

Phases Evolution of Bioactive Glasses during Crystallization for Orthopaedic and Tissue Engineering Applications

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INTRODUCTION: Bioactive glass 45S5 is currently used for dental and ear implants. We aim at extending its application to the orthopaedic and tissue engineering fields, via the processing of porous scaffolds. Our goal is the optimisation of the porous bioactive glasses mechanical and biological properties, via a careful understanding of the process–microstructure–biomechanical properties relations. In this study we report on the thermal transformation of the glass.

METHODS: High purity SiO₂, Na₂CO₃, CaCO₃ and P₂O₅ powders were mixed and melted in a Pt crucible to obtain the 45S5 bioaglass[®] (45%SiO₂; 24,5% Na₂O; 24,5% CaO and 6% P₂O₅ in weight). The melt were quenched in water and ground to a fine powder.

The thermal transformations of the material were first characterized via dilatometric measurements and differential thermal analysis (DTA). The crystallization process and the transformation kinetics were investigated by Differential Scanning Calorimetric analysis coupled with TGA (DSC/TGA). Several thermal treatments in the range of 600 to 1000°C were carried out on the glass powder. The different crystallized phases were studied with XRD and Infrared analysis. A rietveld analysis was performed on the XRD results to measure the cells parameters. Furthermore, SEM and TEM techniques were used on all the samples to observe the microstructure.

RESULTS: TGA analysis gives two main weight losses at 100 and 400°C which are due to the departure of free water and -OH groups principally. DTA, DSC and dilatometric analysis show that the glassy transition takes place at 550°C and that the crystallization process begins at 600°C. DSC results allow us to find out the necessary enthalpy need for crystallization and its kinetics. XRD diffractograms shows that the system crystallized principally under the Na₆Ca₃(Si₆O₁₈) phase. This structure shows a separation of its two principals peaks at 800°C. At this temperature a minor phase appears identified as Na₂Ca₄(PO₄)₂SiO₄. This steps corresponds to a shrinkage on the dilatometric curves. Fourier

Transform Infrared analyses confirm the presence of a cristallized phosphate phase and shows that amorphous phosphate is still present. DTA analysis gives a melting point of 1100 °C.

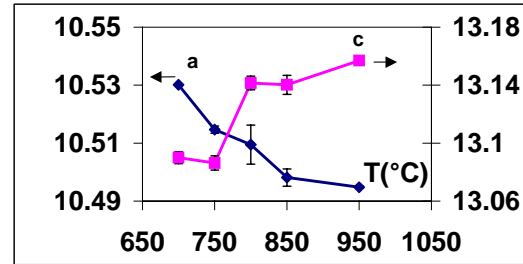


Fig 1: Evolution of the cell parameters with thermal treatment.

DISCUSSION & CONCLUSIONS: Several studies^{[1],[2]} show that the bioglass crystallizes principally in the Na₄Ca₄Si₆O₁₈ with Na₂CaSi₃O₈ as a minor phase. We found no evidence of the second phase and the major phase appears more likely to be Na₆Ca₃Si₆O₁₈ which has the same structure as Na₄Ca₄Si₆O₁₈. On the other hand we found a crystallized phosphate phase which can lead to a decrease in bioactivity of the crystallized 45S5 bioglass after 800°C. After the glassy transition and before the crystallization process, a separation of the glassy phase into two immiscible phases occurs^[3] (one phase rich in silicon and the other rich in phosphorus). We suppose that the first one leads to the major crystalline phase and the second one to the crystalline phosphate phase. The evolution of the crystalline phase (Figure 1) differs from this reported by Oshato and Takéuchi^[4] for pure Na₄Ca₄Si₆O₁₈. The difference between the two evolutions can be attributed to the presence of phosphate glassy phase. The behavior of phosphorous ions is not yet very clear and is under investigation.

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