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Characteristics of Plasma Sprayed Hydroxyapatite Bio-Coatings

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Abstract. Hydroxyapatite (HAp) coated implants are widely used in the medical area and in dentistry. HAp is well known as a bio-active material as it does not provoke adverse reactions in the host body, and on the positive side promotes chemical reactions with the bone tissue close to the implant. HAp coatings produced by plasma spraying on titanium surfaces have been widely investigated. In this study, a Miller SG-100 plasma gun with argon gas to form the arc and helium gas to sustain the arc were used. The HAp powder was prepared by the neutralization method, wherein a phosphoric acid solution was slowly added to a calcium hydroxide suspension. HAp coatings on titanium substrates, with and without an alumina bond coat, also deposited by plasma spraying have been compared. The powders and the coating surfaces have been characterized in terms of particle size distribution and surface roughness and also by scanning electron microscopy and x-ray diffractometry. Crystalline HAp was detected as the main phase in the coatings obtained under different conditions.

Introduction

Synthetic hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$, exhibits great potential for applications in the fields of medicine and dentistry, because of its similarity with the mineral phase of bone tissues. This permits HAp to be used in bone reconstruction. HAp belongs to a group of materials known as "bio-actives" [1,2]. Bio-active materials do not provoke toxic or adverse reactions with tissues surrounding the implant. These materials are divided into two groups, one that reabsorb and those that are surface active. HAp belongs to the second group because of its ability to form chemical bonds with live bone tissue, promoting thereby, bone integration by osteogenetic bonding. Their use in the orthopedic field is however limited, due to their low tensile strength. One of the ways of overcoming this lack of strength is to coat metallic prosthesis with a fine layer of HAp [3,4].

HAp coatings on metallic implants is considered to be one of the best ways to create bio-active bonds in implants, aiding the joining and fixing process. HAp coatings increase the rate of fixing of implants to bone, by bone integration [4].

Among the various coating techniques, plasma spraying is used more often to deposit HAp on metallic substrates. Titanium based alloys such as Ti-6Al-4V are best suited as metallic substrates. This alloy seems to be the most suitable in terms of mechanical properties and bio-corrosion resistance [5,6]. In this investigation, HAp powder was prepared by the neutralization method and deposited on Ti-6Al-4V alloy by plasma spraying.

Experimental procedure

HAp was obtained by slow addition of 0.3M phosphoric acid solution (H_3PO_4) to an aqueous suspension of 0.1M calcium hydroxide ($Ca(OH)_2$). The experiment was carried out in an inert

nitrogen atmosphere and the precipitate was aged for 20 days. The product thus obtained was calcined at 1000°C for 3 hours. Commercial grade alumina (Brodmann Inc., Harvey, L.A.) was used in the as-received condition.

The dimensions of the Ti-6Al-4V alloy substrate were 40x25x3mm. To increase substrate surface roughness, they were grit blasted with alpha alumina particles. After grit blasting, the substrates were ultrasonically cleaned in acetone to remove loose alumina particles. Subsequently, the Ti alloy substrates were preheated to 100°C with the plasma spray gun itself. This preheating improves the adhesion of the coating to the substrate by decreasing thermal shock between the HAp particles and the substrate. It also aids in surface cleaning and mechanical keying of the deposit to the substrate.

During deposition the temperature of the substrate was controlled with an optical pyrometer and it did not exceed 500°C. After the deposition, the substrate/coating system was allowed to cool naturally to room temperature. The specimens were then heat treated at 500°C for 3 hours. The experimental conditions are summarized in Table 1.

Table 1. Plasma spraying parameters used to obtain HAp coatings.

Spray gun	Plasma Miller –SG 100
Power level/ Arc voltage /Arc current	32 kW/ 40 V/ 800 A
Primary gas	Ar
Pressure	50 psi
Flow	20 L/min
Secondary gas	He
Pressure	110 psi
Flow	44 L/min
Carrier gas	Ar
Pressure	35 psi
Flow	4.7 L/min
Spray distance	7.0-7.5 cm

Results and discussion

X-ray diffraction analysis of the prepared and calcined (1000°C / 3h) powder revealed mainly, the presence of a crystalline phase of HAp. (Fig. 1-a). The as-received alumina from Brodmann Inc. showed alpha-alumina to be the main phase, besides some trace impurities. (Fig.1-b).

The micrographs of the powders are shown in Fig. 2. The HAp powder consists of agglomerates of small particles. (Fig.3).

Grain size analysis of the prepared HAp powder revealed average particle/agglomerate size to be around 30 μm. The average grain size of the as-received alumina was about 46 μm.

The roughness (Ra) of the substrates after grit blasting was measured in a perfilometer and found to be around 4.5 μm. The HAp coated substrates showed roughness values of 67 μm and those coated with HAp and an alumina bond layer, 60 μm. The alumina coated substrates showed roughness values of about 45 μm.

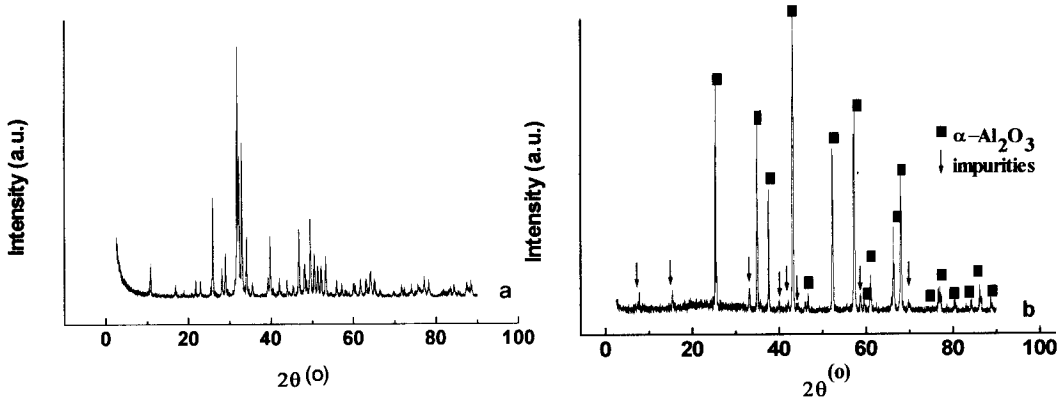

Fig.1. X-ray diffractograms. (a) HAp powder calcined at 1000°C for 3 hours, only hydroxyapatite phase. (b) As- received alumina powder.

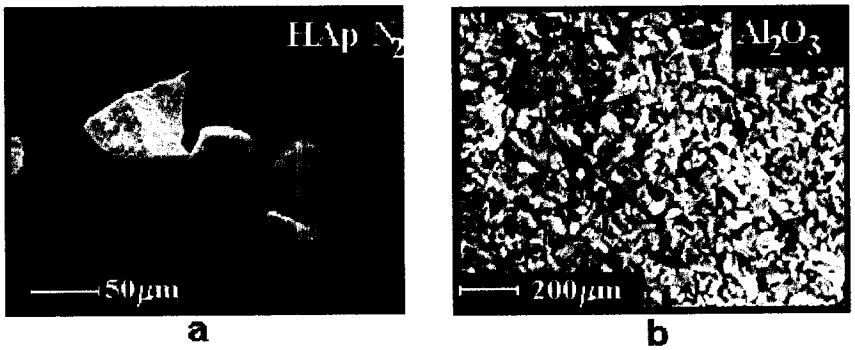

Fig. 2. Micrographs of powders of (a) HAp powder calcined at 1000°C for 3 hours. (b) as-received alumina powder

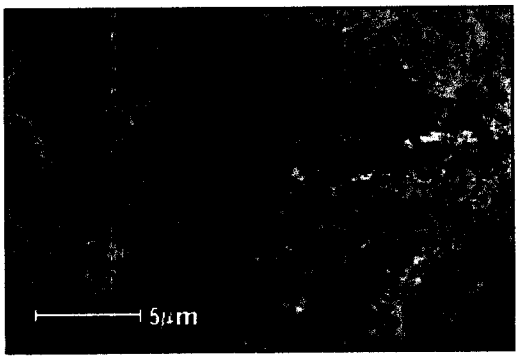

Fig. 3. Powder agglomerates of HAp calcined at 1000°C for 3 hours.

The high temperatures involved in plasma spraying can induce changes in the original HAp, giving rise to coatings with different properties. The HAp melts partially with consequent phase transformation and this was confirmed by x-ray diffraction measurements. Fig. 4a presents HAp as the main phase and small quantities of a secondary phase, beta tricalcium phosphate, $Ca_3(PO_4)_2$, (β-TCP) and calcium oxide.

The alumina powder which presented the alpha phase as the main constituent underwent phase transformation during plasma deposition and showed predominant gamma phase and small peaks of alpha. (Fig. 4-b). The alpha to gamma phase transformation is well known and is related to the rapid cooling of alumina during the plasma spraying process.

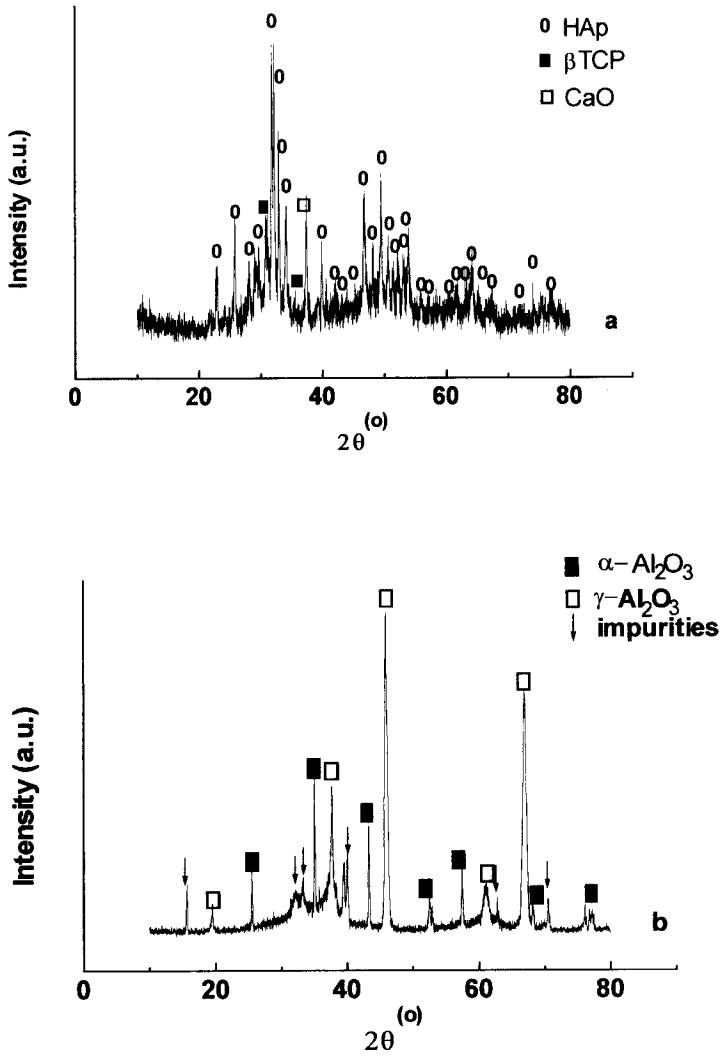

Fig. 4. X-ray diffraction spectra of coated substrates and after heat treatment at 500°C for 3 hours. (a) HAp. (b) Alumina.

Fig. 5 shows the micrographs of the plasma spray coated substrate. Coatings obtained under different conditions revealed small particle splats, pores and cracks. This type of microstructure is characteristic of coatings obtained by plasma spraying. The cracks seen on the surface are due to differences in the coefficients of thermal expansion between the coating and the substrate. The coating/substrate interface does not reveal cracks (as can be seen in the micrographs of cross sections in Fig. 6), indicating good adhesion of the coating.

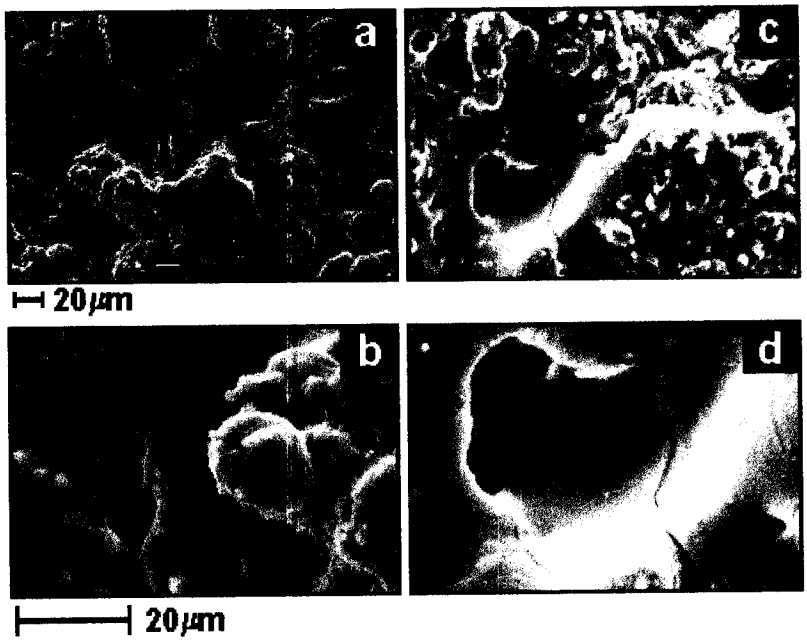

Fig 5. Plasma sprayed coating surfaces after heat treatment at 500°C for 3 hours. (a, b) HAp (c, d) Alumina + HAp.

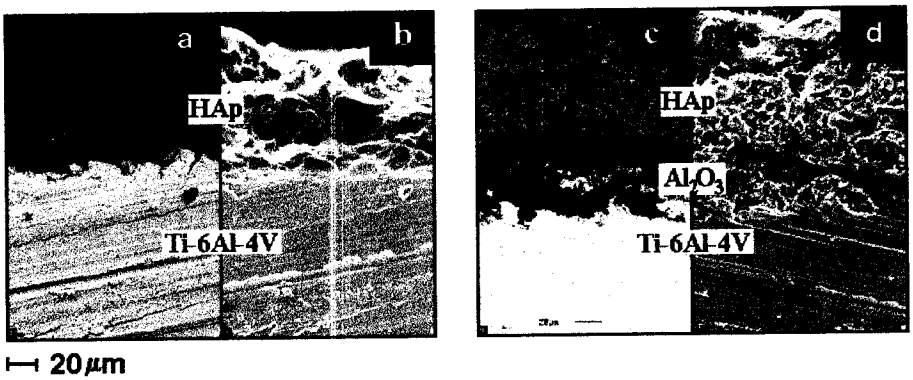

Fig. 6. Micrographs of interfaces Ti-6Al-4V substrate/ HAp coating; (a) BSE, (b) SE; alloy/ Al_2O_3 + HAp (c) BSE and (d) SE

Conclusions

HAp synthesized by the neutralization method in an inert atmosphere was found to be stable at high temperature. The phases, β-TCP and γ-Al_2O_3 formed during the thermal spraying process and were due to the high temperatures followed by rapid cooling. Cracks were found in regions close to the surface and probably occurred due to tensile stresses generated during cooling.

Acknowledgements

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References

[1] T.S.B. Narasaraju, D.E. Phebe, J. Mat. Sci., 31 (1996) p. 1-21.
[2] M.B.El-Kholy, A.A. Khalil, A. M. Hashem Interceram., 47 (1998) p.29-32.
[3] H. Kurzweg, R. B. Heimann, T. Troczynski, J. Mat. Sci.- Mat. in Medicine, 9 (1998) p.9-16.
[4] V. Palka, J. Ivan, E. Postrkova, V. Kolenciak, A Krsek, I. Nfner, H. K. Koerten, J. Mat. Sci.-Mat. in Medicine, 9 (1998) p.369-373.
[5] C.Sittig, M. Textor, N.D. Spencer, M Wieland, P.H. Vallotton, J. Mat. Sci.- Mat. in Medicine, 9 (1999) p.35-46.
[6] B.C. Wang, E.C. Hang, C.Y. Yang, D. Tu, J. Mat. Sci.- Mat. in Medicine, 4 (1993) p.394-403.

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