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Glass Reactivity at High Temperature

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Glasses are metastable materials that can evolve during heat treatment. These transformations can be a desired effect to obtain specific properties (self-healing) or to form materials such as glass ceramics or glass foams. It can also be deleterious and alter the optical and physical properties of glass or degrade its chemical durability. In this work, we will show – through different studies performed during the last 10 years - the interest of using an Environmental Scanning Electron Microscope (ESEM) equipped with a high temperature furnace to directly observe the formation of crystals in glasses, phase separation, chemical reactivity or glass foaming. We will also endeavor to show the contribution of the use of recently developed devices or methodologies to these studies.

Glass elaboration: Glass elaboration from raw materials is a complex process during which many chemical reactions lead to the formation of reaction intermediates. The different stages of formation of these reaction intermediates are directly observed. Depending on their composition, they can contribute to the formation of crystals with particular morphologies at high temperature or lead to phase separation (molten sulfates...) [1].

Glass foam formation: The effect of the process atmosphere composition on the foam formation of glass containing reducing agent *(e.g.* graphite and MnO_2) was studied. Water steam facilitates glass grain sintering. This is probably due to the formation of hydroxyl groups at the glass grain surface that locally decrease the glass viscosity. We have shown that increasing the steam pressure from 50 Pa to 750 Pa decreases both sintering and foaming onset temperatures by approximately 100°C, favouring the formation of closed pores in viscous glass (Figure 1). At high temperature, the presence of water steam promotes foam formation [2].

Self-healing property: The self-healing property of glass-ceramic composites at high temperature is observed. Self-repair is obtained through the oxidation of healing particles (*e.g*. VB) without the need to increase the operating temperature (ranging between 650 and 950°C). It is shown that a crack could be healed by the VB oxidation products (V_2O_5 and B_2O_3) [3, 4].

Glass crystallization: Crystallization pathways of $BaO\text{-}CaO\text{-}Al_2O_3\text{-}SiO_2$ (BCAS) glass were determined as a function of time and temperature. The glass systems are a melted quenched bulk form and a deposited thin-film form. The composition of the crystallized phases depends on the geometry of the glass, and of the applied geometrical constraints. These constraints control the volume fraction of crystallized glass melt as a function of time and temperature, and thus modify the reactional pathways (Figure 2). Five different compounds crystallize in the glass bulk whereas only two different types of crystals are observed at the surface of the glass thin film, at T=960°C [5]. Glass crystallization has also been studied in other systems ($M_2O\text{-}P_2O_5\text{-}MoO_3$ glasses with M = Na, K, Cs and Ag) using classical and innovative techniques [6]. These techniques allow to describe the evolution of the morphology of the objects in 3D, at high temperature or to observe the formation of crystals in the backscattered electron mode at high temperature. All these studies have allowed us to observe the transformations at the microscopic scale on the glass material, to obtain original data and to describe these transformations using the HT-ESEM technique.

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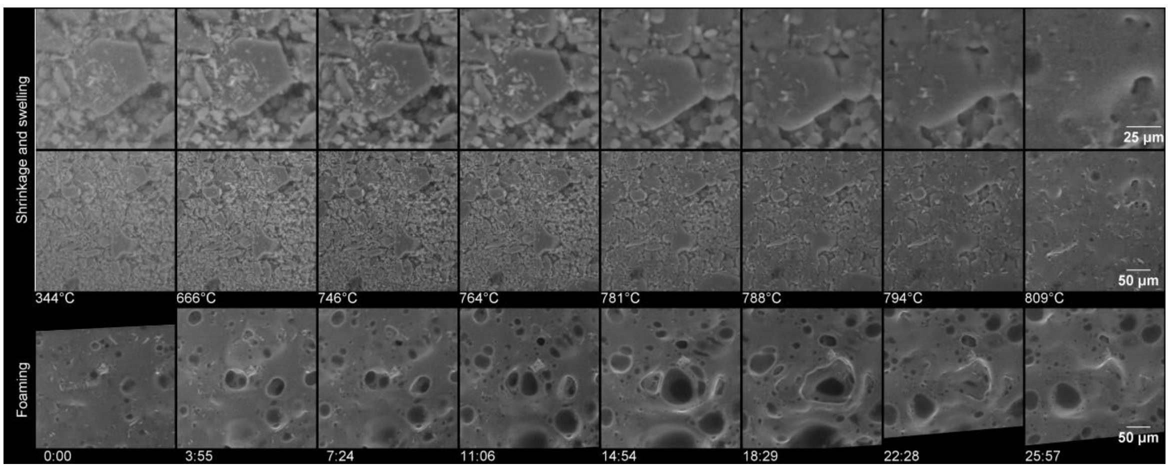

Figure 1. Morphological modifications observed on a "CRT glass + 4.4 wt.% MnO_2 + 0.3 wt.% C" sample during the *in situ* formation of glass foam in ESEM using a 750 Pa water vapour atmosphere.

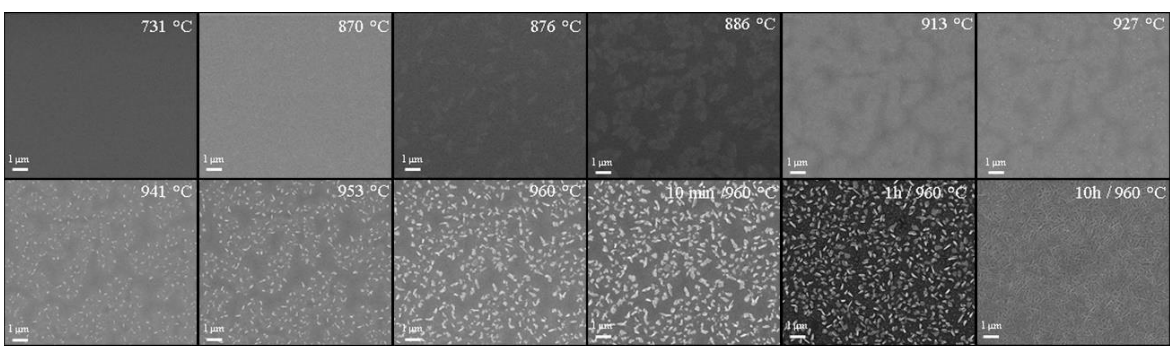

Figure 2. HT-ESEM micrographs showing the crystallization phases shapes of BCAS glass thin-film *vs* temperature and time at 960 °C.

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