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Devitrification studies of wollastonite–tricalcium phosphate eutectic glass

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Abstract

The present paper describes and discusses the devitrification and crystallization process of wollastonite–tricalcium phosphate (W–TCP) eutectic glass. This process was studied *in situ* from room temperature up to 1375 °C, by neutron diffractometry in vacuum. The data obtained were combined and compared with those performed in ambient atmosphere by differential thermal analysis and with those of samples fired in air at selected temperatures, and then cooled down and subsequently studied by laboratory XRD and field emission scanning electron microscopy fitted with energy X-ray dispersive spectroscopy. The experimental evidence indicates that the devitrification of W–TCP eutectic glass begins at ~870 °C with the crystallization of a Ca-deficient apatite phase, followed by wollastonite-2M ($CaSiO_3$) crystallization at ~1006 °C. At 1375 °C, the bio-glass-ceramic is composed of quasi-rounded colonies formed by a homogeneous mixture of pseudowollastonite ($CaSiO_3$) and α-tricalcium phosphate ($Ca_3(PO_4)_2$). This microstructure corresponds to irregular eutectic structures. It was also found that it is possible to obtain from the eutectic composition of the wollastonite–tricalcium phosphate binary system a wide range of bio-glass-ceramics, with different crystalline phases present, through appropriate design of thermal treatments.

Keywords: Glass-ceramics; Wollastonite; Tricalcium phosphate; Apatite; Neutron diffraction

1. Introduction

Natural and synthetic materials have been used clinically for many years to reconfigure anatomic structures for aesthetic and therapeutic reasons in several different surgical situations [1–6]. Calcium phosphate-based bioceramics have been used successfully in traumatology, dentistry and maxilla-facial surgery for over 30 years for bone repairing, primarily because of their biocompatibility, bioactivity and osteoconductivity [1,4]. In the last decade, intensive research has been devoted to preparing doped calcium phosphate materials to improve the osteogenesis, bioreabsorption rate, strength and phase composition of the resulting bioceramics. In particular, silicon [7–16] has received great attention as a constituent in phosphate-based bioceramics and glass-ceramics for biomedical applications. Silicon plays an essential role in the metabolic events conducive to endochondral and intramembranous bone formation [17–18] and, together with calcium, sodium and phosphorus (as released from 45S5 Bioglass), acts on the expression of certain genes responsible for controlling the cell cycle of animal and human osteoblasts and stimulates osteoproduction [19–21].

According to the above considerations, calcium phosphates with silicon additions are promising candidates for

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preparing bioceramics and glass-ceramics with improved osteogenic properties. In order to provide adequate levels of silicon, calcium and phosphorus ions to the biological environment at the same time as the material is replaced by new bone tissue, it should be biodegradable. Therefore, many attempts to improve the bioactivity level of ceramics and glass-ceramics have been carried out with formulations within the SiO_2–CaO–Na_2O–P_2O_5 quaternary system and within each of its constituent systems [1–4,22] and adding small amounts of different elements such as magnesium (A/W glass-ceramic) [23].

Therefore, the bioactivity and the total osteointegration of these bioceramics, bioactive glasses and glass-ceramics in the human body are extremely sensitive to the composition of the crystalline phases and/or glass present. However, the behavior of ceramic implants depends not only on composition but also on their microstructure.

When bioactive materials are implanted in a living body, the interaction between the bone tissue and these materials usually takes place only on their surfaces, with the remaining bulk of the material unchanged, often causing unfavorable shear loaded interfaces [24–29]. To improve the ingrowth of new bone into implants (osteointegration), the use of materials with an appropriate interconnected porous structure has been recommended [5,30–33]. The design of a porous ceramic implant material has the potential of controlling bone ingrowths. However, porous ceramic materials have very poor mechanical properties.

A new approach to overcoming this problem was proposed by De Aza et al. [34,35]. This is based on designing dense crystalline bioactive ceramic materials with the ability to develop an *in situ* porous hydroxyapatite-like (HA) structure when they are implanted into a living body [34,35]. The material designed was composed of two phases, pseudowollastonite ($CaSiO_3$ = psW) and α-tricalcium phosphate (α-$Ca_3(PO_4)_2$ = α-TCP). In an attempt to simulate bone structure, the crystalline microstructure of the material was developed by controlled slow solidification of the eutectic composition of the binary system wollastonite–tricalcium phosphate (W–TCP) (60 wt.% W and 40 wt.% TCP) [36]. This consisted of quasi-rounded colonies of alternating lamellae of psW and α-TCP. Such bioceramics are also known as Bioeutectics (De Aza PN, Guitián F, De Aza S. Bioeutectics. Internacional Trademark No. 1.780.697. Owner: Universidad de Santiago de Compostela, Spain; 1994).

This Bioeutectic ceramic has the property to restructure its morphology during exposure to simulated body fluid (SBF) [37] or human parotid saliva [38], by dissolution of the psW phase and subsequent pseudomorphic transformation of α-TCP into HA. *In vitro* studies carried out in a dynamic flow of SBF showed that the entire psW–α-TCP dense ceramic transforms into the porous apatite phase as a function of time [39].

Therefore, this Bioeutectic ceramic is a bioactive material which is totally replaced by HA in SBF [39]. Consequently, as expected, it behaves similarly in *in vivo* experiments, facilitating the osteointegration of the implant. Although, these *in vivo* studies are being carried out nowadays [5,40], the procedure used for the synthesis of these W–TCP potential implants restricts their size and even their shape [41].

However, by means of processing science, it is possible to tailor the size, shape and microstructure of this bioceramic potential implants. Here, it is appropriate to draw attention to glass-ceramic processing. Increasing interest in bioactive glass-ceramic materials [22,42–45] in the biomedical field has been aroused by two interesting advantages. First, these materials can be obtained in large pieces and with highly complex shapes; in fact, the first step of the process involves producing a glass that can be obtained using a variety of well-known inexpensive techniques [46,47]. The other advantage is that, by the effect of subsequent crystallization of the glass, glass-ceramic materials usually exhibit a controlled microstructure containing few or no residual pores. These features result in improved mechanical properties of the end product. However, the crystallization process requires a well-founded knowledge of the nucleation and growth mechanisms of the crystal phases [46–50].

Consequently, the present investigation focuses on the devitrification and crystallization study of W–TCP eutectic glass as a preliminary stage to obtaining this new Bioeutectic biomaterial in large pieces and complex shapes with controlled microstructure. This is the first stage to try to develop W–TCP implants with better bioactivity and improved mechanical properties by means of processing science.

Among the techniques used to understand the devitrification process of glasses, conventional thermal analysis has been widely used, e.g., thermo-gravimetric analysis, differential thermal analysis (DTA) and differential scanning calorimetry [51–53], but these techniques by themselves cannot help to identify the reaction products or the transient phases that result from each thermal event. Therefore, although it is possible to spot the temperatures at which the reactions happen, they do not provide a precise indication of the phases present. However, conventional methods of analysis require the reaction process to be abruptly interrupted, hence introducing external interference. This procedure makes this approach less reliable. That is why diffraction methods, such as neutron diffraction (ND), have also been used in the present work to identify phases that form and disappear as the temperature rises. Another important advantage of using neutrons is the ready penetration of thick samples. The experimental data so collected from the process taking place in the bulk of the sample are truly representative, as the diffraction signal comes from the whole specimen and not from the surface layer.

Therefore, the present paper describes and discusses the devitrification of this W–TCP eutectic glass studied *in situ* from room temperature up to 1375 °C, by neutron diffractometry (ND) in vacuum. The data obtained were combined and compared with those performed in ambient

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