

## Non-isothermal Devitrification Study of Wollastonite-Tricalcium Phosphate Bioeutectic<sup>®</sup> Glass.

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**Abstract.** This document describes and discusses the non-isothermal devitrification process of the wollastonite-tricalcium phosphate (W-TCP) eutectic glass. This eutectic glass has been studied *in situ*, from room temperature up to 1375 °C, by Neutron Diffractometry (ND) in vacuum. The data obtained were complemented and compared with those performed on ambient atmosphere by Differential Thermal Analysis (DTA) and with those of samples fired in air, at selected temperatures, and then cooled down and subsequently studied by laboratory X-ray Powder Diffraction (LXRD) and Field Emission Scanning Electron Microscopy (FE-SEM) fitted with Energy X-Ray Dispersive Spectroscopy (EDS). Selected samples have been investigated by quantitative full-phase analysis (including the amorphous content) using the Rietveld method. 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 (Ca<sub>9.92</sub>(P<sub>5.85</sub>O<sub>23.54</sub>)(OH)<sub>2.03</sub> (H<sub>2</sub>O)<sub>2.194</sub>) followed by wollastonite-2M ( $\alpha$ -CaSiO<sub>3</sub>) crystallization at ~1006°C. At 1375°C the bio glass-ceramic is comprised of quasi-rounded colonies formed by a homogeneous mixture of pseudowollastonite ( $\beta$ -CaSiO<sub>3</sub>) and  $\alpha$ -tricalcium phosphate ( $\alpha$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>). This microstructure corresponds to irregular eutectic structures and is similar to that of Bioeutectic<sup>®</sup> W-TCP material obtained previously, via controlled slow solidification of the eutectic composition, by some of the present authors. It has also been found that from the eutectic composition of the wollastonite – tricalcium phosphate binary system is possible to obtain a wide range of bio glass-ceramics through appropriate design of thermal treatments.

### Introduction

Pseudowollastonite ( $\beta$ -CaSiO<sub>3</sub> =  $\beta$ -W) -  $\alpha$ -tricalcium phosphate ( $\alpha$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> =  $\alpha$ -TCP) Bioeutectic<sup>®</sup> ceramics obtained by slow controlled solidification [1] have the property to restructure its morphology during exposure to simulated body fluid (SBF) or human parotid saliva [2] by dissolution of the  $\beta$ -W phase and subsequent pseudomorphic transformation of  $\alpha$ -TCP into hydroxyapatite (HA). *In vitro* studies carried out in a dynamic flow of SBF showed that the entire  $\beta$ W- $\alpha$ TCP dense ceramic transforms into porous apatite phase as a function of time [3]. Nevertheless, to date the procedure used for its synthesis restricts the size and even the shape of the potential implants [1-3]. At this point, glass-ceramic methodology has two interesting advantages. Firstly, these materials can be obtained in large pieces and with highly complex shapes. The other advantage is that glass-ceramic materials usually exhibit a controlled microstructure, containing few or no residual pores.

The present document describes and discusses the devitrification study of the W – TCP Bioeutectic<sup>®</sup> glass as a preliminary stage to obtain complex shapes with controlled microstructure, better mechanical properties and improved osteointegration after implantation in the human body.

## Materials and Methods

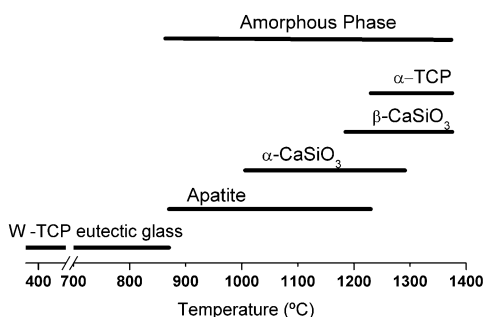
The stoichiometric eutectic composition (60.0 wt% W – 40.0 wt% TCP) was prepared from a mixture of reagent-grade  $\text{CaCO}_3$  (99.5 wt%, Merck), high-purity washed  $\text{SiO}_2$  Belgian sand (99.9 wt%) and high-purity synthetic TCP. The used TCP batch chemical composition determined by X-ray fluorescence analysis and expressed as weight percentage was: 54.22 CaO; 45.74  $\text{P}_2\text{O}_5$ ; 0.33 MgO; 0.10  $\text{Na}_2\text{O}$ ; 0.008  $\text{K}_2\text{O}$ ; 0.013 MnO; 0.037  $\text{Fe}_2\text{O}_3$ ; 0.004 SrO and 0.012  $\text{TiO}_2$ ; being 1.50 the Ca/P molar ratio.

The thoroughly mixed batch was melted using a Pt-10 wt% Rh crucible at 1600°C for 30 min. The obtained glass was subsequently annealed close to the glass transition temperature ( $T_g = 795^\circ\text{C}$ ) to relieve the internal stresses. Subsequently, a significant amount of glass was grounded to less than 65  $\mu\text{m}$  and characterized by X-ray fluorescence analysis to quantify the stoichiometric eutectic composition of the glass.

The non-isothermal devitrification process of this eutectic glass has been studied *in situ*, from room temperature up to 1375 °C, by Neutron Diffractometry (ND) in vacuum. The data obtained were complemented and compared with those performed on ambient atmosphere by Differential Thermal Analysis (DTA) and with those of samples fired in air, at selected temperatures during 6 min dwell time, and then cooled down and subsequently studied by laboratory X-ray Powder Diffraction (LXRD) and Field Emission Scanning Electron Microscopy (FE-SEM) fitted with Energy X-Ray Dispersive Spectroscopy (EDS). Selected samples have been investigated by quantitative full-phase analysis (including the amorphous content) using the Rietveld method. A protocol for such analyses can be found elsewhere [4]. Mixtures with a weighed amount (30.000 wt%) of a suitable standard,  $\text{CaF}_2$  (99.99%, Sigma-Aldrich) and the investigated samples were prepared. The powder patterns of the bio glass-ceramics were analyzed by Rietveld method with the GSAS (General Structure Analysis System) suite of programs [5].

## Results and Discussion

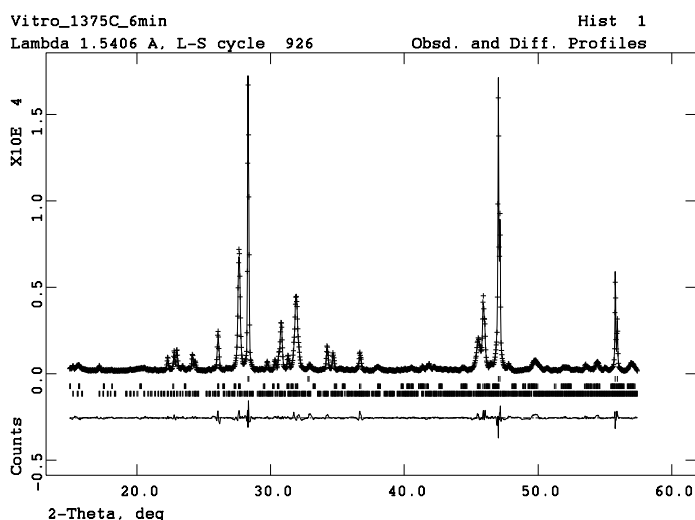
**Fig. 1** summarizes the results from neutron diffraction data. It has to be borne in mind that this is a non-equilibrium or dynamic diagram; the data used to construct the figure were recorded while heating the samples at a rate of  $5^\circ\text{C min}^{-1}$  from 600°C up to 1375°C, while neutron diffraction spectra were continuously registered. Each diffraction pattern (from 10 to 90°) is the result of the accumulation of the spectra recorded over 2.5 min. i.e., from 600 to 1375°C a pattern was obtained each 12.5°C. The existence of phase domains is clearly highlighted by their neutron diffraction peaks.



**Fig. 1.** Dynamic phase diagram of phases during the non-isothermal devitrification process of W-TCP eutectic glass at a rate of  $5^\circ\text{C min}^{-1}$ . Neutron diffraction data.

The results of room temperature laboratory X-ray Powder Diffraction (LXRD) and Rietveld quantitative amorphous content analysis (RQACA) from the heat-treated samples are summarized in **Fig.2** and **Tables 1-2**. These show the phase evolution with temperature at 900, 1100 and 1375°C respectively, with a holding time at each temperature of 6 min. Considering a standard free of

amorphous phases, RQACA relates the overall amorphous content to the overestimation of the internal crystalline standard in the Rietveld refinement [4]. The Rietveld plot ( $15-58^\circ/2\theta$ ) for the  $1375^\circ\text{C}$  analyzed sample is shown in **Figs. 2** as an example. The values of the pattern-dependent,  $R_{\text{WP}}$  disagreement factor [5,6] were evaluated, and they are listed in **Table 1**. The values are smaller than 10%, indicating good fits. Furthermore, the values of the phase-dependent,  $R_{\text{F}}$ , disagreement factor [5,6] are quite small; see **Table 1**, which indicates that fits to any given phase are very satisfactory. The final phase compositions for the three bio glass-ceramics from the full RQACA are given in **Table 2**. The overall amorphous phase contents of the analyzed bio glass-ceramics were derived from the refined  $\text{CaF}_2$  phase ratios and the phase fractions of the crystalline components obtained directly in the Rietveld study were renormalized by taking into account the overall non-diffracting fraction.



**Fig. 2.** GSAS Rietveld plot ( $15-58^\circ/2\theta$ ) for the  $1375^\circ\text{C}$  analyzed sample with the observed (crosses), calculated (line) and difference (bottom line) powder patterns. The marks correspond to the Bragg peaks of the different phases, from bottom to top:  $\alpha$ -TCP;  $\beta$ -W and  $\text{CaF}_2$  (internal standard).

**Table 1.** Some Rietveld refinement results for the bio glass-ceramics mixed with  $\text{CaF}_2$ .

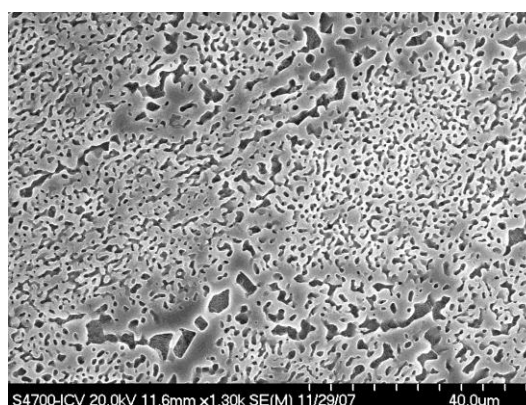
Sample	$R_{\text{WP}}$ %	$R_{\text{F}}$ $\text{CaF}_2$ %	$R_{\text{F}}$ Apatite %	$R_{\text{F}}$ $\alpha$ - $\text{CaSiO}_3$ %	$R_{\text{F}}$ $\beta$ - $\text{CaSiO}_3$	$R_{\text{F}}$ $\alpha$ -TCP
$900^\circ\text{C} - 6 \text{ min.}$	9.0	5.8	7.7	--	--	--
$1100^\circ\text{C} - 6 \text{ min.}$	8.6	3.8	4.1	5.3	--	--
$1375^\circ\text{C} - 6 \text{ min.}$	9.8	2.4	--	--	6.4	9.8

**Table 2.** Phase composition of the bio glass-ceramics from full quantitative Rietveld analysis.

Sample	Apatite wt%	$\alpha$ - $\text{CaSiO}_3$ wt%	$\beta$ - $\text{CaSiO}_3$ wt%	$\alpha$ -TCP wt%	Amorphous wt%
$900^\circ\text{C} - 6 \text{ min.}$	40.7(6)	--	--	--	59.3(4)
$1100^\circ\text{C} - 6 \text{ min.}$	34.6(7)	20.9(8)	--	--	44.5(5)
$1375^\circ\text{C} - 6 \text{ min.}$	--	--	36.6(7)	35.7(8)	27.7(6)

**Fig. 3.** Chemically etched surface of the samples fired at  $1375^\circ\text{C}$   $6 \text{ min}^{-1}$  in air and studied by FE-SEM /EDS. See text for details.

The microstructure of the sample thermal treated up to  $1375^\circ\text{C}$  is shown in **Fig. 3**. FE-SEM / EDS observation of the etched samples (5 vol% acetic acid for 1s) showed that is comprised of quasi-rounded colonies of W-TCP. The colonies are formed by an interlocked phase of  $\beta$ -W, which encloses well dispersed  $\alpha$ -TCP. The morphology of the material corresponded to irregular eutectic structures. This



microstructure is similar to that of Bioeutectic<sup>®</sup> W-TCP materials obtained by controlled slow solidification of the eutectic composition as can be seen elsewhere [1-3].

## Conclusions

With the information obtained, the following concluding remarks can be made:

1. The devitrification and crystallization behavior of the stoichiometric eutectic composition (60.0 wt% W – 40.0 wt% TCP) is similar in air and vacuum.
2. The first phase that nucleates and growth from the bulk glass is Ca-deficient apatite:  $\text{Ca}_{9.92}(\text{P}_{5.85}\text{O}_{23.54})(\text{OH})_{2.03}(\text{H}_2\text{O})_{2.194}$ . The apatite phase crystallization is detected from  $\sim 870^\circ\text{C}$ . This phase entirely decomposed at about  $\sim 1291^\circ\text{C}$ . This fact suggests that water is present in the glass in the form of OH groups and in an adsorbed form.
3. The second phase that begins to crystallize is  $\alpha$ - $\text{CaSiO}_3$  that appears at  $\sim 1006^\circ\text{C}$ . This low temperature phase totally disappears at  $\sim 1303^\circ\text{C}$ .
4. At  $\sim 1185^\circ\text{C}$  crystalline  $\beta$ - $\text{CaSiO}_3$  is detected and remains growing up to  $1350^\circ\text{C}$ .
5.  $\alpha$ - $\text{CaSiO}_3$  and  $\beta$ - $\text{CaSiO}_3$  coexist in a non-equilibrium condition from  $\sim 1185$  to  $\sim 1303^\circ\text{C}$  during the devitrification process.
6. At  $\sim 1230^\circ\text{C}$   $\alpha$ -TCP begins to crystallize. This phase is formed at the expense of the Ca-deficient apatite and remains growing up to  $1350^\circ\text{C}$ .
7. At  $1375^\circ\text{C}$  the devitrified eutectic glass is comprised of quasi-rounded colonies formed by a homogeneous mixture of  $\beta$ - $\text{CaSiO}_3$  and  $\alpha$ -TCP crystals, where  $\beta$ - $\text{CaSiO}_3$  is the continuous interlocking phase and  $\alpha$ -TCP is evenly distributed within it. The microstructure of the material corresponds to an irregular eutectic structure.
8. It has been found that from the eutectic composition of the wollastonite – tricalcium phosphate binary system is possible to obtain a wide range of bio glass-ceramics through appropriate design of thermal treatments.
9. Quantitative full-phase analysis (including the amorphous content) by Rietveld method using laboratory X-ray powder diffraction is a suitable technique to characterize the mineralogical composition of bio glass-ceramics.

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