JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE, 5 (1994) 855–857

Post-deposition treatment effects on hydroxyapatite vacuum plasma spray coatings

F. BROSSA
Institute for Advanced Materials, Joint Research Centre, Ispra (VA), Italy
A. CIGADA, R. CHIESA, L. PARACCHINI, C. CONSONNI
Dip. Chimica Fisica Applicata, Politecnico di Milano, Italy

The purpose of this work is to evaluate the effects of post-deposition heat treatments on high and low crystallinity hydroxyapatite coatings on Ti6Al4V alloy. HA layers were produced by the vacuum plasma spray (VPS) technique, and the desired degrees of crystallinity were obtained by changing the deposition parameters. An analysis of the mechanical properties of the coatings and their adhesion to the substrate has been done by shear strength test. X-ray diffraction analysis was used to detect the structure and the chemical components in which HA dissociates during the deposition process and heat treatments. The data obtained indicates that heat treatments can increase the crystallinity of HA, but they also introduce a mechanical degradation of the coatings. After heat treatments, it was also observed that a large amount of tetracalcium phosphate was formed.

1. Introduction

In the non-cemented femoral prosthesis, hydroxyapatite [HA, $Ca_{10}(PO_4)_6OH_2$] coatings are currently widely used. This kind of prosthesis, if properly manufactured, permits a strong and durable joint of the prosthesis stem to the bone [1]. Biological data indicates that in living tissues low-crystallinity hydroxyapatite coatings have a greater dissolution rate than those with high crystallinity. Consequently, the crystallinity of HA coatings is a very important factor that has a great influence on the biological system of bone-to-metal prosthesis bonding [2]. In the HA-coated prosthesis on a sand-blasted metallic substrate, a high degree of crystallinity is generally required while lower crystallinity is preferable for HA coatings deposited on porous metallic interlayers. It has been noted that the degree of crystallinity of the HA coatings is related to their adhesion on the substrate: higher crystallinity generally being associated with lower mechanical strength [3]. This work considers the effects of heat treatments on the adhesion properties of both high- and low-crystallinity HA coatings.

2. Materials and methods

HA coatings on Ti6Al4V alloy, were produced by the vacuum plasma spray technique (VPS): this technique, in comparison with air plasma spray (APS), offers higher coating quality and the possibility of operating effectively in the desired crystallinity range [4, 5]. For the mechanical testing of the adhesion of the HA coating on the metallic substrate, cylindrical samples (diameter 15 mm and width 40 mm) coated with HA along half their length were prepared. The structural analysis was done, using optical and electronic microscopy, on samples prepared by traditional metallographic techniques. Chemical and crystallographic analysis were carried out by the X-ray diffraction technique on metal sheets (20 × 40 × 1 mm). For each set of deposition conditions, five cylindrical samples and one sheet were coated. Two samples were tested without other treatments, while the remaining three samples were heat treated before the adhesion test.

The adhesion was determined by measuring the value of the shear strength of the coating on the substrate. The test consisted of a shear stress test on a cylindrical sample in which the lateral surface (20 mm in width) was joined to an AISI 316 counter sample (Fig. 1) using a high resistance adhesive (type 3M 2214).

The sheets for X-ray analysis were cut into two pieces (1 × 20 × 20 mm); one part was heat treated along with the three cylindrical samples. Using this technique it was possible to evaluate the effect of the heat treatment on the crystallinity by direct comparison with the untreated samples.

The heat treatments considered were:

- 950 °C – 1 h, 1.33×10^{-4} Pa
- 950 °C – 12 h, 1.33×10^{-4} Pa
- 950 °C – 24 h, 1.33×10^{-4} Pa

Heating and cooling rates of 6 °C/min were used. The influence of the heat treatment was evaluated for both high-crystallinity and low-crystallinity HA coatings.

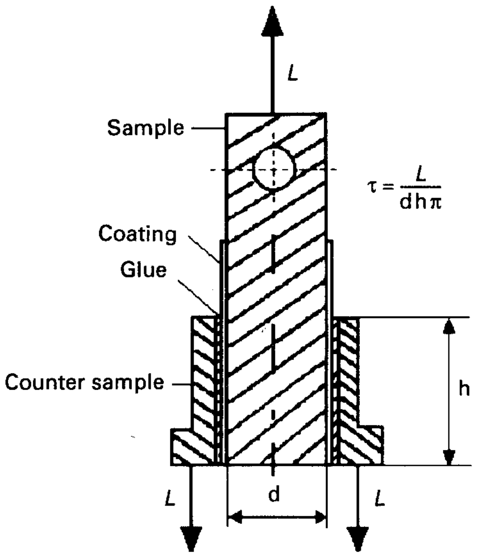

Figure 1 Sample used for mechanical testing: $d = 15$ mm, $h = 20$ mm.

3. Discussion

The VPS process, and the heat treatment always introduce the same changes in composition and structure of the original HA [6, 7]. In particular, the VPS process lowers the crystallinity and partially decomposes HA into β-tricalcium phosphate (β-TCP, β-$Ca_3(PO_4)_2$) and lime (CaO). The post-deposition heat treatments increase crystallinity and decompose a large amount of HA into tetracalcium phosphate [$Ca_4O(PO_4)_2$] (Figs 2, 3, and 4) [8].

From the data analysis (Table I) it was observed that:

- For the shear test on non-heat-treated coatings, the strength decreased from a maximum (38.1 ± 0.8 MPa) for the low-crystallinity coatings to a minimum (28.9 ± 3.1 MPa) for the high-crystallinity coatings.
- Heat treatments increased the crystallinity of HA coatings with some modification of the structure: X-ray diffraction indicates that a significant quantity of tetracalcium phosphate was formed, while the crystallinity values were similar to the values of the non-heat-treated high crystallinity coatings (Figs 2, 3, 4);
- Heat treatments caused a decrease in the shear strength of both low-crystallinity coatings (950 °C – 1 h, 28.8 ± 2.7 MPa; 12 h, 31.2 ± 2.7 MPa; 24 h 23.0 ± 1.8 MPa) and high-crystallinity coatings (950 °C – 1 h, 23.1 ± 3.8 MPa; 12 h, 23.6 ± 5.6

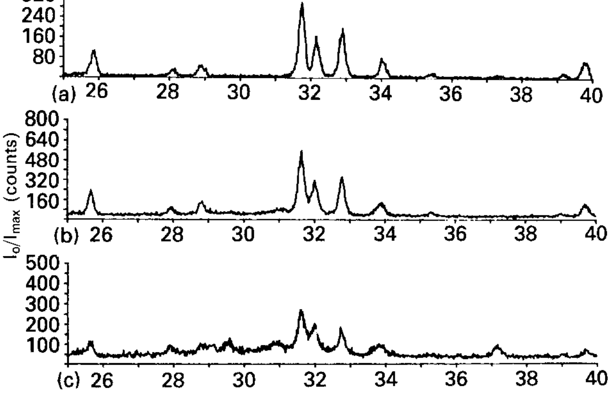

Figure 2 (a) Diffractogram of HA powder; (b) high-crystallinity HA coating as sprayed; (c) low-crystallinity HA coating as sprayed.

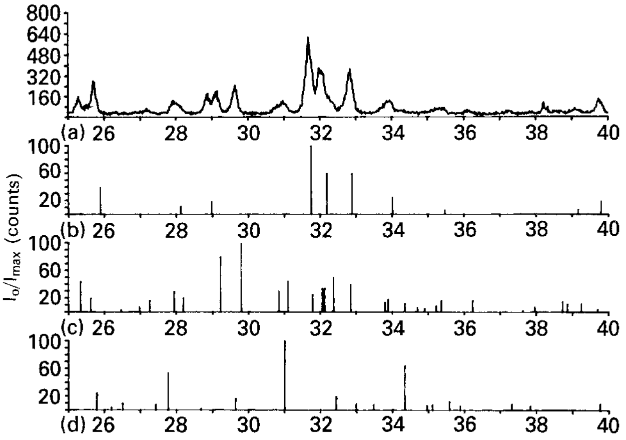

Figure 3 Diffractogram of (a) heat-treated (950 °C – 12 h, 1.33 × 10^{-4} Pa vacuum) low-crystallinity HA coatings with the reference patterns of (b) Ha (JCPDS 9-432), (c) tetracalcium phosphate (JCPDS 25-1137) and (d) β-tricalcium phosphate (JCPDS 9-169): note the presence of the JCPDS 25-1137 peaks.

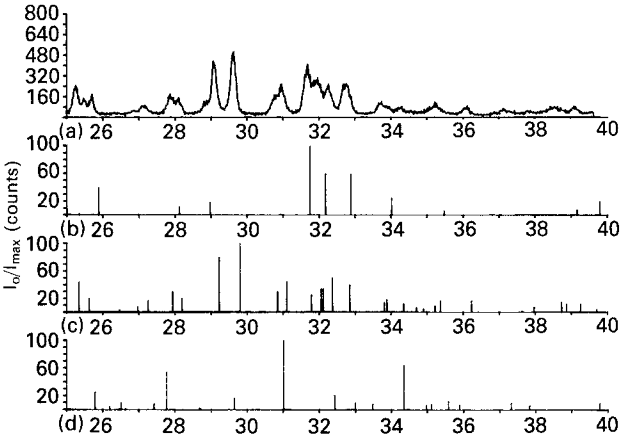

Figure 4 Diffractogram of (a) heat-treated (950 °C – 12 h, 1.33 × 10^{-4} Pa vacuum) high-crystallinity HA coatings with the reference patterns of (b) Ha (JCPDS 9-432), (c) tetracalcium phosphate (JCPDS 25-1137) and (d) β-TCP (JCPDS 9-169).

TABLE I Mechanical testing data

Heat treatment	Crystallinity (before heat treatment)	Adhesion (MPa)
no	high	28.9 ± 3.1
no	low	38.1 ± 0.8
1 h – 950 °C	high	23.1 ± 3.8
1 h – 950 °C	low	28.8 ± 2.7
12 h – 950 °C	high	23.6 ± 5.6
12 h – 950 °C	low	31.2 ± 2.7
24 h – 950 °C	high	20.9 ± 1.6
24 h – 950 °C	low	23.0 ± 1.8

MPa; 24 h, 20.9 ± 1.6 MPa); this decrease becomes more evident with increasing time of treatment. This phenomena could be caused by different mechanisms: the different thermal expansion coefficients of the titanium alloy and of hydroxyapatite, the sudden change of volume of the alloy at the $\alpha \rightarrow \beta$ transition temperature, and probably a progressive oxidation of the metallic substrate caused by traces of oxygen. The adhesion of high crystallinity HA non-heat-treated coatings is however better (35.7 ± 1.2 MPa) than that of the low-crystallinity HA coatings which have been heat-treated to increase the crystallinity (31.2 ± 2.7 MPa).

4. Conclusions

It seems that high-temperature heat treatments are not particularly useful. For both high- and low-crystallinity coatings, the adhesion of untreated VPS coatings is always better than that of the coated and heat-treated deposits. Heat treatments of high crystallinity coatings only introduce undesired new chemical components, and are of no value.

Heat treatment may be useful only in the case where it is not possible to manufacture high-crystallinity coatings (for example with the APS technique): in this case high-crystallinity coatings can be obtained, but with a decrease in the mechanical properties, and with the unexpected formation of tetracalcium phosphate.

References

1. L. L HENCH, *J. Amer. Ceram. Soc.* **74** (1991) 1487.
2. P. FRAYSSINET, F. TOURENNE, N. ROUQUET, G. BONEL and B. GIAMMARA, in Proceedings of the International Thermal Spray Conference & Exposition, Orlando, Fl, USA, 1992, p. 477.
3. F. BROSSA, A. CIGADA, R. CHIESA, L. PARACCHINI and C. CONSONNI, *Biomed. Mater. Engng* **3** (1993) 127.
4. J. G. C. WOLKE, W. J. A. DHERT, C. P. A. T. KLEIN, K. DE GROOT and J. M. A. DE BLIECK-HOGERVOST, Proceedings of the International Thermal Spray Conference & Exposition, Orlando, Fl, USA, 1992, p. 471.
5. M. S. BLOCK, J. N. KENT and J. F. KAY, *J. Oral. Maxillofac. Surg.* **45** (1987) 601.
6. H. GRÜTZER, in Second Plasma-Technik Symposium, edited by H. Eschnauer, P. Huber and A. R. Nicoll, Wohlen, Switzerland, 1988. Plasma-Technik AG, **3** p. 351.
7. C. C. BERNDT and K. A. GROSS, in Proceedings of International Thermal Spray Conference & Exposition, Orlando, Fl, USA, 1992, p. 465.
8. M. J. FILIAGGI, R. M. PILLIAR and N. A. COOMBS, *J. Biomed. Mater. Res.* **7** (1993) 191.