

## Laser cladding of bioactive glass coatings

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### ABSTRACT

Laser cladding by powder injection has been used to produce bioactive glass coatings on titanium alloy (Ti6Al4V) substrates. Bioactive glass compositions alternative to 45S5 Bioglass<sup>®</sup> were demonstrated to exhibit a gradual wetting angle–temperature evolution and therefore a more homogeneous deposition of the coating over the substrate was achieved. Among the different compositions studied, the S520 bioactive glass showed smoother wetting angle–temperature behavior and was successfully used as precursor material to produce bioactive coatings. Coatings processed using a Nd:YAG laser presented calcium silicate crystallization at the surface, with a uniform composition along the coating cross-section, and no significant dilution of the titanium alloy was observed. These coatings maintain similar bioactivity to that of the precursor material as demonstrated by immersion in simulated body fluid.

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### 1. Introduction

For many years the standard consideration when choosing a material to be used in the body was that the best material is the most inert material. Nowadays there is an increasing interest in materials that develop a “bioactive fixation” where the interface between implant and tissue develops a biological bond. Among these materials are bioactive glasses, which are able to promote implant–bone bonding and bone proliferation [1].

In order to solve the lack of strength of bulk bioactive glasses for load-bearing applications, coatings of these bioactive glasses on metallic prostheses have been developed. The first applied coating methods (enameling, plasma spraying and rapid immersion) presented some problems: frequently, the coating porosity and cracks penalized the adhesion strength reliability at the metal–glass interface [2]. More recently other methods have been tested to produce bioactive glass coatings on implants, i.e. pulsed laser deposition [3,4], ion beam sputtering [5] and sol–gel technique [6]. To overcome the common difficulties of obtaining a sound bioactive glass coating, composition variations from 45S5<sup>®</sup> bioactive glass were developed to match the thermal expansion coefficient of the metallic substrate, avoiding an excessive glass reactivity with the substrate and even modifying the glass viscosity.

In the glass system Na<sub>2</sub>O–K<sub>2</sub>O–MgO–CaO–P<sub>2</sub>O<sub>5</sub>–SiO<sub>2</sub>, the thermal expansion coefficient (CET) is increased by Na<sub>2</sub>O, K<sub>2</sub>O and CaO content [7,8]. Diverse empirical correlations allow one to estimate the CET as a function of the glass composition and thus

different compositions can be tailored to match the metal alloy CET. Nevertheless, these changes on glass composition produced a significant reduction of glass bioactivity compared to that of 45S5<sup>®</sup> bioactive glass [1,9]. Furthermore, bioactive glass viscosity–temperature dependence and the surface tension–temperature dependence are important properties in coating processes. The wettability over a metallic substrate is determined by the surface tension and viscosity of the bioactive glass, thus high viscosity–temperature variations can penalize coating wettability. Again, the composition is a factor affecting the bioactive glass viscosity–temperature evolution; therefore, viscosity reductions can be achieved by modification of the glass components proportions [7,10].

Laser cladding is a coating technique that has demonstrated several advantages in the metallurgical field such as the following [11]:

- controlled shape of the clad within certain limits
- localized heating which reduces thermal distortion and the size of the heat-affected zone
- flexibility of the process
- controlled levels of dilution
- smooth surface finish, near isotropic mechanical properties, fine quench microstructures and good fusion bonding
- minimum surface preparation required
- high deposition rate.

In the biomedical field this technique has already been applied to produce calcium phosphate coatings on Ti6Al4V alloy [12–16] but not for bioactive glass coatings. Therefore, the purpose of the

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present study was to investigate the potential of the laser cladding technique to produce a bioactive glass coating on Ti6Al4V alloy substrate.

## 2. Materials and methods

### 2.1. Precursor materials

The bioactive glass compositions considered in this work are listed in Table 1. The reagents used to prepare the glass precursor mixtures were high-purity  $\text{SiO}_2$ ,  $\text{CaCO}_3$ ,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{K}_2\text{CO}_3$ . The bioactive glasses with composition equivalent to 45S5 and 52S4.6 Bioglass® were obtained from the decarbonation and melting (3 h at 1250 °C) of the mixture and subsequent refinement at 1400 °C for 1 h in a Pt crucible. The glass of composition S520 was prepared following the method described in Ref. [17]. All glass melts were rapidly quenched in water and subsequently dried. The obtained glass frits were ground by means of an agate mill and sieved to a particle size between 60 and 150  $\mu\text{m}$ .

Ti alloy (Ti6Al4V) plates with a thickness of 6 mm and dimensions of  $40 \times 20 \text{ mm}^2$  were used as substrates without a special surface finishing after normal machining. The composition of the Ti6Al4V plates is as follows: 0.02% C, 0.001% H, 0.19% Fe, 6.27% Al, 4.02% V and 89.50% Ti.

### 2.2. Physical characterization of precursor materials: hot-stage microscopy (HSM)

A side-view hot-stage microscope (HSM), EM 201, with image analysis system and electrical furnace, 1750/15 Leica, was used. The microscope projects the sample image through a quartz window and onto the recording device. The computerized image analysis system automatically records and analyses the sample geometry during heating. HSM software calculates the percentage decrease in height, width and area of the sample images relative to the initial shape of the sample as well as the contact angle.

During shrinkage stage (sintering), the dimensions of the HSM sample are reduced but the shape keeps substantially invariable. In glasses, the driving force for sintering is the decrease in surface tension. The surface tension provokes the formation of necks between glass particles that will later soften. The sintering stage finishes when the sample reaches the maximum density and there is a temperature range in which the dimensions do not significantly change until the vitreous phases are fluent enough.

The determination of the characteristic viscosity points (temperatures of first shrinkage ( $T_{FS}$ ), maximum shrinkage ( $T_{MS}$ ), softening ( $T_S$ ), half ball ( $T_{HB}$ ) and flow ( $T_F$ )) by means of hot-stage microscopy (HSM) was carried out according to the procedure described in Refs. [18,19]. Thermal properties such as glass transition temperature ( $T_g$ ), crystallization temperature ( $T_c$ ) and melting point ( $T_m$ ) were obtained by differential thermal analysis (DTA). These DTA measurements were performed with a Setaram instrument Model Setsys Evolution 16/18 using powdered  $\text{Al}_2\text{O}_3$  as inert reference material and employing  $50 \pm 5 \text{ mg}$  of glass powder.

The definition for temperature of first shrinkage and maximum shrinkage are well explained in Ref. [19]. The softening point takes place when the liquid phases formed in the sample emerge at the

surface. From this point, the shape of the sample suffers substantial variations controlled by the surface tension of the liquid phases. The software of the HSM determines specific points in the deformation and flow rates according to geometrical considerations. The sample shape factor is a measure of the difference between the test piece's shadow and an ideal semicircle. The softening temperature is the first temperature at which the sample shape factor has changed by 1.5% with respect to the first image and the tracked corner angle has increased by 10%.

The half ball point is the first temperature at which the shape factor is at least 0.985 and the test piece's height is half of its base width. If glass behaves in a normal way, the contact angle at this temperature is near 90°. But in many cases, the contact angle can be much higher; the sample can look like a ring bell. These anomalies are attributed to the formation of heterogeneous phases in the interior of the sample such as crystallizations or phase separation.

The flow temperature is the first temperature at which the test piece is melted to either a third of its original height (DIN 51730 1984) or a third of its height at hemisphere temperature (DIN 51730 1998-04/ISO 540 1995-03-15). At this temperature the sample is completely liquid and melted.

In order to explore the glass wettability on the titanium alloy as close as possible to the laser cladding processing conditions, measurements were conducted on Ti6Al4V as substrate at a heating rate of  $10 \text{ °C min}^{-1}$  and in a protective Ar atmosphere. Glass powders with a particle size  $<60 \mu\text{m}$  were cold pressed into cylindrical shape samples of 3 mm height and 3 mm diameter and placed on  $10 \times 15 \times 1 \text{ mm}$  titanium plates. The temperature was measured with a Pt/Rh (6/30) thermocouple placed under the plate and in contact with it. The maximum temperature of the experiment was 1300 °C.

### 2.3. Laser cladding

The lateral powder feeding technique was applied to obtain the coating by laser surface cladding. This technique involves blowing particles of the precursor material by a carrier gas over the metallic substrate that is moving across this powder flow and the laser beam (Fig. 1). A stationary high-power laser radiation is directed to the surface of the substrate. The laser beam heats up the precursor material cloud and creates a molten pool on the metallic substrate where the particles impinge. A shielding inert gas is applied on the interaction zone to avoid oxidation. Rapid quenching of the molten pool takes place as it goes away from the laser irradiated area. Thus, the final result is a coating on the surface of the metallic substrate.

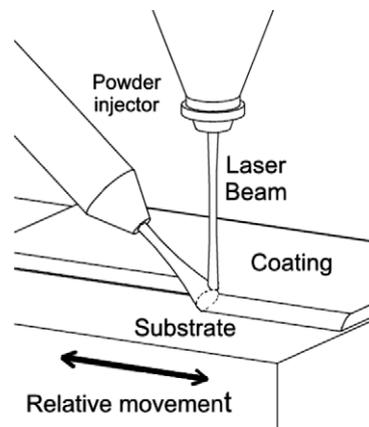


Fig. 1. Sketch showing the principle of operation of laser cladding.

Table 1  
Composition in mol.% of the glasses studied.

Denomination	$\text{SiO}_2$	CaO	$\text{Na}_2\text{O}$	$\text{P}_2\text{O}_5$	$\text{K}_2\text{O}$
45S5	46.1	26.9	24.4	2.6	–
S520	52.0	18.0	20.9	2.0	7.1
52S4.6	52.1	23.8	21.5	2.6	–

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