



Enamelled coatings produced with low-alkaline bioactive glasses



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ABSTRACT

Enamelling is a relatively easy and inexpensive technique to produce glass coatings. In this contribution, three different low-alkaline bioactive glasses, modified with Na₂O and/or K₂O for a total alkaline content of 4.6 mol%, were enamelled on Ti6Al4V substrates for potential orthopaedic applications. The glasses in powder form were applied by means of a precipitation-based method and thermally treated in the 800–850 °C range; in particular, the enamelling temperature required to obtain uniform coatings increased with increasing K₂O amounts. The SEM observation revealed that the coatings were about 100 μm thick, with a crack-free interface with the metal substrate mediated by the development of titanium oxides. Even if the low-alkaline glasses are characterised by a high crystallization temperature, the coatings underwent a partial devitrification, especially in the presence of K₂O. However, the development of bioactive crystalline species, such as wollastonite, was beneficial, in that the new phases not only improved the local mechanical properties (in terms of Vickers microhardness, from 232.1 ± 76.8 HV for the Na₂O-modified glass coating to 317.9 ± 48.8 for the K₂O-modified one), but still preserved the apatite-forming ability in a simulated body fluid.

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1. Introduction

Bioactive glasses are ideal candidates for the fabrication of orthopaedic implants. In fact, it is widely recognized that bioactive glasses, especially silicate ones, are able to interact with the host bone tissue after implantation, creating a stable interface which is a preliminary requirement for the prosthesis' fixation [1,2]. Moreover the ions released by silicate bioactive glasses may exert a stimulatory effect on the genes responsible for the bone regeneration process [3–6]. In particular, the glasses belonging to so-called Bioglass® family, proposed by Prof. Hench at the end of the 1960s, are the target of an intense research activity, due to their strong bone-bonding ability. The 45S5 Bioglass®, which is the main representative of this group, has been approved by the US FDA and it has been applied in clinical practice for the treatment of periodontal diseases, for middle-ear surgery and for orthopaedic implants [7–9]. In order to overcome their intrinsic brittleness, bioactive glasses are mainly used as functionalizing coatings on metal substrates, which, in turn, offer the required mechanical reliability also for load-bearing applications. As a consequence, single-phase, as well as composite and multi-layered coatings based on bioactive glasses have already been proposed in the literature on account of their excellent osteo-integration ability. Over the years, significant contributions have been put forward by various research groups, such as Tomsia et al. [4, 5,10–18], Verné et al. [19–21] and also by other authors [22–25].

Several techniques are currently available to deposit glass coatings [26,27]. Nonetheless, enamelling is still widely diffused, since it is

relatively easy and inexpensive. Moreover, since the enamelling technique is based on a simple thermal treatment, a kiln may be sufficient so that complicated facilities are not required. At most, the thermal treatment may be carried out under controlled atmosphere (low vacuum) [28]. However, in spite of its apparent simplicity, the enamelling technique requires an accurate setting of the thermal schedule. Indeed, the temperature must be high enough to make the glass soften and spread on the substrate uniformly. However, an excessive temperature may comport a degradation of the substrate. For example, the $\alpha \rightarrow \beta$ transformation occurs between 885 °C and 950 °C for unalloyed Ti and between 955 °C and 1010 °C for Ti6Al4V, depending on the impurity nature and content [15]. The process is relatively more straightforward with alumina and other ceramic substrates, which indeed are stable up to very high temperature; as a drawback, high-temperature treatments are expected to promote the diffusion of Al³⁺ or other ions from the substrate towards the coating, thus altering the original bioactivity of the glass [20]. Another problem with enamelling is the possible heat-induced devitrification of the glass. In fact, the aforementioned 45S5 Bioglass® and most of the bioactive glasses derived from its formulation are prone to crystallize even at low temperature. It is known from the literature that the 45S5 Bioglass® experiences a glass-in-glass phase separation at 570 °C, and this catalyses the subsequent extensive crystallization which occurs already at 610 °C [29–32]. Strictly speaking, the growth of new crystalline phases, mainly sodium-calcium silicates for the 45S5 Bioglass®, does not inhibit the bioactivity of the glass completely. Nevertheless, the devitrification greatly retards the reaction kinetics of the glass in a physiological environment and, hence, it delays the development of a stable interface with the bone tissue after implantation [33].

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The present contribution is focused on the production of enamelled coatings with low-alkaline bioactive glasses. The relatively low content of glass modifiers changes the thermal behaviour of these glasses with respect to the 45S5 Bioglass®, retarding the devitrification and promoting the crystallization of wollastonite instead of sodium–calcium–silicates. This is a key issue, since silicate bioactive glasses with sodium–calcium–silicate crystallization are really reactive to high-temperature treatments, whereas glasses with wollastonite crystallization are more stable at working temperatures [34,35]. This is expected to make the enamelling process much easier.

More in detail, each one of the three glasses under exam contains alkaline oxides (Na₂O and/or K₂O) for a total amount of 4.6 mol%. As shown in Table 1, the so-called BG_Ca glass was derived from the standard 45S5 Bioglass® by reducing the Na₂O content down to 4.6 mol%, which is the lowest limit for the “bioactive area” of the Na₂O–CaO–SiO₂ system with 2.6 mol% of P₂O₅ [36,37]; the BG_Ca–Mix glass was obtained from the BG_Ca by replacing 2.3 mol% of Na₂O with K₂O [38] and the BG_Ca–K glass was formulated by substituting Na₂O with K₂O completely [38,39]. According to previous contributions [37–39], all these glasses crystallize at high temperature (over 850 °C, but still below the $\alpha \rightarrow \beta$ transformation temperature of Ti6Al4V; see Table 1) with the development of wollastonite as the main phase, and therefore they represent an optimal choice for the enamelling process on Ti6Al4V substrates. However, the presence of Na₂O and/or K₂O affects the specific behaviour of the glasses and indeed the target of the present research is to determine the impact of the alkaline oxide nature (and relative amount) on the properties of the final coatings.

Some metallic materials, such as cobalt-based alloys or Al- and V-free Ti-based alloys, are now emerging as new substrates for orthopaedic implants due to their properties. For example, some β and near- β Ti alloys, if adequately processed, show a lower elastic modulus (values as low as 44–51 GPa) with respect to “conventional” $\alpha + \beta$ alloys such as Ti6Al4V, whose elastic modulus is about 110 GPa. This is useful to limit the so-called stress-shielding effect [40]. Nevertheless, in the present contribution the well-established Ti6Al4V alloy was considered as the substrate because Ti and its alloys, especially the aforementioned Ti6Al4V, have been used increasingly for the fabrication of orthopaedic devices for more than 40 years [40] and the Ti6Al4V, in particular, is still the most commonly used $\alpha + \beta$ titanium biomedical alloy [41]. Moreover, the same enamelling technique, proposed here for Ti6Al4V substrates, can be in principle applied also to other metals and alloys, provided that the firing temperature is adjusted to the thermal stability limits of the new substrate.

2. Materials and methods

The detailed analysis of the production, properties and thermal behaviour of the BG_Ca, BG_Ca–Mix and BG_Ca–K glasses has already been proposed in previous contributions [37–39]. The main results are briefly summarized here in view of the coatings' deposition. All the low-alkaline bioactive glasses under exam were produced from commercial raw materials in powder form (Na₂CO₃ and/or K₂CO₃, CaCO₃, Ca₃(PO₄)₂, SiO₂, all analytical grade from Carlo Erba Reagenti, Italy). The powders were weighted, mixed and melted in a Pt crucible at 1450 °C after a decarbonation step at 1100 °C. The molten glass was

quenched in room-temperature water, dried and milled to a final size lower than 70 μ m. The Differential Thermal Analysis, DTA (NETZSCH, DSC 404), performed on 30 mg of glass powder from room temperature to 1400 °C with a heating rate of 10 °C/min, revealed very high values of both the glass transition temperature, T_g , and the crystallization temperature, T_c , for all the three glasses. In fact, as reported in Table 1, the T_g increased from 700 °C to 725 °C and the T_c increased from 850 °C to 920 °C for increasing amounts of K₂O [37–39].

The substrates were Ti6Al4V plates, cut to a final size of 10 mm \times 10 mm (thickness: 3 mm). Just before enamelling, the surface to coat was polished with 1 μ m diamond paste and cleaned with acetone to limit the presence of impurities.

In order to produce the coatings, for each formulation the glass powder was dispersed in isopropanol and the suspension was poured on the metal substrates previously placed in a beaker. After that, the beaker was left in a kiln at 60 °C for 24 h to evaporate the liquid medium and to make the glass powder settle on the substrates. As described in detail by Vitale-Brovvarone et al. [21], the final thickness of the coating (t) can be controlled through the sedimentation parameters, since it depends on the amount (mass) of glass in the suspension (m_g), on the glass density (ρ_g), and on the bottom area of the beaker (A_b) according to the relation [21]:

$$t = \frac{m_g}{\rho_g A_b} \quad (1)$$

Even if the exact density slightly differs from glass to glass, in a first approximation the same value of $\rho_g = 2.99 \text{ g/cm}^3$ was used for all the compositions [42]. The planned thickness (t) was set to 100 μ m.

After removing the isopropanol completely, the samples were heat-treated to induce the glazing process. For each glass composition, several schedules were attempted, working between T_g and T_c , with and without a heating ramp of 10 °C/min from room temperature to the maximum temperature, and with and without an isothermal step of 1 h at the maximum temperature. As discussed in the following section, the best results were achieved heating the samples at 10 °C/min from room temperature to 800 °C for the BG_Ca glass, to 820 °C for the BG_Ca–Mix glass and to 850 °C for the BG_Ca–K glass (Table 2), and performing a final isothermal step of 1 h.

The surface and the polished cross-section of the final coatings were observed with an Environmental Scanning Electron Microscope, ESEM (Quanta 200-FEI Company, run in high vacuum mode), coupled with X-ray energy dispersion spectroscopy, X-EDS (Oxford INCA-350). The images of the cross-sections (400 \times) were analysed to determine the average thickness of the coatings, which was calculated on 5 different locations for each coating.

An X-ray diffraction, XRD (X'pert PRO, PANalytical, Almelo, The Netherlands), was performed on the surface of the as-produced coatings to investigate the possible development of new phases. Data were collected employing the CuK α radiation; the scans were processed in the angular range 10–70° 2 θ , with a step size of 0.017° 2 θ and a scan step time of 51.8 s.

Vickers micro-indentation tests (Wolpert Group, Micro-Vickers Hardness Tester digital auto turret, Mod. 402MVD) were carried out on the coatings' cross-section. A maximum load of 100 g_f was applied for 10 s and at least 10 indents (clear and crack-free) were considered and analysed for each coating [43].

Table 1
Glass compositions (in molar percent) and characteristic temperatures (glass transition temperature, T_g , and crystallization temperature, T_c) [37–39].

Glass	Composition (mol%)					Temperatures (°C)	
	Na ₂ O	K ₂ O	CaO	P ₂ O ₅	SiO ₂	T_g	T_c
BG_Ca [37]	4.6	–	45.6	2.6	47.2	700 °C	850 °C
BG_Ca–Mix [38]	2.3	2.3	45.6	2.6	47.2	720 °C	880 °C
BG_Ca–K [38,39]	–	4.6	45.6	2.6	47.2	725 °C	920 °C

Table 2
Enamelling temperature (T_{en}), indicative thickness (estimated variability: $\pm 5 \mu$ m), Vickers hardness (100 g_f) and mineralogical phases of the low-alkaline glass coatings.

Glass coating	T_{en}	Thickness	HV (100 g _f)	Phases
BG_Ca	800 °C	$\approx 108 \mu$ m	232.1 \pm 76.8 HV	Glass
BG_Ca–Mix	820 °C	$\approx 113 \mu$ m	329.0 \pm 81.0 HV	Glass, Wollastonite, SiO ₂
BG_Ca–K	850 °C	$\approx 121 \mu$ m	317.9 \pm 48.8 HV	Glass, Wollastonite, SiO ₂

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