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Preliminary study of hydroxyapatite coatings synthesis using solution precursor plasma spraying

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ABSTRACT

The liquid precursors of calcium hydroxide and diammonium hydrogen phosphate were injected into the plasma jet generated by the SG-100 torch to synthesize the hydroxyapatite (HA) coatings. Three operational deposition process parameters, namely: (i) electric power, (ii) spray distance, and (iii) scan speed were varied. The process enabled synthesization of coatings with HA as major phase onto stainless steel substrates. The coatings were deposited to reach the thickness of about 50 μm with high rate ranging from 3 μm to nearly 7 μm by pass of torch. The X-ray diffraction (XRD) analysis of coatings enabled finding of HA accompanied by calcium phosphates, calcium oxide, and calcium carbonate. The presence of the carbonates was confirmed by Fourier Transform Infrared (FTIR) spectroscopy and by elemental mapping made with the use of Electron Dispersive X-ray Spectroscopy (EDS). The morphology of coatings, observed using scanning electron microscope (SEM), revealed fine-grained microstructure and porosity in the range of 1.3 to 5.1%. The adhesion of coatings obtained using scratch test characterized by critical force was in the range of 2.5 to 3.6 N.

1. Introduction

Solution precursor thermal spraying is a relatively new deposition technique used for the first time in the end of the 90s of the last century to synthesize alumina coating with the use of aluminum nitrate solution in isopropanol injected into a combustion flame [1]. The application of plasma jet instead of combustion flame enabled the development of the solution precursor plasma spraying (SPPS) processes. The process has been used in recent years to synthesize such oxides as e.g. yttria stabilized zirconia [2], yttrium iron garnet [3] or cobalt ferrite [4]. The important issues related to the synthesis using solution precursor thermal spraying process were reviewed recently [5,6]. One of the particularly interesting oxides is hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) which is used to obtain the bioactive coatings onto metallic implants for orthopedic and dental applications. The development of the SPPS method is an important step forward in the development of hydroxyapatite coatings. It is well known that the industrial method for the development of HA is via conventional powder plasma spraying which uses powders having 100 μm in size [7]. Another way of HA coating deposition started with milling of coarse HA powder to obtain fine particles with a few micrometer mean size. Such fine powder was used to formulate a water suspension, which was applied to a process called suspension plasma spraying (SPS) to obtain coating [8]. The coatings obtained using APS and SPS processes included some phases of the HA decomposition, namely tricalcium phosphate (TCP,$Ca_3(PO_4)_2$), tetracalcium phosphate (TTCP, $Ca_4P_2O_9$) and calcium oxide (CaO). The phases of decomposition are less bioactive that HA and it is interesting to find a process enabling deposition of coatings composed of crystalline HA. The SPPS may be such a process. The major motivation behind the development of the SPPS is the reduction of the tedious process of powder feedstock preparation and/or suspension formulation. These processes can be eliminated since the chemically precipitated HA aqueous solution is fed directly to the plasma. Another advantage of this method is that during wet chemical precipitation, morphology and size of the resulting precipitates can be controlled and the homogeneity at molecular level can be exploited.

The synthesis of HA coatings was tested with the use of SPPS method by Garcia et al. [9] and Huang et al. [10]. Garcia and his co-workers used the organic route to prepare Ca-P sol–gel solution according to the method proposed by Liu et al. [11] in which calcium nitrate tetrahydrate and triethyl phosphite were used as calcium and phosphorus precursors. Huang and his colleagues [10] used calcium nitrate $Ca(NO_3)_2$ and diammonium hydrogen phosphate $(NH_4)_2HPO_4$ to obtain HA following the reaction:

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

The present paper is a continuation of the previous studies of our research group in which a powder synthesized with the use of reaction shown by Eq. (1) was used to formulate a suspension, applied to plasma

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Table 1
Solution precursor plasma spray parameters.

Working gas composition and flow rate, sLpm	Ar + H_2 and 45 + 5 sLpm
Solution feed rate, mL/min	35 mL/min
Type of injection	Nozzle inside torch having 0.3 mm internal diameter oriented radially at 90° relative to the plasma jet axis.
Injection pressure, bar	0.5
Number of scans	2 passes per shot with 9 s interruption after each pass. Each shot is hold to allow the samples to cool down to ~50 °C before performing the next shots of spraying.
Scan pattern	Rectangular patterns with offset distance of 3 mm after each torch run.

spray of coatings [12,13]. However, it was decided to use calcium hydroxide instead of calcium nitrate to simplify the reaction which does not need any pH control. Moreover, the liquid precursor was, after aging, injected directly to plasma jet to form coatings. The present study has a preliminary character and should show a feasibility of synthesis of HA coatings of acceptable quality from the used precursors.

2. Experimental methods

2.1. Preparation of liquid precursor

The wet chemical precipitation method was employed for the preparation of the hydroxyapatite liquid precursor using calcium hydroxide (ACS Reagent 95%, Sigma Aldrich) and diammonium hydrogen phosphate (ACS Reagent 98%, Sigma Aldrich) as calcium and phosphorous ions sources respectively. Consideration of the above-mentioned precursors was based on the fact that, calcium hydroxide is relatively cheap and, moreover, the addition of ammonium hydroxide to control pH is not necessary for such preparation. In order to achieve the stoichiometric Ca/P ratio of 1.67, 150 mL of 0.3 M of diammonium hydrogen phosphate aqueous solution was added drop-wise into a stirred 250 mL of 0.5 M calcium hydroxide aqueous solution ($pH = 12.4$). For comparison, $pH = 11$ in the paper of Huang et al. [10] to obtain HA coatings. The mixed solution precursor was then magnetically stirred and heated at bath temperature of 70 °C for 3 h in a reaction vessel. The prepared liquid precursor was then aged for at least 24 h in ambient temperature and was submitted to an ultrasonic treatment prior to injection into plasma jet. During the wet chemical precipitation of HA solution, the particles that started to be formed were amorphous and aging of this solution induced crystallization of the precipitates because of the chemically active environment of the solution. The solution precursors were supposed to react in the plasma jet as follows:

$$10Ca(OH)_2 + 6(NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 12NH_3 + 18H_2O \quad (2)$$

2.2. Plasma spraying of coatings

The plasma torch SG-100 (Praxair S.T., Indianapolis, IN, USA) mounted on 5-axis IRB-6 robot (ABB, Zürich, Switzerland) was employed for the deposition of HA liquid precursors. The injection of HA liquid precursor was realized using a mechanical injector installed inside the anode-nozzle of the torch. The liquid precursor was submitted to a magnetic stirring while delivering to plasma jet from a solution container. The operational plasma spray parameters, kept constant during all the coating experiments, are listed on Table 1. The variable parameters used in the experimental runs are shown in Table 2. The coatings were sprayed onto stainless steel 316 having diameter 25 mm and thickness 5 mm and Ti plates having size 20 × 20 × 1 mm. The temperature profile during each spraying run was monitored using Impac IN 5 Pyrometer (LumaSense Technologies, Santa Clara, CA, USA). The substrates were prepared using sand alumina blasting prior to spraying.

2.3. Characterizations of liquid precursor and of coatings

The precursor was characterized with Fourier Transform Infrared Spectroscopy (FTIR) with the use of spectrum one set-up of Perkin Elmer (Waltham, MA, USA). The precursor was dried, before testing, at 100 °C to obtain fine powder and grinded together with 0.1 g of potassium bromide. Functional groups of the obtained coatings were also determined by means of Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) using Nicolet 6700 (Thermofisher) spectrometer at scan range of 400–4000 cm^{-1} with 4 cm^{-1} resolution over 32 scans. The thermal behavior of the precursor was tested by thermogravimetric analysis and differential scanning calorimetry (TG-DSC) with the use of Labsys set-up of Setaram (Caluire, France). The fine powder formed in liquid precursor prior to spraying was tested using light particle size analyzer type Zetasizer Nano ZS of Malvern Instruments .(Malvern, UK). Scanning electron microscope (SEM) Philips XL30 (Eindhoven, Netherlands) coupled with electron dispersion spectrometer (EDS) was used to characterize the splats. The structural characteristics of fine powder and coatings were determined using X-ray diffraction (XRD) using Bruker D8 Advance diffractometer (Billerica, MA, USA) under Bragg-Brentano configuration with Cu Kα radiation. The resulting diffractogram was analyzed using Diffrac + EVA Software equipped with JCPDS-ICDD database. The following standards were used for phases' identification:

- Hydroxyapatite (HA) — JCPDS 00-009-0432;
- Calcium phosphate (α-TCP) — JCPDS 00-009-0348;
- Calcium phosphate (β-TCP) — JCPDS 00-009-0169;
- Tetracalcium phosphate (TTCP) — JCPDS 00-25-1137;
- Calcium oxide (CaO) — JCPDS 01-082-1690;
- Calcium carbonate ($CaCO_3$) — JCPDS 00-017-0763.

Table 2
Experimental design of SPPS experiments.

Run no.	Power input (kW)	Spray distance (mm)	Scan speed (mm/s)	No of torch passes over the substrate	Total[a] thickness, μm	Thickness in one pass, μm/pass	Maximum temperature of coatings, °C	Coating porosity, %	Critical load, N
1	36	60	400	22	63	2.9	671	1.6	3.3
2	36	60	600	17	60	3.5	670	1.3	2.5
3	36	80	400	10	66	6.6	617	2.2	3.6
4	36	80	600	16	58	3.6	692	1.6	3.0
5	40	60	400	14	65	4.6	617	2.1	2.7
6	40	60	600	12	54	4.5	564	2.3	2.7
7	40	80	400	10	51	5.1	836	5.1	2.9
8	40	80	600	12	51	4.3	465	4.7	2.5
9	38	70	500	12	59	4.9	897	4.6	2.8

[a] The smallest value taken from 5 measurements made using an optical microscope on the coatings' cross-sections.