JTTEE5 17:679–684
DOI: 10.1007/s11666-008-9220-2
1059-9630/$19.00 © ASM International

Peer Reviewed

Synthesis and Preliminary Tests of Suspension Plasma Spraying of Fine Hydroxyapatite Powder

Roman Jaworski, Christel Pierlot, Lech Pawlowski, Muriel Bigan, and Maxime Quivrin

(Submitted April 30, 2008; in revised form September 8, 2008)

The synthetic hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) is a very useful biomaterial for numerous applications in medicine, such as e.g., fine powder for suspension plasma spraying. The powder was synthesized using aqueous solution of ammonium phosphate ($H_2(PO_4)NH_4$) and calcium nitrate ($Ca(NO_3) \cdot 4H_2O$) in the carefully controlled experiments. The synthesized fine powder was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The powder was formulated into water and alcohol based suspension and used to carry out the initial tests of plasma spraying onto titanium substrate. The phase analysis of sprayed coating was made with the XRD.

Keywords biomedical coatings, hydroxyapatite, powder manufacturing, suspension plasma spraying

1. Introduction

Suspension plasma spraying is a new coating technique which enables obtaining relatively thin and finely structured coatings by the use of water (alcohol) based suspension of fine powders (Ref 1). The technique was reviewed recently (Ref 2) and can be used to obtain relatively thin ceramic coatings of TiO_2 (Ref 3, 4), yttria-stabilized zirconia (Ref 5), and hydroxyapatite (Ref 6-8). The latter is a bioceramic material used intensively as a plasma-sprayed coating material to promote osseointegration of the femoral stems (Ref 9, 10). Initial studies of suspension plasma sprayed HA made by our research group have been made by the use of commercial spray-dried powder (Ref 8). The powder crushed using a milling machine with zirconia balls. The present paper shows the way of synthesis of 600 g of HA starting from pure calcium nitrate and diammonium phosphate. The synthesis of HA by wet chemistry is well described in the literature and the reaction starting from phosphoric acid and calcium hydroxide were reported (Ref 6, 11). The present paper was inspired by the study of Hornez et al. (Ref 12). The synthesis was optimized in order to increase the productivity of the reaction by modifying concentration of calcium and phosphorus and volume the ammonium hydroxide in the reactor, and keeping under control the by-products of the reactions. The product of the reaction was subsequently calcined and crushed. The resulting fine powder was used to formulate water-based suspension and to carry out the initial test of plasma spraying.

2. Experimental Methods

2.1 Synthesis of Hydroxyapatite

The HA was synthesized using calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (M = 236.15 g/mol) commercialized by Arcos Organics, purity of 99% and ammonium phosphate, $(NH_4)_2HPO_4$ (M = 132.06 g/mol) of Arcos Organics, purity of 99% and ammonium hydroxide, NH_4OH concentration of 28-30 mass%, (M = 35.95 g/mol) of Arcos Organics. The solution of each product in ionized water was made in the way to keep the ratio of concentrations (in mol/L) of [Ca]/[P] = 1.6. The pH of final solution was controlled by the ammonium hydroxide volume. The reaction of the synthesis is as follows:

$$6(NH_4)_2HPO_4 + 10Ca(NO_3)_2 + 8NH_4OH \rightarrow 6H_2O + 20NH_4NO_3 + Ca_{10}(PO_4)_6(OH)_2 \qquad \text{(Eq 1)}$$

The procedure is shown schematically in Fig. 1 and includes the following stages:

- introduction of $Ca(NO_3)_2 \cdot 4H_2O$ solution in deionized water followed by heating and agitation;

This article is an invited paper selected from presentations at the 2008 International Thermal Spray Conference and has been expanded from the original presentation. It is simultaneously published in *Thermal Spray Crossing Borders, Proceedings of the 2008 International Thermal Spray Conference*, Maastricht, The Netherlands, June 2-4, 2008, Basil R. Marple, Margaret M. Hyland, Yuk-Chiu Lau, Chang-Jiu Li, Rogerio S. Lima, and Ghislain Montavon, Ed., ASM International, Materials Park, OH, 2008.

Roman Jaworski and **Lech Pawlowski**, Service of Thermal Spraying at Ecole Nationale Supérieure de Chimie de Lille, BP 90180, 8 avenue Mendeleïev, 59650 Villeneuve d'Ascq, France; and **Christel Pierlot**, **Muriel Bigan**, and **Maxime Quivrin**, LCOM, UMR CNRS 8009, ENSCL, BP 90108 F-59652 Villeneuve d'Ascq Cedex, France. Contact e-mail: lech.pawlowski@ensc-lille.fr.

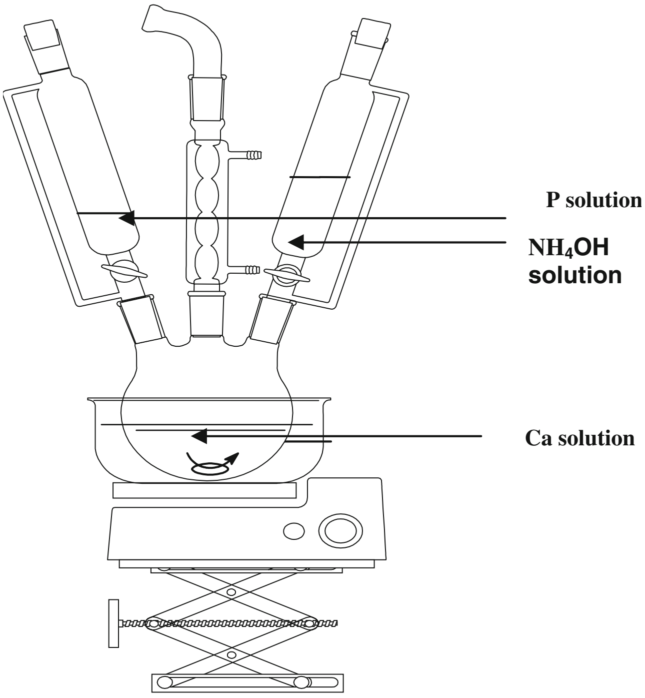

Fig. 1 Reactor of HA synthesis

- adding of NH_4OH at $T = 80$ °C and determination of pH (initial);
- adding of $(NH_4)_2HPO_4$ solution in deionized water in a "droplet by droplet way" during 15 min;
- 3-h heating and agitating and measuring pH (final);
- filtration and drying after 24 h of resting;
- calcinations at $T = 1000$ °C (for 4 h, 2 h of increasing of temperature up to maximum).

The experiments were designed in order to improve the productivity of reaction by using following variables:

- Concentration of [Ca] in mol/L, X_1: The lowest concentration was 0.5 and the highest was 4. The concentration of [P] was resulting from the condition $[Ca]/[P] = 1.6$ kept constant in all experiments.
- Volume of ammonium hydroxide in mL, X_2: The smallest volume was 10 mL and the greatest was 100 mL.
- Time of reaction in min, X_3: Two periods were used—15 min and 180 min.
- Time of resting, X_4: Two periods were tested—0 and 24 h.

First group of experiments were made in a small reactor (250 mL) and then a bigger one was used (1 L). The values of pH on the beginning of reaction were in the range of 11 to 12.5. The coefficient decreased after reaction to be in the range of 8.7 to 10. The optimized procedure of powder production enabled about 600 g of powder to be produced. The batches of 40 g after the optimized reaction and calcination were mixed together and ball milled using moliNEx system (Netzsch, Germany) with 1.85 mm diameter zirconia balls, and ethanol added as cooling medium. The obtained powder was formulated with distilled water 10 wt.% of the solid content.

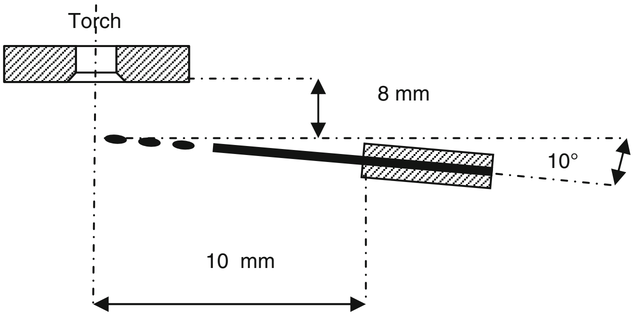

Fig. 2 Geometry of suspension injection to the plasma torch

2.2 Suspension Plasma Spraying

The suspension was fed to plasma jet using a pneumatic feeder described in details elsewhere (Ref 13) and an outlet having diameter of 0.75 mm in a way shown schematically in Fig. 2. Plasma torch used throughout all experiments was Praxair SG-100 mounted on 5-axis ABB IRB-6 industrial robot. The torch was alimented with 45 slpm of Ar and 8 slpm of H_2 and the electric power input was of 40 kW. The temperature at spraying was measured using pyrometer In 5 Plus of Impac. The pyrometer was about 90 cm from the sprayed substrates. The temperature variations at coatings deposition were very important, and it was decided to record only the maximal temperature. The torch trajectory over substrate is described elsewhere (Ref 3). There were 20 passes of torch above each substrate and after each five passes there was an interruption of 60 s for cooling. The process variables tested in this article are collected in Table 1. The substrates, being of metallic titanium, had size of 20 × 20 × 1 mm. These substrates were sand blasted using alumina grit with their sizes ranging from 250 to 500 μm at 4 bar of air pressure, directly prior to deposition. The angle of blasting was 90°.

2.3 Powders and Coatings Characterization Methods

The granulometry was tested using a laser device Master Sizer X of Malvern. The x-ray phase analysis of powder was made using a set-up Miniflex of Rigaku with Cu-Kα radiation and the Rigaku software. The synthesis of HA results in a formation of other phases, such as α-TCP, β-TCP (tricalcium phosphate $Ca_3(PO_4)_2$), and TTCP (tetracalcium phosphate, $Ca_4P_2O_9$). The percentage of the other phases with regard to hydroxyapatite were determined from the reference intensity ratio with the method described by Prevey (Ref 14) using the comparison of the strongest peaks' intensities. The XRD investigations of sprayed coatings were done by Bruker

Table 1 Variable spray parameters and coating thicknesses

Sample no.	Torch linear velocity, mm/s	Spray distance, cm	Maximal coating temperature at spraying measured with a pyrometer, °C	Coating thickness, µm
1	125	5	860	10
2	125	6	450	13
3	250	5	560	Very thin
4	250	6	290	33

Table 2 Experimental conditions

N°exp	[Ca], mol/L	[P], mol/L	Volume ammonium hydroxide, mL	Purity of obtained powder (a), % HA	Mass of obtained powder, g
1	1	0.6	20	100	5.0
2	3	1.8	20	46	13.5
3	1	0.6	60	98	5.0
4	3	1.8	60	65	14.4
5	0.57	0.35	40	100	2.8
6	3.4	2.1	40	60	16.2
7	2	1.2	11.7	85	9.9
8	2	1.2	68.3	98	10.0
9	2	1.2	40	99	9.9
10	2	1.2	40	100	9.8
11	2	1.2	40	100	9.8

(a) Obtained by the analysis of X-ray peaks intensities

apparatus type D8 with Cu-Kα radiation in the range of 2θ angles from 20° to 80° or 20° to 60°. The patterns were identified using Diffrac^{plus} Eva software which is based on the International Centre of Diffraction Data JCPDS-ICDD. Following peaks were considered:

- Hydroxyapatite, peak: 210, d = 3.08 Å, JCPDS 9-0432;
- α-TCP, peak: 441, d = 2.905 Å, JCPDS 9-348;
- β-CP, peak: 0.2.10, d = 2.88 Å, JCPDS 9-169;
- TTCP, peak: 040, d = 2.995 Å, JCPDS 25-1137;
- CaO, peak: 200, d = 2.405 Å, JCPDS 4-0777;

Amorphous calcium phosphate was identified as a halo with a maximum intensity at d = 2.97 Å. The percentage of phases was calculated as a ratio of areas of the strongest peak with regard to the area of the strongest peak of hydroxyapatite, according to French norm (Ref 15). The SEM investigations of powders and coatings were made using a Leo 982 scanning electron microscope working under low acceleration voltage.

3. Results

3.1 Powder Synthesis

After the selection of the best experimental conditions of synthesis in the small reactor, the optimization of synthesis in the big reactor was carried out. The optimization included two variables: concentration of calcium [Ca] and volume of ammonium hydroxide. The results of the experiments realized are collected in Table 2. Their design and the mathematical model are explained in detail elsewhere (Ref 16); the isopleths of constant purity of HA (Fig. 3) enabled us to find the optimal experimental conditions. Finally, optimal concentration of calcium nitrate was found to be about:

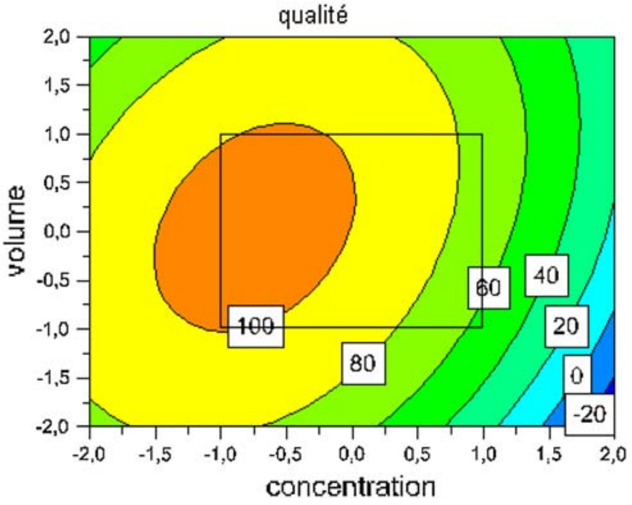

Fig. 3 Isopleths of constant purity of synthesized HA powder for two process variables: concentration of [Ca] and volume of ammonium hydrate (in normalized units)

- 1.26 mol/L of calcium nitrate (and correspondingly 0.76 mol/L of diammonium phosphate);
- 41 mL of ammonium hydroxide.

A quantity of 600 g of HA powder was manufactured using the optimized conditions. The morphologies of the

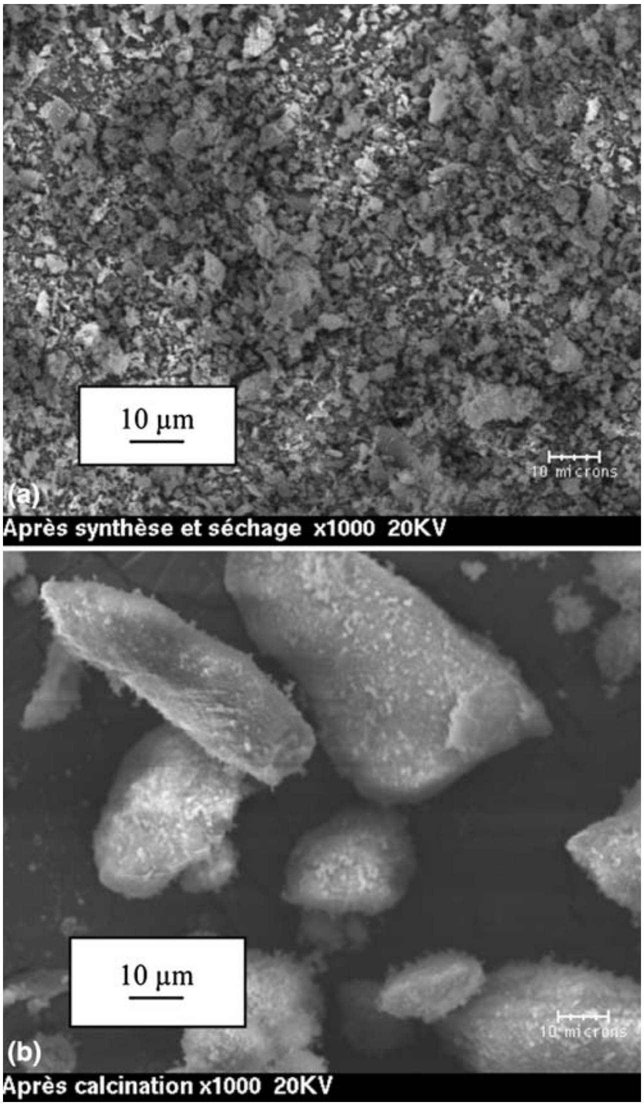

Fig. 4 Morphologies of HA powder particles after synthesis and drying (a) and after calcinations (b)

powder after synthesis and crushing and after calcinations are shown in Fig. 4. The powder after synthesis is fine grained, the grains become larger after calcination. The final stage of the powder processing was crushing and the granulometry of final powder has the mean diameter, d_{VS}, varying between 1.0 and 4.4 µm and the distribution is shown in Fig. 5. There are two maxima in the distribution: the first one in the submicrometer range and the second one at about 30-40 µm. Most probably, the latter results from the agglomeration of fine particles.

3.2 Coatings

The sprayed coatings were very thin (Table 1) and their color turned to be dark. The phases' content of sprayed coatings is shown in Table 3. Among the HA decomposition phases, the α-TCP is most present in the sprayed followed by β-TCP and TTCP. CaO and amorphous phosphate are only seldom present in sprayed coatings. The view of a typical surface of sprayed coatings is shown in Fig. 6.

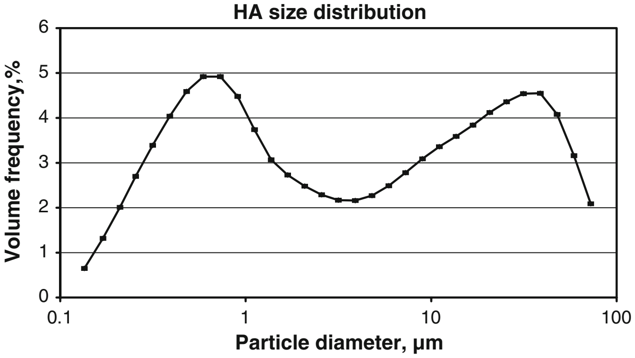

Fig. 5 Size distribution of synthesized HA powder particles

4. Discussion

Suspension-plasma-sprayed HA coatings included the following phases: HA, α-TCP, β-TCP, TTCP, CaO, and amorphous calcium phosphates (ACP). The phase diagram shown in Fig. 7 for a low content of water allows, to a degree, predicting the phenomena at flight of HA particles. The formation of amorphous calcium phosphates (ACP) can be attributed the rapid cooling of melt. Similarly, α-TCP and TTCP formed on heating of HA and their presence in the coatings was explained at spraying of large particles by freezing of these phases at impact with substrate (or previously deposited coating), (Ref 18). Finally, the presence of HA can be explained by the fact that some particles, or their parts remain unheated or heated to the temperatures below the temperature of phase transformation to TTCP and α-TCP (see Fig. 7). The presence of β-TCP is unusual and the phase was not observed when sprayed with the same HA powder having coarse particles in water and/or onto substrate (Ref 19). The possible explanation is related to the small size of powder particles. The particles are a solid part of a water solution being injected into plasma jet. The jet of liquid is injected into plasma jet. Knowing that the size of suspension delivery outlet is 700 µm, the sizes of droplets must have diameter of a few hundreds of micrometers (see Fig. 2). It is possible that the jet of liquid was not injected perfectly in the middle of plasma jet, it could have remained on the periphery of the plasma jet and the fine particles inside get only heated without melting. If the jet were injected into the hot temperature region of plasma jet, the droplets of liquid would be accelerated in the plasma jet and disintegrated into smaller droplets. Simultaneously, water boiled and got evaporated. The solid particles inside any droplet get closer and may start to agglomerate by sintering in flight. Some of the solid droplets got molten in the initial part of their trajectory. Fauchais (Ref 2) estimated that the fine particles of 0.1 µm size gets molten after a distance of 2.5 mm in its trajectory

Table 3 Crystal phases' content in suspension plasma sprayed coatings obtained by the analysis the peaks on the x-ray diagrams

Sample no.	α-TCP/HA, %	β-TCP/HA, %	TTCP/HA, %	CaO/HA,%	Amorphous/HA, %
1	31	21	12	Absent	Absent
2	37	2	Absent	Absent	3
3	12	10	10	6	Absent
4	Absent	33	Absent	5	Absent

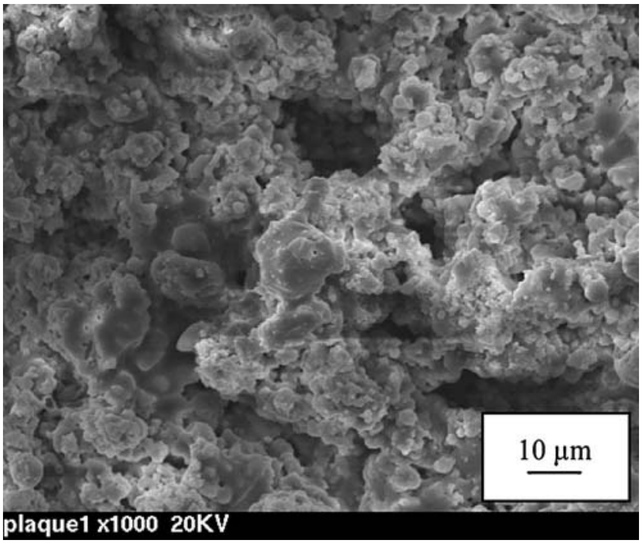

Fig. 6 SEM (secondary electrons) morphology of suspension plasma HA sample no. 1

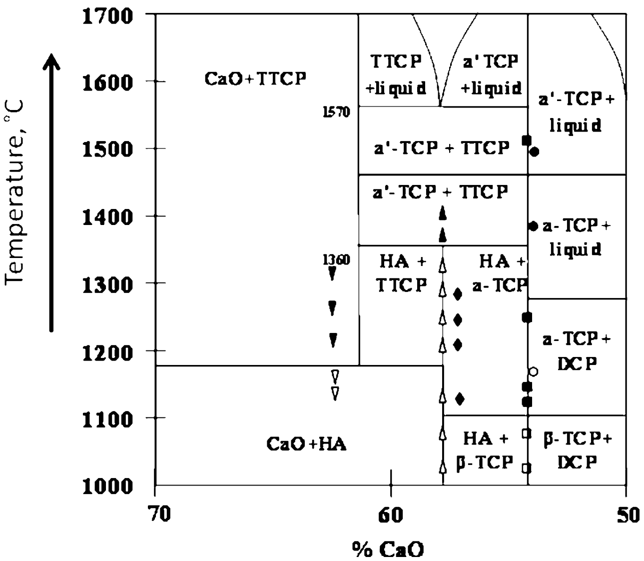

Fig. 7 Phase diagram of the system CaO-P_2O_5 at high temperature for the partial pressure of H_2O equal to 10 Torr (Ref 17)

in the plasma jet. In fact, the plasma gets colder because of evaporation of water. Subsequently, the fine particles may get agglomerated by sintering with other particles and/or evaporated. The agglomeration progresses until an impact with the substrate. Temperature of a few fine particles that remained on the periphery of the plasma jet may be greater than that of the transformation temperature of HA into α-TCP and TTCP. β-TCP could have been formed from α-TCP on cooling down. Similarly, CaO could have been transformed from TTCP. The cooling of particles being on the periphery of the jet is less intensive than that being in the center of the jet making possible such transformations. The β-TCP phase is present in all the sprayed coatings, and in the sample 4, all α-TCP transformed into β-TCP and all TTCP transformed into CaO (see Table 3). The spray conditions seem to be, however, far from optimal and it is hard to understand the influence of individual parameter onto the phase content.

5. Conclusions

The HA powder was synthesized using aqueous solution of ammonium phosphate ($H_2(PO_4)NH_4$) and calcium nitrate ($Ca(NO_3).4H_2O$) using a design of experiments. The synthesized fine powder was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM). The powder was formulated into water-based suspension and used to carry out the initial tests of plasma spraying onto titanium substrate. The phase analysis of sprayed coating was made with the used of XRD and the phase content was related to the phenomena that could have happened in plasma jet. The process of suspension plasma spraying needs further optimization.

Acknowledgments

Mr. Marc Martel enabled us to realize the synthesis of HA powder in his laboratory, and the discussions with Dr. Hornez were helpful in initiating the synthesis of HA.

References

1. L. Pawlowski, The Science, Engineering of Thermal Spray Coatings, 2nd ed., Chichester, Wiley, 2008, p 101
2. P. Fauchais, Solution/Suspension Plasma Spraying of Finely Structured Coatings, *1st Scientific Workshop on Thermal Spraying of Suspensions*, Tours, France, 14 and 15 June 2007, available upon request
3. R. Jaworski, L. Pawlowski, F. Roudet, S. Kozerski, and A. Le Maguer, Influence of Suspension Plasma Spraying Process Parameters on TiO_2 Coatings Microstructure, *J. Therm. Spray Technol.*, 2008, **17**(1), p 73-81

4. R. Jaworski, L. Pawlowski, F. Roudet, S. Kozerski, and F. Petit, Characterization of Mechanical Properties of Suspension Plasma Sprayed TiO_2 Coatings Using Scratch Test, *Surf. Coat. Technol.*, 2008, **202**, p 2544-2553
5. K. Wittmann-Ténèze, K. Vallé, L. Bianchi, P. Belleville, and N. Caron, Nanostructured Zirconia Coatings Processed by PROSOL Deposition, *Surf. Coat. Technol.*, 2008, **202**, p 4349-4355
6. E. Bouyer, F. Gitzhofer, and M.I. Boulos, Suspension Plasma Spraying for Hydroxyapatite Powder Preparation by R.F. Plasma, *IEEE Trans. Plasma Sci.*, 1997, **25**(5), p 1066-1072
7. F. Gitzhofer, E. Bouyer, and M.I. Boulos, ‘‘Suspension Plasma Spraying,’’ US Patent 5 609 921, 3 November 1997
8. R. Jaworski, C. Pierlot, R. Tomaszek, L. Pawlowski, Z. Znamirowski, and J. Zdanowski, Optimization of Dielectric Properties of Suspension Plasma Sprayed Hydroxyapatite Coatings, *Mat.-wiss. u. Werkstofftech.*, 2007, **38**, p 125-130
9. R. Heimann, Thermal Spraying of Biomaterials, *Surf. Coat. Technol.*, 2006, **201**, p 2012-2020
10. S.M. Best, A.E. Porter, E.S. Thian, and J. Huang, Bioceramics: Past, Present and for the Future, *J. Eur. Ceram. Soc.*, 2008, **28**(7), p 1319-1327
11. M. Markovic, B.O. Fowler, and M.S. Tung, Preparation and Comprehensive Characterization of Calcium Hydroxyapatite Reference Material, *J. Res. Natl. Inst. Stand. Technol.*, 2004, **109**, p 553-568
12. J.-C. Hornez, F. Chai, F. Monchau, N. Blanchemain, M. Descamps, and H.F. Hildebrand, Biological and Physico-Chemical Assessment of Hydroxyapatite (HA) with Different Porosity, *Biomol. Eng.*, 2007, **24**(5), p 505-509
13. L. Pawlowski, Finely Grained Nanometric and Submicrometric Coatings by Thermal Spraying: A Review, *Surf. Coat. Technol.*, 2008, **202**(18), p 4318-4328
14. P.S. Prevey, X-ray Diffraction Characterization of Crystallinity and Phase Composition in Plasma-Sprayed Hydroxyapatite Coatings, *J. Therm. Spray Technol.*, 2000, **9**(3), p 369-376
15. S 94-067, *Détermination qualitative et quantitative des phases étrangères présentes dans les poudres, dépôts et céramiques à base de phosphate de calcium*, AFNOR, Paris, France, 1993
16. R. Jaworski, C. Pierlot, L. Pawlowski, M. Bigan, and M. Martel, Design of the Synthesis of Fine HA Powder for Suspension Plasma Spraying, submitted for publication in *Surf. Coat. Technol.*
17. C. Santos, A. Pazo, F. Guitan, Water Vapour Pressure Influence on $CaO-P_2O_5$ System Phase Diagram, *Mater. Clinic. Appl.*, 1995, p 11-18
18. S. Dyshlovenko, L. Pawlowski, B. Pateyron, I. Smurov, and J.-H. Harding, Modelling of Plasma Particles Interactions and Coating Growth for Plasma Spraying of Hydroxyapatite, *Surf. Coat. Technol.*, 2006, **200**, p 3757-3769
19. S. Dyshlovenko, L. Pawlowski, P. Roussel, D. Murano, and A. Le Maguer, Relationship Between Plasma Spray Operational Parameters and Microstructure of Hydroxyapatite Coatings and Powder Particles Sprayed into Water, *Surf. Coat. Technol.*, 2006, **200**, p 3845-3855