

# **NEW CERAMIC FRIT APPLICATIONS: BIOACTIVE GLASSES**

**Eugeni Cañas Recacha, Mónica Vicent Cabedo, M<sup>a</sup> José Orts Tarí,  
Enrique Sánchez Vilches**

**Instituto de Tecnología Cerámica (ITC). Asociación de Investigación de las  
Industrias Cerámicas (AICE). Universitat Jaume I (UJI), Castellón, Spain.**

## **1. ABSTRACT**

Companies in the frit, glaze, and ceramic colour producing subsector know a great deal about the different frit-manufacturing process stages such as raw materials milling and mixing, as well as fusing the raw materials mixture to obtain the frit. This knowledge can be used to break new ground in frit applications and to obtain products with high added value, such as bioactive glasses.

Bioactive glasses are amorphous materials that are able to interact with bone cells, thanks to surface growth of a hydroxycarbonate apatite (HCA) layer when they enter into contact with a biological fluid. This bioactivity, together with their relatively low cost compared to that of the materials used at present, makes such materials particularly attractive for obtaining prosthesis and implant coatings. Among the numerous coating methods, atmospheric plasma spraying is one of the most widely used techniques for industrial-scale deposition of this type of coating owing to its versatility, simplicity, and relatively low cost.

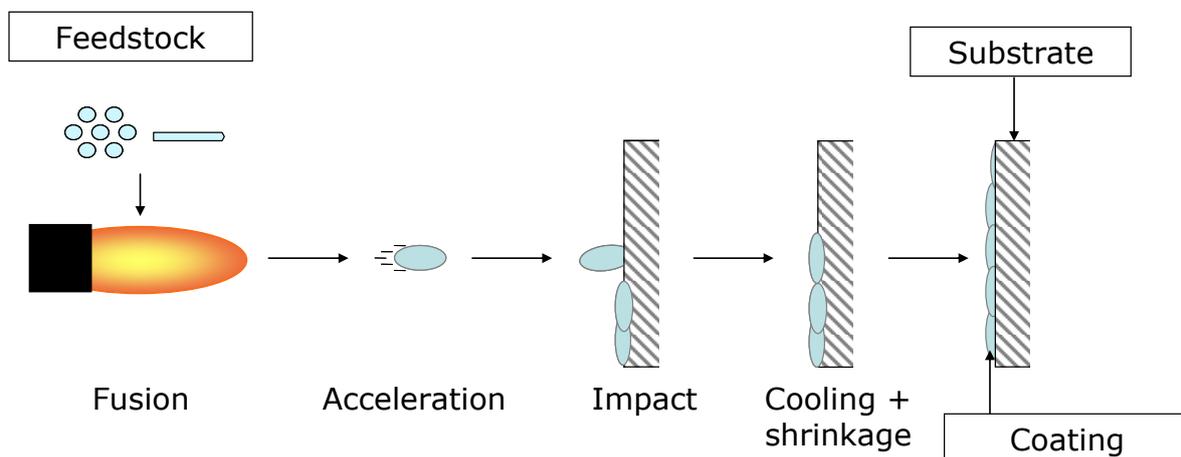
This study presents a methodology for obtaining bioactive glass coatings by thermal plasma spraying. The methodology includes: frit synthesis; design, preparation and characterisation of appropriate powders and bioactive glass

suspensions for thermal plasma spraying; optimisation of the deposition conditions for the obtainment of coatings from powders as well as from suspensions; and characterisation of the end coatings.

It was verified that, after deposition, the resulting coatings exhibited the typical microstructure of layers deposited by thermal plasma spraying. In this case, as feedstock of a glassy nature was involved, the microstructure consisted of a matrix of flattened drops of molten glass, together with rounded pores and cracks. The results obtained also indicated that the amorphous nature of the jetted frit was maintained in the end coating, as was intended. However, low adhesion to the substrate was also observed, it being necessary to use a bonding layer between the substrate and the bioactive glass layer. Consequently, further investigation is needed to improve the bond strength and other properties of these coatings, as well as to evaluate their bioactivity.

## 2. DESCRIPTION OF THE STEPS FOR OBTAINING A BIOACTIVE COATING

Bioactive glass coatings can be obtained, among other techniques, by thermal plasma spraying, which consists of fusing the feedstock (which may be made up of dry powders or suspensions) and accelerating the material towards a substrate. On hitting the substrate, the material cools and shrinks, forming a coating of solidified drops (Figure 1). This approach for obtaining bioactive coatings is very interesting because there is no crystallisation during deposition, owing to the high temperatures in the plasma torch, the short residence time in the torch, and the rapid cooling (quenching) of the material upon deposition. The amorphous character of the coatings is a key property in this type of application because crystallinity reduces the material's bioactivity.



**Figure 1.** Scheme of thermal plasma spraying

The feedstock was obtained by the typical frit manufacturing process used in the ceramic industry (Table 1). For the selected composition, the raw materials mixture consisted of silicon oxide ( $\text{SiO}_2$ ), calcium carbonate ( $\text{CaCO}_3$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), and calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ), of the greater possible purity as the resulting material (substrate coated with bioactive glass) was intended for use as a prosthesis [1].

The raw materials were fused, first, according to the fusion method used in ceramic frit preparation (Figure 2). The melt was quenched to obtain the frit, this being a critical step in maintaining an amorphous structure and avoiding crystallisation or devitrification.

The frit or resulting bioactive glass was then dry milled and sieved by the same procedure as that used in the ceramic sector to obtain a frit (Figure 3). This milled frit or grit was the first feedstock for the thermal plasma spraying system [2].

The dry milled frit was subjected to wet milling by a procedure similar to that used in glaze preparation (Figure 4), in this case using an organic suspending medium. The resulting suspension was then the second feedstock for the thermal plasma spraying system [3]. When particle size of a suspension is to be reduced to an average diameter of a few micrometres, the suspension is milled again in a bead mill in the same way as ceramic ink is prepared for an injection system.

<p><b>Fusion</b></p>	<p>Raw materials</p> <p>Proportioning</p> <p>Mixing</p> <p>Feed hopper</p> <p>Melting furnace</p> <p>Cooling</p> <p>Water</p> <p>Air</p> <p>Drying</p> <p>Glass</p> <p><b>Figure 2.</b> Bioactive glass manufacturing process</p>
<p><b>Dry milling</b></p>	<p>Milling</p> <p>Sieving</p> <p><b>Figure 3.</b> Process used to obtain bioactive glass powder fractions</p>
<p><b>Wet milling</b></p>	<p>Milling</p> <p>Obtainment of a suspension</p> <p><b>Figure 4.</b> Process used to obtain a bioactive glass suspension</p>

**Table 1.** Analogy between the ceramic frit and glaze preparation methodology and the methodology for preparing glass as feedstock for obtaining bioactive coatings

### 3. EXPERIMENTAL DEVELOPMENT AND RESULTS

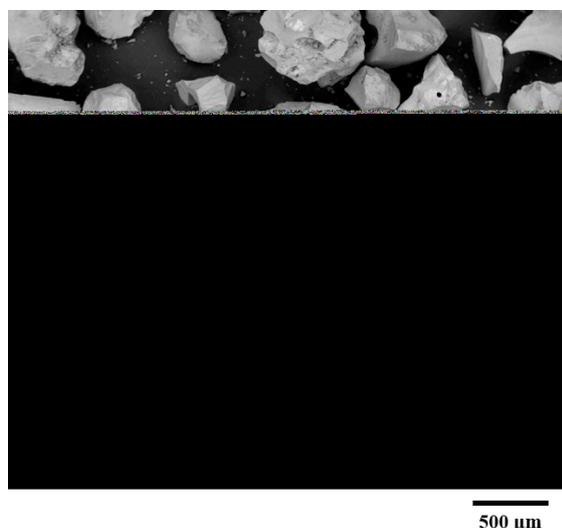
The raw materials were fused in a pilot plant furnace used to obtain ceramic frits. Table 2 details the chemical analysis of the frit obtained and that of the nominal frit, corresponding to that of a commercial bioactive glass (Bioglass®). It may be observed that the frit obtained in the laboratory was similar to the commercial glass.

Oxide (%)	SiO <sub>2</sub>	Na <sub>2</sub> O	CaO	P <sub>2</sub> O <sub>5</sub>
Nominal composition	45	24.5	24.5	6
Frit	47.6	24	23.1	5.3

**Table 2.** Chemical analysis of the nominal frit and the frit obtained in the pilot furnace

The frit (bioactive glass) was dry milled in a hammer mill and the resulting powder was sieved to different mesh apertures between 63  $\mu\text{m}$  and 700  $\mu\text{m}$  in order to obtain different working powder fractions as feed for the thermal plasma spraying system. By way of example, figure 5 shows the morphology of the powder fraction 200–700  $\mu\text{m}$ .

Owing to the poor flowability of the fine fraction ( $d < 63 \mu\text{m}$ ), in order to be able to feed the powder homogeneously into the spraying system, it was necessary to add 1% pyrogenic hydrophobic silica fluidiser.



**Figure 5.** Micrographs of the dry milled and sieved glass at 200–700  $\mu\text{m}$

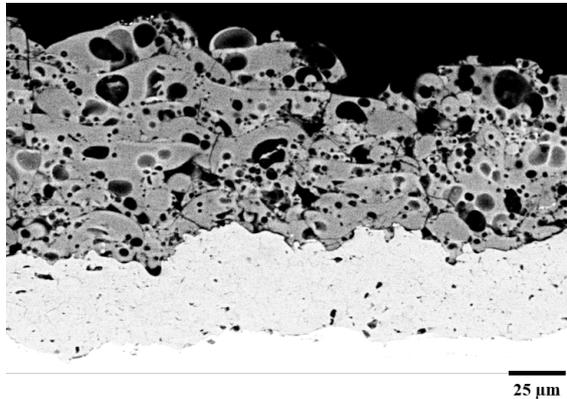
The finest powder fraction was then wet milled in a planetary ball mill for 60 minutes using dipropylene glycol methyl ether as medium. The resulting suspension was ground in a bead mill for 180 minutes, yielding a bioactive glass suspension with an average particle size of 2.2  $\mu\text{m}$ . This suspension was also used as feedstock for the thermal spraying system.

Both the powder (milled frit) and the bioactive glass suspension were used in the thermal plasma spraying system, their amorphous character being verified by X-ray diffraction (XRD). With a view to obtaining coatings with good bonding between the metallic substrate and the glass layer, a titanium oxide layer was previously jetted as bonding layer.

The microstructure of the coatings resulting from the milled frit exhibited the typical microstructure of plasma-deposited layers. However, unlike other coatings obtained from refractory oxides such as alumina or zirconia, owing to the thermal treatment undergone by the material during jetting through the plasma torch, liquid phase was generated and, when this hit the substrate, it led to partial sintering of the coating and generated closed porosity. As a result, the porosity was greater than that corresponding to a refractory material (alumina or zirconia) coating and, in addition,

the pores were rounded. The microstructure of a bioactive glass coating obtained from the powder is depicted in figure 6, which shows the features described.

The microstructure of the coating obtained from a glass particle suspension is shown in figure 7, in which a different, thinner microstructure may be observed, owing to the difference in particle size between the two feedstocks.



**Figure 6.** Micrograph of the coating obtained from the bioactive powder (milled frit)



**Figure 7.** Micrograph of the coating obtained from the bioactive glass suspension

Finally, the amorphous character of every coating was verified by XRD. Coating bioactivity was determined by dipping tests in simulated body fluid (SBF) at the University of Erlangen (Germany), verifying their bioactive character.

## 4. CONCLUSIONS

A methodology is presented for the obtainment of bioactive glass coatings by thermal plasma spraying. The feedstock preparation method is similar to the unit operations used in the ceramic frit and glaze manufacturing process.

The methodology enabled both bioactive glass powders and suspensions to be obtained, which were subsequently used as feedstock for a thermal plasma spraying system, yielding coatings with appropriate properties for use as products with high added value in prostheses.

## ACKNOWLEDGEMENTS

The authors of this study thank Universitat Jaume I of Castellón for the support provided in funding the project RECUBIO (P1-1B2013-69) and thank the company FRITTA, S.L. for the fusion of the material in a pilot furnace.

## REFERENCES

- [1] Jones JR (2013) Review of bioactive glass: From Hench to hybrids. *Acta Biomater* 9:4457-4486.
- [2] López V, Vicent M, Bannier E, Cañas E, Boccaccini AR, Cordero L, Sánchez E (2014) 45S5 bioactive glass coatings by atmospheric plasma spraying obtained from feedstocks prepared by different routes. *J Mater Sci* 49:7933-7942.
- [3] Bolelli G, Bellucci D, Cannillo V, Gadov R, Killinger A, Lusvarghi L, Müller P, Sola A (2015) Comparison between Suspension Plasma Sprayed and High Velocity Suspension Flame Sprayed bioactive coatings. *Surf Coat Technol* 280:232-249.