purposes. X-ray diffraction was used to control the crystallinity of the coatings, scanning electron microscopy for the surface and cross-sectional morphology, and the pull test to determine the tensile strength of the coatings. This study reveals that the pulsed-laser deposition technique appears to be a very good candidate to replace the plasma spray in many biomedical applications, because it overcomes most of the drawbacks of the plasma spray.

1. Introduction

Calcium phosphate ceramics, especially hydroxyapatite (HA) are currently used as biomaterials for many applications in both dentistry and orthopaedics, because they form a real bond with the surrounding bone tissue when implanted [1]. Nevertheless, due to the poor mechanical properties of bulk HA ceramics, these cannot be used as implant devices to replace large bony defects or for load-bearing applications [2]. In those cases, titanium-based devices find their field of utilization. For this reason, much effort has been devoted in the last decade, towards the application of HA as a coating on metallic substrates, in order to improve fixation and promote osteointegration of cementless titanium-based implant devices [3].

The plasma-spray (PS) technique is currently the only method commercially available for coating implant devices with HA. But the PS HA coatings, although exhibiting a very good biocompatibility, present some disadvantages affecting the long-term stability of the implant and, therefore, its lifetime. Among these drawbacks, the most significant are the poor coating-substrate adherence (making it necessary to introduce a grit-blasting surface treatment prior to the coating procedure, in order to guarantee a minimum adhesion of the coating) and the lack of uniformity of the coating from two

different points of view: morphology and crystallinity [4–8].

Because of these drawbacks, several techniques have been proposed to apply HA as a coating on metallic substrates, such as the magnetron sputtering deposition [9], ion-beam deposition [10], electrophoretic deposition [11] and pulsed-laser deposition technique (PLD) [12–15]. In this context, the PLD technique appears to be the most promising one, because it allows the intrinsic disadvantages of the PS technique to be overcome.

In this paper we present a comparative study between PS and PLD techniques, from the point of view of the morphology and its implications in the mechanical properties of the coatings.

2. Materials and methods

2.1. PS coatings

High quality commercially PS-coated titanium plates of $52 \times 54 \text{ mm}^2$ and 1.5 mm thick were supplied by Plasma Biotall Ltd, UK. The complete procedure included degreasing, and grit blasting with alumina powder (14 μm) before applying the coating.

The HA powder used to produce the PS coatings was of the same batch as the HA used to obtain the PLD coatings.

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2.2. PLD coatings

The PLD coating system consists basically in a vacuum chamber [16], evacuated up to 10^{-6} mbar, then filled with water vapour up to the working pressure (0.45 mbar). This pressure was maintained by a control needle valve and a rotary pump. The laser beam (ArF, $\lambda = 193$ nm), working at a repetition rate of 20 Hz, was focused on to a HA pellet, achieving an energy density of 0.8 mJ cm^{-2} . The substrate (titanium plates of the same dimensions as those coated by PS), placed at 5 cm from the HA target in front of it, was kept at 455°C during the deposition by means of a halogen quartz lamp heater. The complete procedure also included substrate cleaning by acetone degreasing and surface passivation with nitric acid in aqueous solution in an ultrasonic bath at room temperature.

2.3. Structural and morphological characterization

In order to check the quality of the coatings from the point of view of their crystalline structure, X-ray diffraction (XRD) measurements have been performed, using a Siemens D5000 diffractometer, at 40 kV and 30 mA, in the standard θ - 2θ configuration.

Surface examination of the coatings was carried out by scanning electron microscopy (SEM), in a Philips XL30 series microscope equipped with an EDAX energy dispersive X-ray spectroscopy (EDS) device. The samples were gold coated before their SEM observation in order to increase their electrical conductivity, leading to a reduced noise level and enhanced image contrast.

To perform cross-sectional observations, the samples were embedded in Acryfix acrylic resin. They were then polished with a series of water-lubricated SiC papers up to grade 1000, followed by diamond paste finish, up to $1 \mu\text{m}$ size. After this preparation, the samples were gold coated and examined by SEM, as in the case of the surface observation.

2.4. Mechanical testing

The coating-to-substrate adhesion was determined by measuring its tensile strength by the pull test, following a modified ASTM C633 procedure. Three specimens were used to calculate the bond strength of each type of coating. Fig. 1 represents schematically the procedure followed to perform these measurements: the facings of the stainless steel rods used as probes were sand blasted in order to increase their bond strength to the adhesive. The titanium-coated plates were placed between two of these rods, then heat treated at 300°C for 1 h to cure the epoxy. The prepared samples were placed in an Instron machine and tensile loaded until failure occurred.

3. Results and discussion

XRD spectra of the two studied types of HA coatings (PS and PLD) are of good quality, HA being the

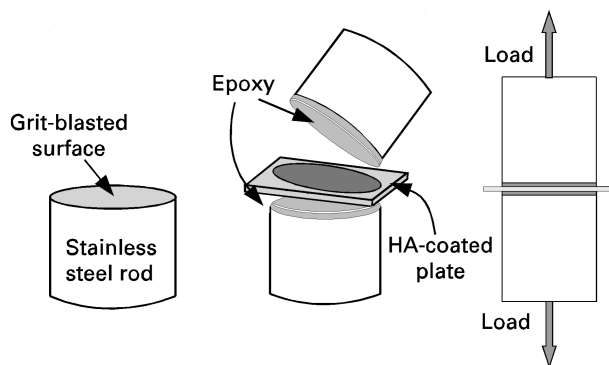


Figure 1 Schematic diagram of the modified ASTM-C633 procedure followed for the tensile strength evaluation.

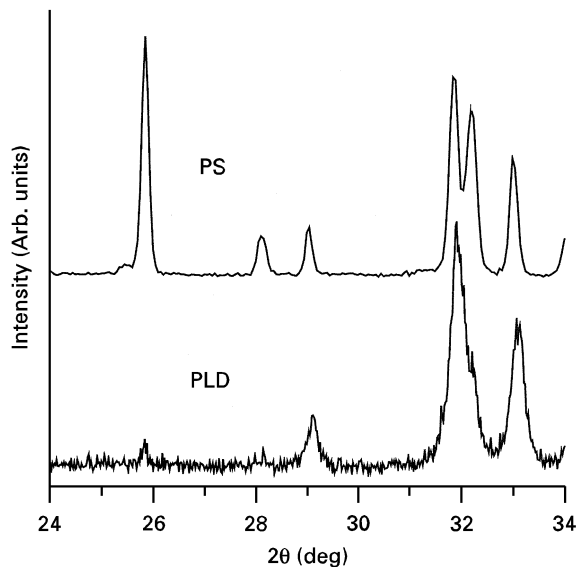


Figure 2 XRD spectra of a PS and a PLD-HA coatings (not to the same scale). The only phase detected in both cases is HA. The PS coating presents a typical crystalline (002) orientation.

only crystalline phase detected. In the case of the PS, a typical crystalline (002) orientation is observed (see Fig. 2).

3.1. Surface observations

Fig. 3 shows the surface morphology of a HA coating produced by the PS technique, revealing that the coating is basically formed by the superposition of partially molten HA particles, leading to the typical splat-shaped structure [17]. These splats measure around $50 \mu\text{m}$ and leave abundant interconnecting porosity in between them. The size of the pores is approximately between 10 and $20 \mu\text{m}$. One other noticeable fact is the presence of cracks, $1 \mu\text{m}$ thick, along the coating surface, which could be attributed to the thermal shock which occurred during the deposition of the coating, when the molten HA particles reach the titanium surface, which is kept at lower temperatures, in order to protect it from oxidation and/or phase transformations.

The severe grit blasting which is necessarily applied to the metallic substrates before the PS coating procedure in order to increase their surface and provide

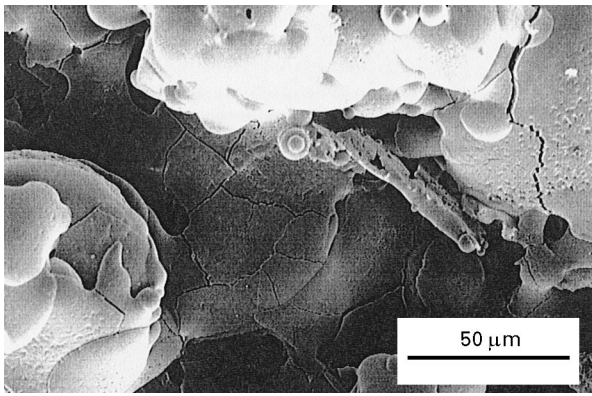


Figure 3 Scanning electron micrograph of the surface of a HA coating produced by PS, showing the typical splat-shaped structure, with interconnecting porosity and microcracks.

them with points of mechanical anchorage for the deposited layer, also contributes to the inhomogeneous appearance of this kind of coatings. Without this surface preparation, the HA PS coating does not remain attached to the substrate, but it falls off in the form of powder.

This typical structure of the HA coatings produced by the PS method, although it could, in principle, promote a better fixation of the implant device by bone ingrowth into the porosity, has been reported to be one of the main reasons for the poor mechanical properties of this kind of coatings [18].

Fig. 4 shows the surface morphology of a HA coating produced by the PLD technique. This surface morphology is totally different from those previously described for the PS coatings. The appearance is quite smooth, and the surface topography of the titanium substrate can be clearly distinguished.

A certain fine structure, noticeable in Fig. 4, is present in the coating. Higher magnifications reveal that, in fact, the coating is formed by a network of superimposed fine polygonal HA crystallites varying in size from 100–500 nm, as can be observed in Fig. 5.

3.2. Cross-sectional observations

The microscopic examination of the surface of the coatings in this study allows an overview of the possible implications of the morphology in the mechanical properties of the coatings. However, the picture would not be completed without an inspection of the cross-section of the coatings, which can provide information directly related to their bond strength performance.

Fig. 6a shows the cross-section of a HA coating produced by PS. The inhomogeneous morphology seen in the surface observation is also reflected in the cross-section. As can be seen in this scanning electron micrograph, the cracks appear not only at the surface level, but penetrate the coating, even reaching the titanium substrate. This micrograph also reveals the presence of a large crack along the coating–substrate interface. This fact explains the need of a grit-blasting step before the PS coating process, and the reason for the poor bond strength shown by the PS coatings: the

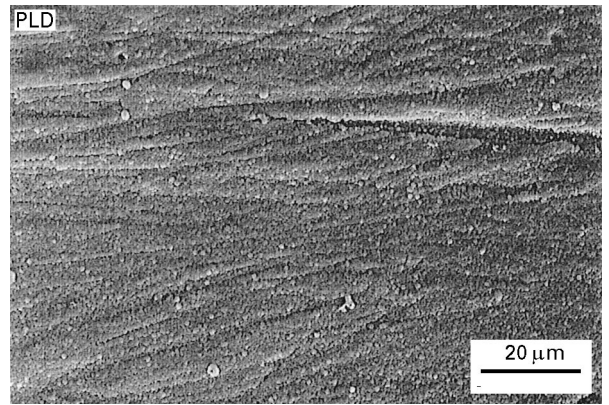


Figure 4 Low-magnification scanning electron micrograph of a PLD-HA coating surface. The surface topography of the titanium substrate can be easily distinguished.

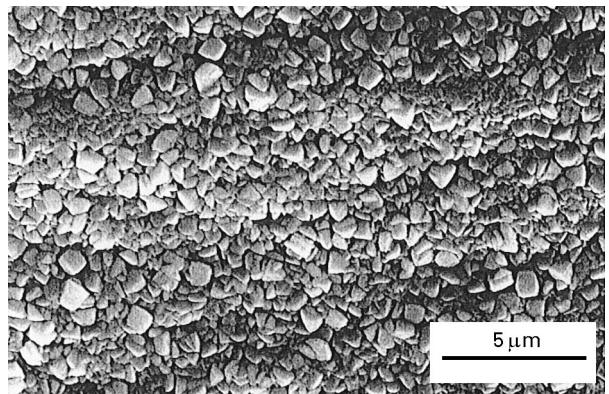


Figure 5 Higher magnification of Fig. 4, revealing that the coating is formed by a network of polygonal-shaped HA crystallites.

PS coating is not really adherent to the substrate; in fact, it is only mechanically anchored to the inhomogeneities introduced in the titanium by the grit blasting. Fig. 6b corresponds to an EDS colour mapping at the same magnification. Two important facts can be reported from this picture.

(i) Some alumina grains (black in the figure), coming from the grit blasting, remained embedded in the titanium substrate. It has been reported that an excess of aluminium in contact with bone could inhibit the osteogenic activity of the osteoblast cells [19]. Therefore, the presence of remaining grains of alumina is not advisable for implant devices that base their fixation in the bone ingrowth into their surface irregularities, because this bone ingrowth could be negatively affected by the aluminium ions released to the physiological medium.

(ii) The resin employed in the sample preparation (green in the picture) penetrates through the coating, reaching the substrate. This fact is very important, because if the resin reaches the substrate and remains bonded to it, in the same way, the adhesives habitually used for the tensile bond strength measurements of this kind of coating could lead to greatly incorrect results, because the measurement would no longer be of the adhesion coating–substrate, but epoxy–substrate [17].

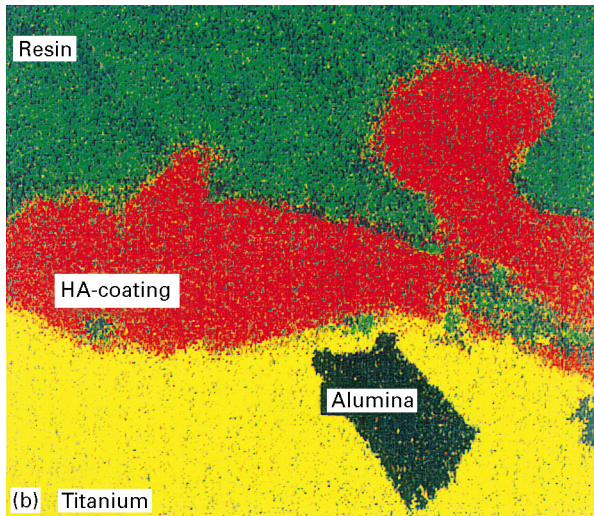
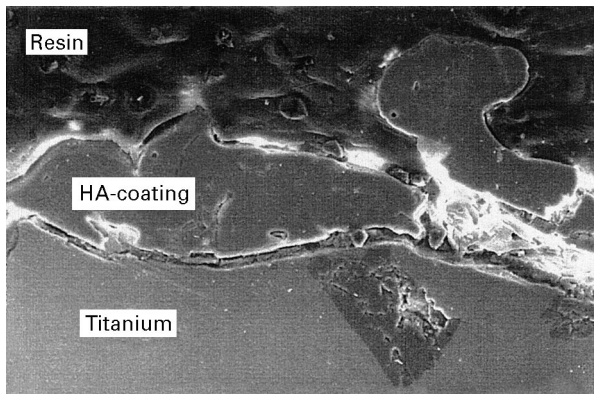


Figure 6 (a) Cross-sectional view of a PS-HA coating, revealing the presence of microcracks penetrating the coating surface, and even reaching the substrate. A large crack along the coating–substrate interface can be clearly appreciated. (b) EDS colour mapping of the same area (C, green; Ca, red; Ti, yellow; Al, black).

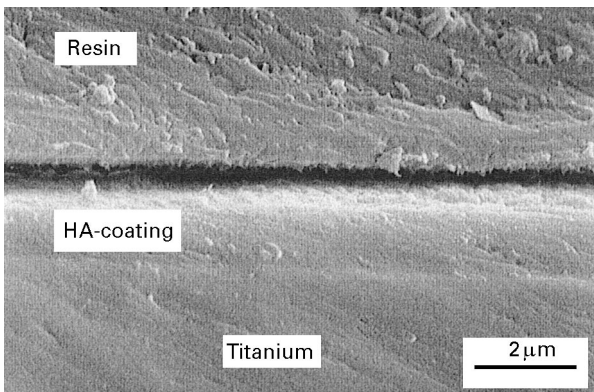


Figure 7 Scanning electron micrograph of the cross-section of a PLD-HA coating, showing the good adherence between coating and substrate. The sample preparation does not allow the cross-sectional structure of the coating to be distinguished.

The cross-section of a PLD coating is shown in Fig. 7. The coating is dense and homogeneous, and no cracks can be detected along it. The acrylic resin used in the metallographic-like sample preparation is slightly separated from the surface of the coating, allowing the surface microstructure of the HA coating described in Figs 4 and 5 to be seen. The detachment of the resin is due to its shrinkage, produced by the effect of the electron beam during the SEM

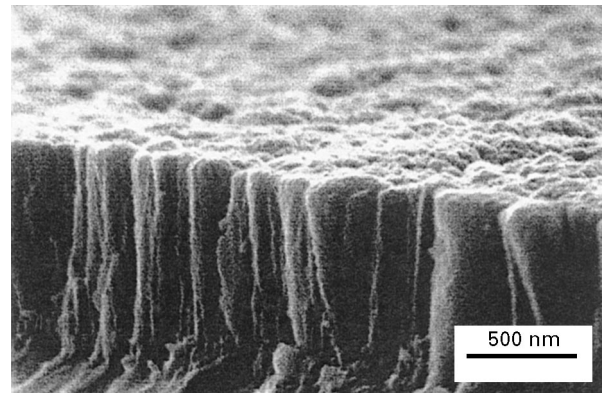


Figure 8 Fracture surface of a PLD-HA coated silicon wafer, showing the cross-sectional columnar structure of the PLD coatings.

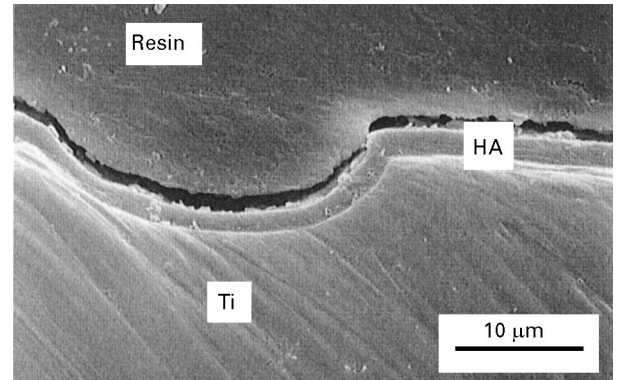


Figure 9 Cross-sectional view of a PLD-HA coated textured titanium rod: the substrate surface texture is perfectly followed by the coating, without cracks or spallations.

observation. In spite of this resin shrinkage, the coating remained firmly attached to the titanium substrate, without any evidence of spallation. This fact constitutes evidence of the good adhesion between coating and substrate. In this figure the metallographic preparation of the sample does not allow any cross-sectional structure of the PLD coatings to be discerned. This structure can, nevertheless, be seen in Fig. 8. This scanning electron micrograph corresponds to the fracture surface of a HA coating produced by PLD on a silicon wafer with this purpose, under the same conditions as those deposited on titanium. In this figure it can be seen that the coating grows in the form of overlapped columns which are firmly anchored to the substrate.

Fig. 9 shows the excellent possibilities offered by the PLD technique when a homogeneous coating on micro-textured surfaces is required. This micrograph corresponds to the cross-sectional view of a titanium cylinder coated by PLD with HA. The surface texture is perfectly followed by the coating without cracks or spallations. This fact constitutes one of the main performances of the technique, establishing capital differences between the PLD and the PS techniques.

3.3. Mechanical evaluation

The results of the pull test applied to the coatings confirm the SEM observations. For the PLD coatings,

the tensile strength values obtained were higher than 58 MPa, being the fracture at the adhesive in all cases, without spallation of the coating. This is a very good result, considering the fact that the titanium substrates were not grit blasted, and therefore, the surface in contact with the adhesive was notably lower than the surfaces employed in the PS coatings. The values obtained must be normalized to be able to establish direct comparisons with those reported for the PS.

4. Conclusions

A comparative study was performed between HA coatings produced by two different techniques, the plasma spray (PS), currently commercially used for the coating of orthopaedical and dental implant devices, and the pulsed-laser deposition (PLD), still under investigation but with enormous possibilities to overcome the drawbacks of the PS.

The differences detected between the two types of coatings emanate from the fact that they correspond to two different coating philosophies, and the results must therefore be different. Nevertheless, some points should be considered, and can be summarized as follows:

1. The PS technique produces HA coatings which are thick, brittle and inhomogeneous, resulting in the poor mechanical strength values reported in the literature.
2. The PLD technique allows the deficiencies detected for the PS to be overcome, and appears to be a good candidate to replace it in the near future in many biomedical applications. This technique allows well-adhered thin and homogeneous coatings to be obtained, without the brittleness of those produced by PS.

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