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Mechanical properties of suspension plasma sprayed hydroxyapatite coatings submitted to simulated body fluid

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ABSTRACT

Home synthesized (HA) powder was formulated with water and alcohol to obtain a suspension used to plasma spray coatings onto titanium substrate. The deposition process was optimized and the resulting coatings were soaked in simulated body fluid (SBF) for the periods of 3, 7, 14, 28, and 60 days at controlled temperature of 37 °C. The microstructural research enabled to find in the as-sprayed deposits two characteristic zones: (i) *dense zone* corresponding to the lamellas, observed usually in thermally sprayed coatings; (ii) *sintered zone* containing fine hydroxyapatite grains corresponding to the fine solids from initial suspension. The *sintered zone* disappears after soaking in SBF and the pores get filled by the reprecipitated calcium phosphates. The adhesion of the soaked coatings to the substrate was characterized by the critical load in the scratch test and was about 10 to 12 N. The Young modules of the coatings were determined with help of depth-sensing indentation test by the use of the technique developed by Oliver and Pharr. The modules were not depending on the time of soaking and their mean values were 15.6 and 28.4 GPa, depending on the coating operational parameters. The scratch test enables to determine the hardness of the coatings, which remained fairly constant during the time of soaking in the range of 3 to 5 GPa. This hardness was compared to that the Martens microhardness which doubled with time of soaking to reach up to 1 GPa.

1. Introduction

The biomaterials interact with biological systems without causing any unacceptable harm to the body. In particular, hydroxyapatite, $Ca_5(PO_4)_3OH$, has been used since 1990 as coating on the prostheses of e.g. hips, knees, teeth in order to enhance their biointegration to a bone [1]. The most popular coatings technology is plasma spraying. On the other hand, there are a lot of different deposition processes being able to compete with plasma spraying if a particular coating property should be enhanced [2]. One of the recent modifications of plasma spray processes consists of using a suspension of fine solids in water or alcohol. This technology enables production of nanometric microstructures and was recently reviewed [3]. The key issue at suspension plasma spraying, initiated in late nineties of the last century in The University of Sherbrooke in Canada, is injection of liquid into plasma jet [4]. This occurs, in the majority of present torches, radially with regard to the torch axis in a form of a continuous or an atomized liquid stream. The appropriate penetration of suspension into high temperature core of plasma is necessary in order to assure the heat treatment of the feedstock. The slurry dries up and the fine particles get possibly sintered in plasma and molten before striking the substrate. Previous studies of our research group were concentrated on the characterization of the coatings sprayed using atomizer injector [5, 6] and, more recently, on the coatings processed with the use of continuous stream injector [7, 8]. The coatings were characterized microstructurally with the scanning electron microscope, electron microprobe microanalysis and with X-ray diffraction. The latter investigation enabled the quantitative phase analysis in as-sprayed and those soaked in SBF deposits. The mechanical properties of suspension plasma HA deposits were also tested with the scratch test [8]. The previous works on mechanical properties of hydroxyapatite coatings have been concentrated on as-sprayed samples processed with dry powder feedstock. Fu et al. [9] tested adhesion of sprayed coatings using the tensile test and their elastic modulus using indentation test. Similar characterizations were made by Morks and Kobayashi [10] for high power plasma torch. Recently, nanoindentation test was used to characterize flame sprayed coatings [11]. The mechanical properties of coatings soaked in SBF were tested for the deposits obtained by aerosol [12].

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2. Experimental methods

2.1. Suspension preparation

HA powder was synthesized by a *wet method* using calcium nitrate and diamonium phosphate in ammoniacal solution in the way described elsewhere [13, 14]. The powder has a monomodal size distribution with the mean diameter of about 1 μm when tested in ethanol. The distribution, while tested in water, was bimodal with agglomerates in the range from 3 to 10 μm. The suspension was formulated by taking about 20 wt.% of dry powder with 40 wt.% water and 40 wt.% ethanol.

2.2. Plasma spray parameters

The coatings were sprayed onto titanium substrates having size in mm $20\times20\times0.8$ washed with ethanol before processing. The substrates were roughened with the corundum grit having size of $-125+88$ μm, blasted under pressure of 0.4 MPa. The internal injection was made through a 0.5 mm internal diameter nozzle inserted into the anode-nozzle of the torch. The *SG-100* torch of *Praxair* S.T. (Indianapolis, IN, USA) was mounted on 5-axis *IRB-6* of ABB (Zürich, Switzerland) industrial robot. The plasma of 40 slpm of Ar with 5 slpm H_2 was used in all experiments. The electric power of 30 kW and spray distance of 60 mm were used in the experimental run no. 1. The power of 27 kW and spray distance of 50 mm were used in the experimental run no. 2 (see also [7]). The coatings thicknesses were in the range of 50 to 100 μm. The surface temperature at coatings' deposition was recorded using a pyrometer IN 5 Plus of *Impac* (Erstein, France) which is sensible in the wavelengths' range from 8 to 14 μm.

2.3. In vitro corrosion test

The samples were submitted to a corrosion test in a liquid having a composition proposed by Kokubo et al. [15]. After having mixed all the components, the pH was adjusted to reach the value of pH = 7.4 (see also [7]). Each sample was immersed in SBF and closed in a small container kept in a constant temperature of 37 °C. Prior to the characterizations, the tested samples were cleaned using distilled water and dried during a night at the temperature of 60 °C. The codes of characterized samples are shown in Table 1.

2.4. Microstructure observations

XRD investigations of sprayed coatings were done by Bruker AXS (Karlsruhe, Germany) apparatus type D8 with Cu-Kα radiation (see more details in [7]). The percentage of the phases in coatings were determined from the reference intensity ratio (RIR) method described by Prevey [16], which uses the comparison of strongest peaks intensities. RIR were calculated using the following files of the JCPDS data base:

- HA, hydroxyapatite, JCPDS 73-1731;
- α-TCP, tricalcium phosphate $Ca_3(PO_4)_2$, JCPDS 70-0374;
- β-TCP, tricalcium phosphate $Ca_3(PO_4)_2$, JCPDS 70-2065;
- TTCP, tetracalcium phosphate, $Ca_4P_2O_9$, JCPDS 70-1379;
- CaO, calcium oxide, JCPDS 82-1690.

Table 1
Codes of the samples tested *in vitro* and submitted to the characterizations (as sprayed-1 and as sprayed-2 correspond to the different samples sprayed in the run).

Run no	Days of immersion					
	As-sprayed	3	7	14	28	60
1	100	103	107	114	128	160
2	200	203	207	214	228	260

SEM investigations were made using JEOL (Tokyo, Japan) set up of type JSM 5800 LV.

2.5. Mechanical properties

2.5.1. Scratch test

The scratch test was realized with a *MicroCombiTester* of *CSM Instruments* (Peseux, Switzerland) equipped with a Rockwell diamond indenter having a tip radius of 0.2 mm. The scratches were linear with progressively increasing load. The experimental conditions were similar to that presented previously [8, 17]. As the coatings are very porous, the acoustic signal could not be used for the estimation of critical load, L_c. Instead, the following indications enabled the load to be found in the way described in details elsewhere [17]. In present work, the critical load was defined at the onset of the coating loss associated with the beginning of visibility of metallic substrate inside the scratch channel. This measurement was made with the help of optical microscope. The tester enabled also to find the friction coefficient at the critical load. The scratch hardness HS_L (Pa) was estimated following the specification of ASTM G171-03 norm:

$$HS_L = \frac{8\cdot L}{\pi\cdot d^2} \tag{1}$$

where L (N) is the applied normal force (the loads of 3, 6 and 9 N were selected) and d (m) is the corresponding scratch width. The scratch hardness is a fair indicator of coating cohesion.

2.5.2. Indentation test

Depth-sensing indentation (DSI) tests were performed using a Micro-hardness Tester 2-107 from CSM instrument. The indenter used is a Vickers pyramidal. All indentation experiments were carried out at a constant room temperature of 20 °C. The indentation test consists of applying the indenter by using a continuous loading ranging between 0 to P_{max} to obtain a load–depth curve. For determining the bulk modulus and for studying the hardness–load dependence, the curves obtained at various maximum loads are required. In this work, the maximum indentation loads, P_{max}, were selected between 50 mN and 1000 mN. The typical loading rates in nanoindentation are from a few μN/s up to a few mN/s for peak loads equal to 10 μN and to 10 mN respectively [18]. In microindentation, the same rule is applied. Based on this rule, the loading/unloading rates are calculated with a linear relationship as a function of the maximum load. The rates, expressed in N/min, are then equal to twice the value of the maximum load expressed in Newton. The dwell time at the maximum load is equal to 15 s in agreement with the duration recommended by the standard Vickers hardness testing. For each tested sample, we have performed at least 10 indentation tests at different P_{max} on the cross-section of the coating in order to avoid influence of the surface roughness.

2.5.3. Elastic properties

The calculations were made by the model of Oliver and Pharr [19] based on the original work of Doerner and Nix [20]. Different corrections [21–23], introducing the instrument compliance and the coefficient γ, were also introduced. Finally, we applied the following relation applied to the unloading curve:

$$\frac{1}{S} = \left(\frac{dh}{dP}\right) = C_t = C_f + \sqrt{\frac{\pi}{24.5}}\frac{1}{2\cdot(\beta\gamma)\cdot E_R}\cdot\frac{1}{h_c} \tag{2}$$

where C_t is the total compliance, C_f is the frame compliance, β is a correction factor depending on the shape of the indenter (1.05 for a Vickers indenter) and h_c the contact indentation depth. Moreover to consider additional assumptions in Sneddon's solution, Hay et al. [23]