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Mechanical properties by instrumented indentation of solution precursor plasma sprayed hydroxyapatite coatings: Analysis of microstructural effect

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ABSTRACT

The mechanical properties of solution precursor plasma sprayed hydroxyapatite (SPPS-HA) coatings were investigated by instrumented indentation test in relation to their microstructural characteristics. The morphology of the coatings using solution that is more concentrated shows cauliflower-like surface with fine particles and agglomerated fragmented shells while dome-like formations with spherical particles around were observed for coatings from less concentrated solution. The coatings had elastic modulus and hardness values in the range of 5.0 to 22.0 GPa and 0.04 to 0.17 GPa, respectively. The strong disparities in elastic modulus and hardness values were attributed mainly to the morphology and crystallinity of the coatings. The coatings prepared from more concentrated solution precursors had average elastic modulus and hardness nearly two times greater than the coatings prepared from solution of low concentration. Variation of hardness values was due to the densification of the coating material upon indentation. Models employed enabled to describe the hardness and elastic modulus of coatings as a function of crystallinity volume fraction. Moreover, for the HA coatings to exhibit bone-like microstructure, it was found that the crystallinity volume fraction should be within 0.56–0.86.

1. Introduction

Hydroxyapatite (HA) is a very important bio-ceramic material employed in medical applications due to its exceptional biocompatibility and its close resemblance to the physico-chemical characteristics of the mineral component of human bone [1]. Synthetic HA has been greatly considered as an osteoconductive bone substitute and commonly used in research and development field for studying the nature of biomineralization of the human bone. However, properties of synthetic HA such as purity, composition and morphology among others, are very dependent and sensitive to experimental conditions [2]. The presence of impurity phases during synthesis is undesirable since it leads to inferior characteristics of the resulting HA.

It is well known that powder plasma spraying [3,4] is the standard method in producing HA coatings for bone implant applications. The relatively coarse powder is directly injected to the plasma jet. The coatings sprayed in this process exhibit cracking and large splat boundaries that significantly affect the biomechanical properties of HA especially when submitted to physiological fluids. For obtaining finely structured HA coatings, innovation of this process resulted in the use of suspension plasma spraying [5] or high velocity suspension flame spraying [6]. The further progress in plasma spray technology led to the development of HA coatings using solution precursor plasma spraying (SPPS) [7]. This process enables to synthesize the coating directly from liquid precursors without using powder. The molecularly mixed calcium-phosphate solution precursors are injected radially into the free expanding plasma jet. The coatings were dense and had good deposition rate. On the other hand, the calcium carbonate was present in the coatings together with the phases of decomposition of HA what lowered the quality of the coatings. Consequently, the precursors were modified [8].

It is important to know the mechanical properties of HA coatings in order to predict their behavior in service and, in particular, compare them to that of the natural bones. The previous studies of the mechanical properties of HA coatings were focused on the conventional plasma spray process using powder feedstock [9,10] and suspension plasma spraying [11] by means of nano-indentation method performed on a prepared surface of the coatings.

In the present work, the mechanical properties of solution precursor plasma sprayed hydroxyapatite (SPPS-HA) coatings are studied using instrumented indentation technique (IIT). The mechanical properties are determined by means of indentation experiments in the micro loads range in order to limit the influence of the heterogeneity of the microstructures as well as the roughness over the surface of the coating

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for which the effects are predominant in nano-indentation. Elastic modulus and hardness of the SPPS-HA coatings were compared to the mechanical characteristics of HA coatings plasma sprayed using powder and suspension feedstocks. The microstructural effect, specifically, the role of morphology and crystallinity of the SPPS-HA coatings on mechanical properties is illustrated and discussed regarding the application of some models related to this aspect. Furthermore, the results obtained from the applied models enabled us to estimate the elastic modulus and hardness of the SPPS-HA coatings as a function of crystallinity volume fraction.

2. Experimental methods

2.1. Preparation of calcium-phosphate solution

The calcium-phosphate solution was prepared using calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) and triethyl phosphite ($P(OEt)_3$) as precursors. Triethyl phosphite was hydrolyzed initially using deionized water and appropriate amount of calcium nitrate solution was added dropwise to reach the 1.67 Ca/P stoichiometric ratio. Two different concentrations of solutions were used, namely high solution concentration having Ca/P ratio of [0.5 M/0.3 M] and low solution concentration of [0.167 M/0.1 M] Ca/P ratio. The detailed explanation of the chemistry of the solution and of the plasma spraying parameters used in this work is shown elsewhere [8].

2.2. Plasma spraying of HA coatings

The solution precursor plasma spraying of hydroxyapatite coatings was realized using SG-100 torch (*Praxair S.T.*, *Indianapolis*, *IN*, *USA*) mounted on 5-axis ABB IRB-6 robot (*Zürich*, *Switzerland*). The experiments were designed following a two-level, 2^{4-1} plan by varying solution concentrations (0.167/0.1 M and 0.5/0.3 M), injection rate (38 and 50 mL/min), spray distance (50 and 60 mm) and electrical power input to the plasma torch (36 and 40 kW) with more details to be shown in the incoming study [8]. The calcium-phosphate solutions were injected into the plasma jet using a continuous stream injector. Table 1 presents the plasma spraying parameters kept constant in SPPS process.

2.3. Surface roughness of HA coatings

The surface roughness (R_a) of the HA coatings was determined on the surface adjacent to the Berkovich indentation prints using an optical profilometer, WykoVeeco NT9300. Only one specimen for each spray condition was considered. The measurements were realized in a controlled-temperature room at 20 °C. The values of the roughness were obtained by the instrument along six different lines of 2.5 mm length on the surface of each sample. The values were calculated as arithmetic mean of the absolute value of the heights between the actual and mean profile.

Table 1
Process parameters kept constant in the study.

Working gas composition	Ar (45 slpm) + H_2 (5 slpm)
Torch scan speed	500 mm/s
Type of injection	Nozzle inside torch, (0.5 mm internal diameter; oriented at 90° relative to the plasma jet)
Number of scans	Depends on experimental run. Each shot is hold to allow the samples to cool down at ~50 °C before the next shots of spraying.
Scan pattern	Rectangular pattern with off-set distance of 3 mm after each torch run.
Substrate	Stainless steel substrate of 25 mm diameter and 2 mm thickness and sand blasted with alumina sand prior to spraying.

2.4. Microstructural characterization

The microstructures of HA coatings were examined using a scanning electron microscope (SEM) Philips XL30 (*Eindhoven*, *Netherlands*) at their surfaces and at cross sections. X-ray diffraction (XRD) investigation was carried out using a BRUKER D8 ADVANCE diffractometer with Cu Kα = 0.15406 nm wavelength radiation. Phase analysis of the coatings was performed to determine if really HA is their main component. The absence of the decomposition phases of HA such as tri-calcium phosphates, tetracalcium phosphate and calcium oxide that was observed in our previous work [7] could have enhanced the mechanical characteristics of the coatings. Phase analysis was made with the help of *Diffrac + EVA Software* equipped with JCPDS-ICDD database. The crystallinity, which can influence the hardness and adhesion of the coatings, was also determined. The effect of the ratio of crystalline to amorphous HA was also investigated regarding that an increased in crystallinity value may lead to better stability of the coatings. Our further study [8] will describe all the details for the calculation of purity and crystallinity of the SPPS-HA coatings.

2.5. Mechanical properties and indentation background theory

The study of mechanical properties by micro-indentation technique is usually performed on an already prepared surface of a sample that went through polishing procedure. Nevertheless, for the current work, the polishing procedure will change the surface condition of the HA coatings, and the properties that can be obtained by depth sensing would not be necessarily the properties of the material as it was received, and generally, as it would be in the application field. Thus, in order to estimate the properties without changing its original condition, a multi-cycle protocol is used. In this way, it is possible to observe if there is a representative damage in the surface of the sample and also to obtain and analyze the elastic behavior of the material in each cycle from the unloading part of load–depth indentation curve. The indentation experiments were carried out using a micro-hardness tester (CSM 2-107) having a resolution of 100 μN for load measurements and 0.3 nm for acquisition of depth data. The micro-hardness tester was equipped with a Berkovich diamond pyramid indenter having a tip defect (distance between the blunted tip and the ideal pyramid tip) of 50 nm as indicated in reference [12]. Micro-indentation test was conducted directly on the surface of the coatings under a multi-cycle protocol mode using 100 cycles per test and loading–unloading rates (in mN/min) as twice the value of the maximum load (expressed in N) applied [13] as the set-up parameters to assure that all cycles last the same time and into the same place. The maximum load applied in the first cycle was 100 mN and in the last one was 20,000 mN. Loading to unloading values were set at 20% of the maximum load in each cycle and a dwell time of 15 s was imposed at each load between the minimum and maximum loads, according to the standard indentation test procedure ASTM E92-82 [14]. Five indentation tests for each sample were performed randomly on the surface of the HA coatings by applying the indentation parameters described earlier. Fig. 1 shows the plot of the multi-cycle loading–unloading curve where the applied load and the displacement of the indenter are recorded simultaneously.

From each unloading part of the load-indentation displacement curve shown as an example in Fig. 1, the reduced elastic modulus (E_R) can be determined by applying the methodology proposed by Oliver and Pharr [15] expressed as:

$$E_R = \frac{\sqrt{\pi}}{2} \cdot \frac{1}{\sqrt{A_C}} \cdot \frac{1}{C} \quad (1)$$

where A_C is the contact area and C is the compliance term of the sample which is obtained from the total compliance (C_T) and the frame compliance (C_f) of the instrument, i.e. $C_T = C_f + C$. Moreover, it should be noted