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Effect of particle size on processing of bioactive glass powder for atmospheric plasma spraying

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ABSTRACT

The work addresses the effect of the particle size of a bioactive glass feedstock on the processing and microstructure of the resulting coatings obtained by atmospheric plasma spraying (APS). It was observed that the reduction of particle size negatively affects the flowability of the powder. In addition the thermal behaviour (weight losses, glass transitions, crystallisations, etc.) also depended on the particle size of the glass powder.

No coating was obtained with the coarser fractions (higher than 200 μm) due to their low melting degree in the plasma. For the intermediate fractions (200–63 μm) coatings were obtained but insufficient particle melting was produced. On the contrary, the finest fraction (<63 μm) needed a fluidiser which enabled the samples to be sprayed.

1. Introduction

From the sixties there is an important need for bioactive materials to heal or replace damaged areas of the body, due to the ability of these materials to prevent fibrous encapsulation when compared with an inert implant. Bioactive materials include hydroxyapatite (HA) ceramics, glasses, glass-ceramics and surface-active composite materials [1,2]. The most studied of the above materials are glasses, known as bioactive glasses (BGs), because of their higher bioactivity index [3].

BGs are materials based on mixtures of oxides from the SiO_2–CaO–MgO–Na_2O–K_2O–P_2O_5 system. The first BG developed was 45S5 bioactive glass or Bioglass®, which consists of 45% SiO_2, 24.5% CaO, 24.5% Na_2O and 6% P_2O_5 (all percentages in wt%) [4].

BGs preparation techniques include both melting (fusing and crushing) and sol-gel methods [5]. Employing the sol-gel technique, BGs exhibit more bioactivity than those obtained by melting in spite of having lower mechanical properties.

BGs are the most promising materials for bone grafting in several clinical applications, such as orthopaedic, dental, maxillofacial and otolaryngological [6]. Nevertheless, BGs' applications are limited due to their brittleness and poor mechanical properties. In order to solve these problems, BGs can be deposited onto a bioinert substrate to obtain a composite that improves its mechanical strength without changing its bioactivity [4].

There are many techniques to coat a substrate, usually metallic alloys, with BGs. These techniques can be enamelling, sol-gel method, electrophoretic deposition, laser cladding and thermal spraying techniques (plasma spraying and high-velocity oxy-fuel). Nonetheless, the most employed technique to spray BGs, since 1980, is thermal spraying, specifically atmospheric plasma spraying (APS) due to its low cost and industrial feasibility [1–4].

The literature shows many papers about optimisation of plasma spray conditions to obtain BG coatings by APS. Most of these papers also include the characterisation of the resulting coatings [7–12]. However, very few papers have dealt with the effect of the particle size of the bioactive glass feedstock on the processing and final microstructure of the obtained coatings. This aspect is of paramount importance when a glass powder feedstock must be fed into the plasma torch. Fine particle size is required for the powder to sufficiently melt and then adhere on the substrate during splat (melted particle) deposition in the APS process [13]. Moreover, too fine particles dramatically impair powder flowability making it difficult or impossible the pneumatic transport of the powder from the container to the plasma torch. Besides the glass powder particle size strongly affects the liquid phase sintering of the as-deposited

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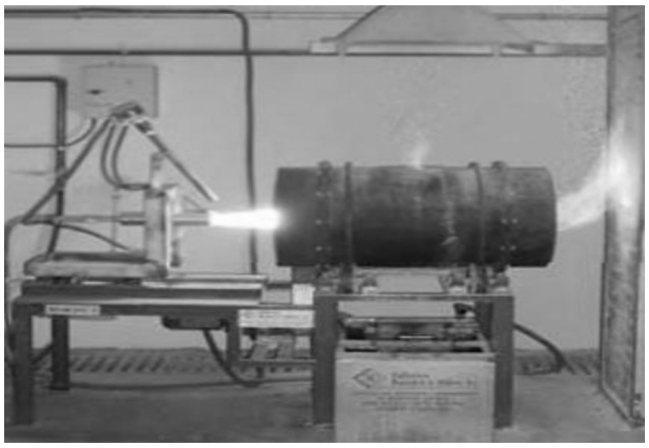

Fig. 1. Rotary furnace employed to obtain the frit.

Table 1
Nominal and as-melted chemical composition of the frit.

Composition (wt%)	SiO_2	P_2O_5	CaO	Na_2O
Nominal	45.0	6.0	24.5	24.5
As-melted	47.6	5.3	23.1	24.0

glass splats as well as the evolving of gas bubbles occurring during the rapid sintering of melted glass particles [14,15]. In other words, particle size of the BG feedstock is expected to drastically impact on the microstructure of the final coatings and therefore on their final properties.

Consequently, the present work aims at addressing the effect of the particle size of a given BG composition prepared by fusing and crushing on the flowability and thermal behaviour of the powder feedstock. The studied BG powder fractions were obtained from a frit by milling and sieving. Then the different BG powder fractions were sprayed onto metallic substrates by APS. The microstructure of the obtained coatings was examined. The final purpose of the research is to provide the necessary information to contribute to optimise the feeding of BG powder feedstocks in the APS process as well as the microstructure of the resulting coatings.

2. Experimental

2.1. Feedstock preparation

A mixture of analytical grade SiO_2, $Ca_3(PO_4)_2$, Na_2CO_3 and $CaCO_3$ was melted in the home-made rotary furnace as shown in Fig. 1, to get the frit. The mixture of raw materials was introduced into the furnace on the left side, whereas the melt was collected on the right side. The maximum temperature reached into the furnace was 1450 °C.

The melt was quenched into water and a BG frit was obtained. The chemical composition of the frit (Table 1) was determined by wavelength dispersive X-ray fluorescence spectrometry (AXIOS, PANalytical, The Netherlands). Table 1 shows the nominal and as-melted glass composition. As observed the frit composition is close to the nominal one. The frit was dry milled in a hammer mill. The milled powder was sieved to obtain different powder size fractions, which were conditioned and used as APS feedstocks. The different size fractions obtained are detailed in Table 2. The morphology of both coarse and fine fractions, with the typical angular shape of milled frit particles, can be observed in Fig. 2.

2.2. Feedstock characterisation techniques

The amorphous/crystalline character of the different size fractions was determined by X-ray diffraction (XRD) using a diffractometer (Advance diffractometer, Bruker Theta–Theta, Germany). The analysis was performed with Cu Kα radiation (λ = 1.54183 Å), generator settings of 30 kV and 40 mA and data were collected in a 2θ range of 5–90° with a step size of 0.02° and a scanning speed of 0.5 s step^{-1}.

Flowability of the BG fractions was determined by means of two different methods, namely Hausner ratio (HR) and angle of repose (α_M). Hausner ratio represents a method to estimate the flowability-cohesiveness of a given powder. Due to its simplicity HR has been extensively used to characterise APS feedstocks [16,17]. HR is defined as the quotient of the tapped density to the bulk (or poured) density of the powder. On the other hand to determine the angle of repose, a home-made device (Fig. 3) which consisted in a powder holder coupled to an angle protractor was used. The holder filled with powder rotates until the powder falls. Then, the clock hand hitched to the holder indicates the angle of repose.

Due to the sensitivity of the BG powder to moisture, flowability tests of some fractions were also carried out with samples which had been left in contact with humid ambient in a climatic chamber in order to determine changes in flowability with adsorbed water [18]. The powder fraction was dried in an oven at 110 °C and then cooled at room temperature in a desiccator. The dry powder was then introduced in the climatic chamber (WK3, Weiss Umwelttechnik, Germany) at 20 °C and 60% relative moisture and the adsorbed water was measured by weighing after 24 h inside the chamber so as to ensure that equilibrium was reached. These temperature and humidity conditions try to reproduce the typical conditions operating in the laboratory during plasma spray experiments.

The feedstocks thermal behaviour was investigated by simultaneous thermal analysis (DTA-TG) and heating microscopy. DTA-TG tests (TGA/SDTA 851e, Mettler Toledo, Switzerland) were carried out using a platinum crucible in air atmosphere, with a heating rate of 10 °C min^{-1} until a maximum temperature of 1200 °C. In order to complement these tests, a heating microscope (Misura 3, Expert Systems Solutions, Italy) was used and some characteristic temperatures for the powders were determined [19,20]. Cylindrical test samples of the powder fractions were prepared by pressing and, in the heating microscope, were subjected to a thermal cycle at a heating rate of 25 °C min^{-1} up to 1250 °C.

2.3. Coating deposition and characterisation

The different size fractions of the BG powder were sprayed onto metallic substrates by APS. Previously to deposition, the substrates (AISI 304) were grit-blasted and cleaned. Grit-blasting was performed using black corundum with a pressure of 4.2 Pa, and then the substrates were cleaned with ethanol. Surface roughness (R_a) of grit-blasted and cleaned substrates was measured with a roughness

Table 2
Size fractions obtained from the BG powder.

Powder fraction reference	BGGS	BGGS1[a]	BGGS2	BGGS3	BGGS4
Particle size distribution (μm)	700–200	400–200	200–100	150–63	<63
Representative size of each fraction (μm)	450	300	150	107	63

[a] The percentage of BGGS1 fraction included in the BGGS fraction is 37.2 ± 0.8%.

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