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Image analysis study of crystallization in two glass compositions of nuclear interest

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ABSTRACT

Few prior studies of the crystallization properties of nuclear glass compositions have focused on the quantification of crystallization rates and the kinetics associated with heat treatments. We have quantified the crystallization of both apatite and powellite in two glass compositions containing simulated fission products using an image analysis technique based on SEM images. Samples are first heat treated at different temperatures (from 600 to 900 °C) and for different durations (from 1 h to 388 h). SEM images are then acquired and the image analysis technique is applied to quantify crystallization by extracting a few relevant crystal morphological parameters. These results permit a quantitative comparison of crystallization in the two glass compositions: nature of crystals, morphologies, thermal domains of crystallization, crystallization rates and kinetics are compared. Results show that image analysis is a suitable method when crystals are homogeneously distributed in the glass matrix. However, this technique should be used carefully in the case of a heterogeneous distribution of crystals in the material.

1. Introduction

The long-term storage of nuclear waste is a major world-wide environmental issue. In France, high-level radioactive wastes (HLW) obtained after reprocessing of spent uranium oxide fuel are commonly incorporated in a sodium aluminoborosilicate glass matrix. The glass composition results from an optimization of several parameters: nuclear waste integration within the glass network, glass feasibility at industrial scale, and glass long-term behavior. In this paper, the devitrification properties of this type of glass are studied.

The crystallization behavior of the sodium aluminoborosilicate host glass has been studied in the past. Crystallization of powellite ($CaMoO_4$), cerianite (Ce/ZrO_2), apatite ($Ca_2Nd_8(SiO_4)_6O_2$) and zincochromites ($ZrCr_2O_4$) has been reported [1–5]. Generally, these studies focus either on characterizing the crystalline phases [1] or on the relationship between structure and glass crystallization [2–4]; however, the degree of crystallization remains to be quantified. Such quantification has been performed in nuclear waste glass by Orlhac et al. [5] by image analysis of optical microscopy images and powder diffraction data refinement using the Rietveld method [6].

In this study, the crystallization rate of two different borosilicate glass compositions containing simulated fission products is quantified with a simple image analysis method based on BSE SEM images. The crystallization behavior of these glasses was studied after extended isothermal heat treatments lasting from 1 h to 120 h.

2. Methods and experimental procedures

Two inactive (non radioactive) glass compositions (Table 1) were studied:

- a simplified (12-oxide) aluminoborosilicate glass referred to below as the “Low Simulated Glass” (LSG);
- a complex (31-oxide) aluminoborosilicate glass, referred to as the “High Simulated Glass” (HSG), which contains Pd and Ru, platinum-group metals (PGM) that are known to form aggregates.

2.1. Glass synthesis

The HSG was obtained by first mixing suitable proportions of reagent-grade oxides (see composition in Table 1).The powder was poured into a platinum crucible, which was heated for 3 hours at 1250 °C. As aggregates of platinum-group metals (RuO_2 and Pd–Te alloys) were expected to form in the melt [5,7], the melt was mechanically stirred while heating to prevent settling of the aggregates [8]. To improve the homogeneity of the material, the glass was then poured onto a steel plate, coarsely ground, placed in a Pt–Au crucible and reheated in a resistance furnace for 15 min at 1200 °C. It was then cast in carbon molds and heated for 6 hours at 630 °C to release glass constraints, before being cut into slices for heat treatment.

A commercial glass frit was used for the LSG. The individual frit pieces measured about 1 $cm^2 \times 1$ mm.

In the active industrial HLW glass, MoO_3, PGM, RE elements, and most of the ZrO_2 come from the nuclear waste solution (obtained by

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Table 1
High simulated and low simulated glass compositions. RE refers to rare earth elements.

	High simulated glass (HSG) , wt.%	Low simulated glass (LSG), wt.%
SiO_2	44.4	46.6
B_2O_3	13.3	14.7
Na_2O	9.2	10.1
Al_2O_3	4.2	5.2
CaO	3.8	4.1
ZnO	2.3	2.5
P_2O_5	0.2	0.0
ZrO_2	2.8	2.4
MoO_3	2.2	0.0
RuO_2 + Pd	2.1	0.0
RE	6.7	7.3
Other oxides	8.8	3.2
Total	100.0	100.0

reprocessing of spent fuel). The other elements come from the glass frit and are incorporated to obtain a glass.

2.2. Heat treatments

Isothermal heat treatments were performed in a high precision AET tubular furnace (the uncertainty on the temperature measurement was less than 2 °C). Two experimental setups were used:

- for the high simulated glass, a glass slice of approximately 10 mm × 5 mm × 1 mm was placed in a small platinum cup;
- for the low simulated glass, several frit grains were placed in a small platinum cup, creating a random number of interfaces between the frit grains.

In both cases, samples were placed in the preheated furnace for the duration of the heat treatment, and were then air-quenched. The heat treatments were performed at temperatures ranging from 700 °C to 900 °C, for durations ranging from 1 h to 120 h. One long heat treatment of 388 h was performed on the two glass compositions at 750 °C. Additional heat treatments lasting about 65 h were performed at temperatures below 700 °C in order to better define the temperature range of crystallization.

2.3. Characterization of glass samples

In order to check the structure of glass before and after thermal treatments, glass samples were studied by XRD, TEM, SEM and microprobe analysis.

XRD data were collected on a PANalytical X′Pert MPD Pro equipped with an X′Celerator detector with Bragg-Brentano parafocusing geometry. For diffraction, Ni-filtered copper radiation ($\lambda = 1.5406$ Å) was used for $2\theta = 15$ to 90° (step size = 0.017°) for 1.5 h. The diffraction patterns were identified using the EVA software.

Transmission electron microscopy (TEM) was performed on a Philips CM20 fitted with an Oxford EDS analyzer. The sample was first crushed in ethanol, and a drop of the solution with the small crystallites in suspension was deposited on a carbon-coated copper grid.

SEM analyses were performed using a Zeiss Supra 55 FEG equipped with a Brucker EDS analyzer. For SEM observations, samples were cut with a circular diamond saw and mounted in epoxy resin before being polished and coated with a thin film of carbon.

Microprobe analyses were performed on a Cameca SX 50 at 15 kV with a 10 nA probe current. Fixed-focus probe mode was used to study crystalline phases, while unfocused mode was used to examine the residual glass in order to minimize sodium losses under the electron beam.

2.4. Characterization of crystals (morphology and kinetics)

2.4.1. Image acquisition

For the study of crystals, each SEM image was acquired with a constant magnification of ×2000 in BSE mode, an acceleration voltage of 15 kV, and a 600 × 450 pixel image resolution. This yielded a stable SEM field area of 148 μm × 111 μm, which gave a pixel size of approximately 0.25 μm.

An average of 200 SEM fields was automatically acquired per heat-treated sample on a rectangular pattern to cover a large area (~3.3 mm^2) compared to the size of crystals (maximum 100 μm). The survey of such a wide area of the sample ensures that the measured results (in terms of quantification of the crystallization) describes the behavior of the crystallization in the whole sample (and not merely in some smaller area of that sample where the nucleation might have been induced by a local heterogeneity). The SEM fields are automatically interlinked by the commercial SEM software to form an image mosaic, which give a good representation of the surveyed plane section.

2.4.2. Image processing and analysis

Image processing and analysis of the SEM images was performed using the *ImageJ* freeware (no additions were made to the software) [9–11]. First, the 200 images were simultaneously opened as a "stack" in the software. The image scale was defined to allow measurement of the actual dimensions of the objects. Manual contrast thresholding [10] was performed to obtain a binary image. The aim of this operation was to select one crystalline phase at a time. This operation was performed separately for each crystalline phase visible in the image. If confusion between crystalline phases remained after the image binarization step, morphological operations (such as opening or closing) or filters (typically 3 × 3 median filter) were applied to the image [12,13]. An example of image processing applied to heat-treated HSG is shown in Fig. 1.

2.4.3. Extraction of particles morphological parameters

Once the binary image had been created, the "analyze particle" algorithm of ImageJ was used to extract the morphological parameters related to a given crystalline phase [10]. Particles cut by the edge of the image were automatically ignored. Also, particles smaller than 0.2 μm^2 were ignored in order not to take into account any remaining lone pixels.

After this step, 33 morphological parameters were acquired for each crystal of the binary. Among these parameters, the most relevant ones for this work are:

- The overall number of crystals, from which we can obtain the crystal surface density and information concerning nucleation in the sample.
- The area of each crystal, from which we can determine the surface area fraction of the crystalline phase.
- The dimensions of the smallest fitting ellipse [14,15] from which we get the crystal size and may determine the growth kinetics of the crystalline phase.
- The angle between the *x*-axis of the image and the direction of the long axis of the best fitted ellipse boxing each crystal of the sample. The distribution of these angles for a given crystal phase gives insight on the potential preferential orientation of crystals for a given sample.

2.4.4. Estimation of the uncertainty

The uncertainty of a specific measurement can be determined with different methods. One can either (a) compare the measured values with data obtained through another experimental method, (b) calculate the error between a modeled response to the measured value and the experimental measurement or (c) repeat the experiments a lot to determine the statistical dispersion of the measurement.