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Synthesis of fluor-hydroxyapatite powder for plasma sprayed biomedical coatings: Characterization and improvement of the powder properties

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ABSTRACT

Fluor-hydroxyapatite (FHA) powder was synthesized by double decomposition in a view to produce bioactive and thermally stable coatings by plasma spray process. This work aims at studying the influence of chemical composition, microstructure and surface energy on the flowability of the FHA particles which is known as a determinant property during plasma spraying for the quality of the product in terms of yield and homogeneity of composition. The as-synthesized FHA powder was sieved in order to obtain two ranges of particles size: 50–80μm and 80–100μm. The phase composition and structure and physical characteristics of FHA particles have been determined by complementary analytical techniques (X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron spectroscopy and laser granulometry). Then, the FHA flowability was determined as recommended by the European Pharmacopeia.

The results showed that the 80–100μm FHA powder has a longer flow time compared to a reference hydroxyapatite powder whereas the 50–80μm FHA particles did not flow. We propose a simple treatment of the FHA particles using ethanol as solvent which showed to significantly improve the flowability of FHA powders.

1. Introduction

Plasma spraying is the most reliable industrial process for surface treatments that can produce adherent apatite coatings on biomedical implants [1–3]. This process consists in melting and transporting apatite particles to the metal substrate with a carrier gas (hydrogen and/or argon). It is also a source of enthalpy for heating particles to their melting point and transforming them into droplets. The coating is then formed by a stack of successive droplets of the molten material onto the metal substrate, which leads, after cooling, to a lamellar structure with a thickness between 15 and 200μm depending on the number of layers deposited by the plasma torch [4–6]. This complex process involves a large number of parameters which determine the final quality of the coating. The adhesion onto the substrate is provided essentially by increasing the roughness of the substrate surface before apatite deposit. Furthermore, the particles must have a sufficient speed at impact to spread over the substrate irregularities or the previously deposited particles [4–6]. In this case the molten state of particles plays an essential role.

Bioactive coatings based on hydroxyapatite (HA) are routinely deposited by thermal spray techniques on the shaft of metal hip prostheses as well as dental screws to improve bone growth and attachment. Despite their excellent clinical performances, prosthesis bio-integration is still limited due to the decomposition of the HA feedstock powder into several foreign phases during plasma spraying leading to a poor adherent HA-coating on the titanium surface [2,7,8]. Indeed due to the high plasma flame temperature (13000K), hydroxyapatite (HA), which is commonly used for plasma spraying, decomposes before its melting point [5,6,9]. This leads to the formation of secondary crystallized phases and an amorphous phase [5,6]. Since the solubility products of these phases are higher, they may dissolve more quickly and lead to coating degradation and prosthesis loosening [4]. Basically, coatings are prepared with HA particles having a size greater than 80μm [10], following conventional plasma spray parameters, the particles do not melt completely and recrystallize into hydroxyapatite [4]. However, this range of grain size causes a thick coating often responsible for peeling and poor adhesion of the coating on the metallic substrate. To limit this effect, new powders which are more thermally stable have been developed, such as chlorapatite (ClA) [9], strontium chlorapatite (Sr-ClA) and fluor-hydroxyapatite (FHA) [10]. These apatites exhibit better thermal stability than HA and consequently lead to a thinner coating with better adherence, which could be a decisive advantage to improve their durability [10,18].

Fluorinated compounds have been used in the biomedical field to treat diseases affecting bone density such as osteoporosis or to increase the resistance of tooth enamel to acid attack [11–13]. Farley et al. [14] have reported that fluoride ions promote mineralization and bone formation by stimulating bone cell proliferation and differentiation. Furthermore, the most promising properties are the thermal stability of fluorinated apatite at high temperatures as well as its bioactivity.

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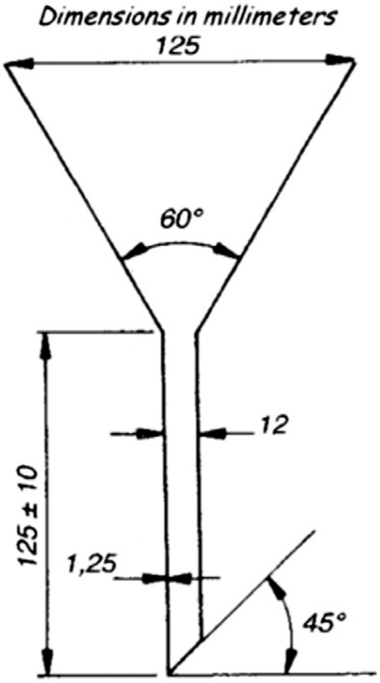

Fig. 1. Dimensions of the funnel used for measuring the flowability.

However, despite the existence of numerous studies demonstrating their bioactivity and thermal stability, very few fluor-based-biomaterials have reached the industrial development, i.e. dental glass ionomers. This problem may be due to the difficulty to produce fluorapatite at an industrial scale as well as the lack of confidence of clinicians in fluorinated materials. Substitution of a part or full of hydroxide ions by fluoride ions in the hydroxyapatite lattice could improve the resistance of these apatites to acidic conditions [15,16]. In addition, the use of fluorinated apatites as orthopedic coatings could promote cell proliferation and bone growth.

The effectiveness of plasma spray process, and characteristics of coatings obtained are strongly influenced by the physical and physico-chemical properties of the injected powders. The powder flow during the plasma processing dictates the coating quality in terms of yield and homogeneity of composition. A high flowability, which is intimately associated to the particle size distribution, shape, chemical composition, moisture and temperature, is a key requirement for the success of this type of process [6,8,10,17]. In addition, the density of powders is also an important parameter that should be considered, because it affects particle acceleration and their heating in the plasma flow. A full understanding of powder-flow behavior is essential when addressing segregation problems. Thus, optimized criteria such as apatite composition, particle size and density are selected in accordance with implant applications [8,17].

In this work, we focus on the manufacture of fluor-hydroxyapatite powders for the development of coatings onto orthopedic implants by plasma spraying. For the intended applications, two particle sizes are considered: 50–80μm and 80–100μm, the latter particle size range being the most widely used industrially. However, since the coating thickness could lead to the prosthesis loosening, we also considered the range 50–80μm with the ultimate goal of providing thin and adherent coatings. The objective of this study is to improve and control the flowability of both FHA powders using a treatment with ethanol and by varying the ratio ethanol/powder as well as the processing time. Surface free energies of hydroxyapatite and fluor-hydroxyapatite powders have been investigated. The nature of the surface of the particles can directly influence their flow properties. Also, surface free energies of biomaterials give information about their behavior after implantation, especially interactions with cells [1].

2. Materials and methods

2.1. Synthesis of FHA powders

The FHA powder synthesis was carried out by double decomposition method in aqueous solution at 80°C following a protocol previously proposed by Ranz et al. [18]. The synthesis was obtained by drop wise addition of phosphate and fluoride salts solution through a peristaltic pump into a reactor containing calcium salt solution while maintaining the pH at 7 with a pH-stat system. The calcium solution was prepared by dissolving 940g of calcium nitrate tetrahydrate ($Ca(NO_3)_2,4H_2O$) in 3500mL of deionized water. Then, di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) and ammonium fluoride (NH_4F) salts were dissolved in two separate flasks (315.65g of di-ammonium hydrogen phosphate in 3000mL of water and 15.56g of ammonium fluoride in 500mL of water).

The pH-stat system controlled the addition of ammonia solution to maintain the pH of the suspension at 7. All reagents were analytical grade and purchased from Sigma-Aldrich chemicals. Once precipitation was completed, the precipitate was slowly cooled to 40°C, filtered on a Büchner funnel and washed with distilled water (about 2 to 3 times the

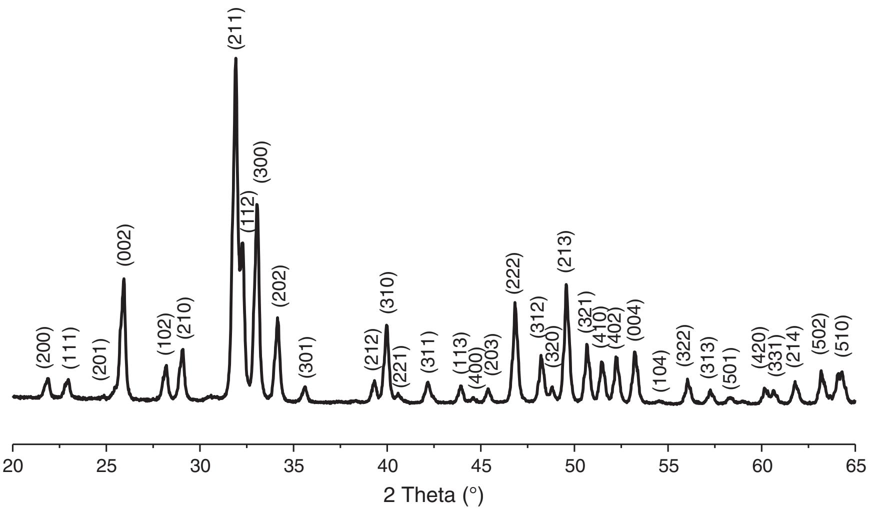

Fig. 2. X-ray diffraction diagram of the synthesized FHA powder.