



HAL
open science

High temperature environmental scanning electron microscopy characterization of transient phase formation during conversion of simulated nuclear waste feed to glass

Renaud Podor, J. Lautru, Richard Pokorný, Z. Nabyl, S. Schuller, Sophie Schuller

► To cite this version:

Renaud Podor, J. Lautru, Richard Pokorný, Z. Nabyl, S. Schuller, et al.. High temperature environmental scanning electron microscopy characterization of transient phase formation during conversion of simulated nuclear waste feed to glass. *Materials Letters*, In press, 10.1016/j.matlet.2024.137619 . hal-04761232

HAL Id: hal-04761232

<https://cnrs.hal.science/hal-04761232v1>

Submitted on 31 Oct 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

High Temperature Environmental Scanning Electron Microscopy characterization of transient phase formation during conversion of simulated nuclear waste feed to glass

R. Podor*¹, J. Lautru¹, R. Pokorny^{2,3}, Z. Nabyl⁴, S. Schuller⁴

¹ ICSM, Univ Montpellier, CNRS, ENSCM, CEA, Marcoule, France

² University of Chemistry and Technology Prague, Technicka 5/1905, 166 28 Prague 6, Czechia

³ Institute of Rock Structure and Mechanics of the Czech Academy of Sciences, V Holesovickach 41,
182 09 Prague 8, Czechia

⁴ CEA, DES, ISEC, DPME, Université Montpellier, Bagnols-sur-Cèze, France

* Corresponding author

Abstract

In-situ High-Temperature Environmental Scanning Electron Microscopy (HT-ESEM) is used to characterize the transient phases formed during the melting of complex glass batch mixtures representing simulated nuclear waste feeds. The first phenomenon that occurs is the formation of oxyanionic salt melt, followed by the reaction of oxyanionic salts with refractory grains containing Si, Al, or Mg through surface reactions to form a molten alkali-alumino-boro-silicate phase. The onset temperatures of gas bubble formation and primary foaming are directly determined from the HT-ESEM measurements. The formation of sulfate lakes as well as the formation of high-temperature transient phases floating at the sample surface are also directly observed and identified. Convection currents are observed and their consequences on glass homogenization are discussed.

Keywords

Transient phase, borosilicate glass, melt, in-situ ESEM, waste glass, high temperature

Introduction

Understanding the formation of transient phases during the production of silicate glasses is essential for the precise control of the industrial glass melting process, such as the selection of suitable chemical and mineralogical forms of batch components, the dissolution time of the components, or the homogenization time of the produced melt. The intermediate phases formed are generally characterized using ex-situ analysis techniques on samples heat-treated to different temperatures [1]. To obtain in-situ information on a local scale, in-situ X-ray computed tomography [2], X-ray synchrotron microtomography [3] and neutron diffraction [4] studies have been carried out, but they are often difficult to implement and interpret. In this work, we demonstrate the contribution of HT-ESEM to the identification of intermediate phases formed during the melting of two types of nuclear glasses through targeted examples. Contrary to the previous techniques, HT-ESEM allows to directly investigate the microstructure and phase evolutions during melting, including the formation of early eutectic salts, glass-forming borate melt, onset of primary foaming, or the formation of segregated crystals or secondary liquid phases.

Materials and methods

The compositions of simulant LAW (low-activity waste) melter feeds used in this study can be found in Supplementary Table S1. The complex waste glass feed mixtures are based on the supernatant composition in respective Hanford tanks AP-107 and AZ-102. AP-107 represents a high-nitrate, high-sodium feed, whereas AZ-102 represents a low-sodium, high-sulfate feed.

A Quanta 200 ESEM (FEI Company) coupled with a FEI 1400 furnace and a Bruker 5010 SDD energy dispersive spectrometer (EDS) detector was used to perform the experiments. Few milligrams of powder are deposited in a platinum crucible that is then introduced in the hot zone of the furnace [5]. The sample is heated to 1000°C (5°C/min heating ramp) while continuously recording images at several magnifications. EDS maps are recorded at different temperatures (following sample cooling to room temperature) to identify the variations of the element distributions during the reactions between the different compounds contained in the sample.

Results and discussion

During the melting of the AP-107 feed, elemental maps were recorded before and after the experiment (full HT-ESEM video is reported in supplementary file S1). The observed morphological evolution of sodium-containing compounds corresponds to previously published x-ray diffraction data (measured ex-situ on samples heat-treated to 1100°C in 100 °C intervals) [6] – above 300°C, they start to melt and become part of the oxyanionic eutectic melt, containing various carbonates, nitrates, sulfates, chromates, halides, perrhenates, and possibly also borates (the degree to which borate is dissolved at temperatures below 500°C still remains unresolved). Above 400°C, the fraction of liquid oxyanionic salt decreases, as nitrates and carbonates start to decompose, forming alkali-borate phases. Above 500°C, this alkali-borate phase starts reacting with silica grains, leading to the formation of a molten alkali-boro-silicate melt on the surface of silica grains visible from 550°C onwards (Fig. 1a). This reaction continues as the temperature increases, and the local melting process accelerates (according to XRD data, the silica dissolution rate peaks at ~600°C). In the images recorded at 619-624°C, the silica grain has moved, but its initial shape remains visible. This indicates that melting processes remain localized on the surface of silica grains, even at high temperatures. As temperature further increases, the

continuous formation of molten phases leads to the encapsulation of the SiO₂ grain (see Fig. 1a, $T = 629\text{--}634^\circ\text{C}$). When considering an MgO-containing grain (olivine, Fig. 1b), molten salts and alkali-borate phases that form at its surface do not seem to react with the MgO grain below $\sim 620^\circ\text{C}$, and the grain is observed to sink in the alkali-alumino-boro-silicate melt above 629°C . In this case, the MgO grain wettability by the liquid silicate probably increases with temperature increase. Thus, this yields to the MgO grain incorporation in the liquid phase.

Two different types of aluminum-containing grains are observed in the sample (Fig. 1c). The small, submicron particles correspond to the aluminum nitrite (present in the nuclear waste), and the larger grains correspond to kyanite (Al₂SiO₅), which is added as glass-forming mineral to increase the durability of the produced glass. Based on XRD data [**Erreur ! Signet non défini.**] (and confirmed by a recent NMR analysis), the small aluminum nitrate grains react between $300\text{--}500^\circ\text{C}$ with the organics in the eutectic melt to produce nano-crystalline Al₂O₃. On the other hand, the Al₂SiO₅ grains become encapsulated by the alkali-alumino-boro-silicate melt and react and dissolve only above $\sim 600^\circ\text{C}$.

As the sample temperature continues to increase, most of the sample becomes liquid and its homogenization is ensured by the formation and coalescence of bubbles and convection related to primary foaming. The effect of foaming on the sample mixing and homogenization can be directly observed in the movie reported as Supplementary File S2. Particles inside the melt rise to the surface and are carried back into the liquid. The effect of convection currents on the mixing of the silicate liquid is clear. The size of the convection cells observed here is on the order of a few tens of micrometers in diameter. The grains stirred up by these convection currents are less than $6\ \mu\text{m}$ long. When the maximum temperature is reached ($T = 1000^\circ\text{C}$), these particles (identified as MgO and FeO-based particles) slowly dissolve in the glass melt while the heat treatment is prolonged

During the melting of AZ-102 glass batch (supplementary file S3), EDS maps have been recorded at different temperatures to more precisely determine the reactions occurring between the different types of grains (supplementary file S4). As displayed in Fig. 2a, the melting process is relatively similar to that for AP-107. Below 500°C , a eutectic liquid is formed, containing various inorganic and organic salts (mainly nitrite, nitrate, carbonate, and sulfate). The aluminosilicate (kyanite) grains are observed to float at the liquid surface and start to dissolve only above 600°C . With increasing temperature, bubbles form and primary foaming starts (Fig. 2b and 2c). When primary foaming stops ($T = 950^\circ\text{C}$), the silicate melt seems to be relatively homogeneous. However, between $T = 700^\circ\text{C}$ and 770°C , segregated molten sulfate phase (composed mainly of Na₂SO₄ with small amounts of CaO, FeO, ZrO₂, and SiO₂) form at the surface of the alkali-alumino-boro-silicate glass melt (Fig. 2d). With increasing temperature, solid Na₂SO₄ grains are observed at the surface of the molten silicate melts and the size of the sulfate lakes further increases. Sulfate lakes move very fast at the silicate melt surface. When temperature reaches 760°C , the sulfate lakes start to disappear, likely due to their volatilization. Segregation of the sulfate phase negatively affects not only the retention of sulfur but also other volatile components that are present in these segregated salt lakes, such as technetium or iodine [7]. At $T = 1000^\circ\text{C}$, small crystals (identified as fayalite containing Fe, Ca, and Zn) formed during high temperature reactions between the silicate melts and raw materials, float at the silicate melt surface and aggregate. These crystals do not seem to be wet by the silicate melt at 1000°C and tend to float at the surface of the liquid.

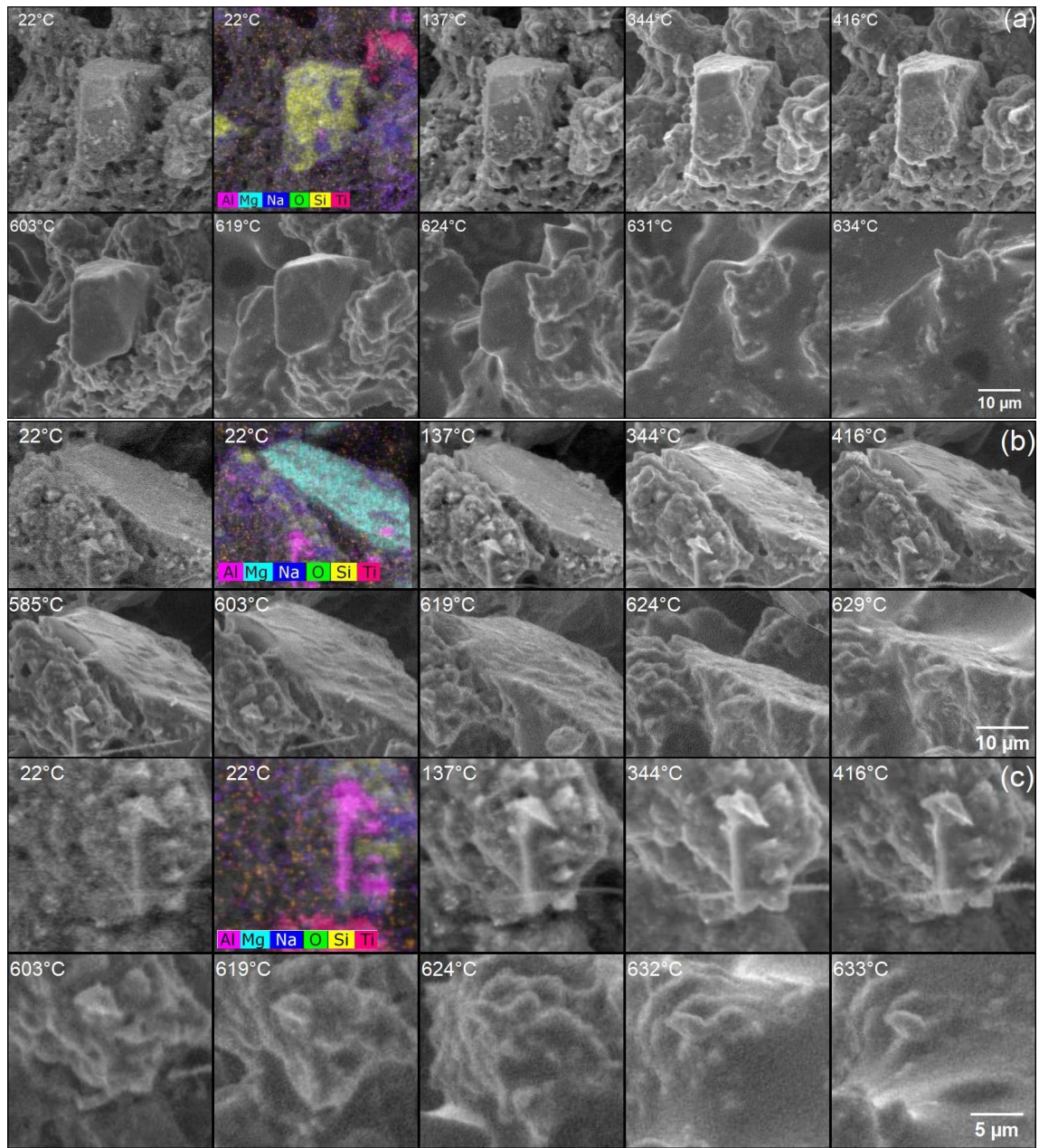


Fig. 1. Series of images showing the formation of a (a) Na_2O -rich liquid phase (blue zone on X-ray map) at the surface of the SiO_2 grains (yellow zone on X-ray map) followed by the slow dissolution of the silica grain into the liquid at higher temperature during the melting of the AP-107 nuclear glass, (b) MgO -containing particles (blue zone on the X-ray map) with the Na_2O liquid and (c) alumina particles (pink zone on X-ray map) with the Na_2O - SiO_2 liquid.

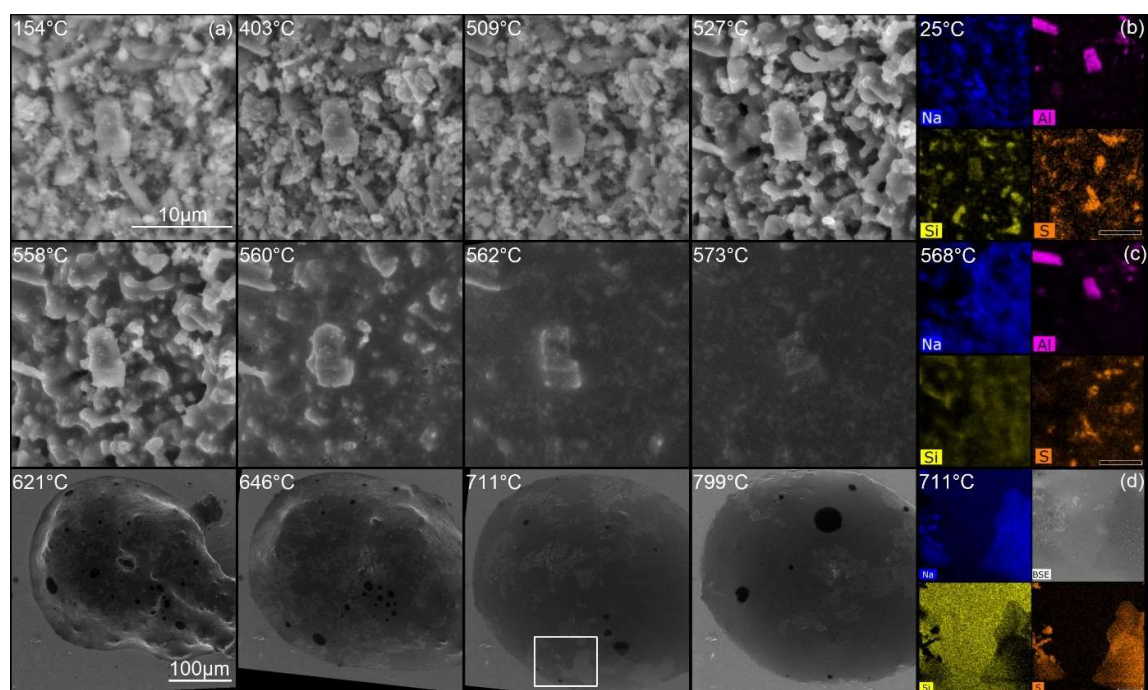


Fig. 2. (a) Series of images recorded at different temperatures during the AZ-102 nuclear glass melting. (b) X-ray maps show Na, Al, Si and S distributions at 25°C (b) and 568°C (c). The white rectangle shown in the image recorded at 711°C corresponds to the formation of sulfate lakes. (d) Enlarged image of a sulfate lake and associated EDS maps showing the distribution of Na, S and Si elements.

Conclusions

The HT-ESEM technique coupled with EDS maps allows to gather information regarding the formation of transient phases during glass batch melting. This technique enables direct observation of reactions taking place within the compounds in the glass batch mixture to form a final glass. The sequences of transient phase formation/dissolution processes can be precisely described, even if they are concomitant or occur within a narrow temperature range. The appearance and behavior of high-temperature molten phases (such as segregated sulfate phases) can be observed directly at high temperatures. Convection currents can be directly observed, the diameter of the convection cells being few tens of micrometers. Associated grain movements at the surface of the liquid indicate that convection currents stir up the liquid and accelerate reaction processes (chemical reactions, dissolution, etc.) within the liquid.

Funding sources

R.P. acknowledges support from the Czech Ministry of Education, Youth and Sports Project No. LUAUS23062.

References

-
- [1] K. Xu, P. Hrma, J. A. Rice, M. J. Schweiger, B. J. Riley, N. R. Overman, A. A. Kruger, Conversion of nuclear waste to molten glass: cold-cap reactions in crucible tests, *J. Am. Ceram. Soc.* 99[9] (2016) 2964-2970. <https://doi.org/10.1111/jace.14310>
- [2] S. A. Luksic, R. Pokorný, P. Hrma, T. Varga, E. L. Rivers, A. C. Buchko, J. Klouzek, A. A. Kruger, Through a glass darkly: In-situ x-ray computed tomography imaging of feed melting in continuously fed laboratory-scale glass melter, *Ceram. Int.* 47[11] (2021) 15807-15818. <https://doi.org/10.1016/j.ceramint.2021.02.153>
- [3] E. Gouillart, M. J. Toplis, J. Grynberg, M.-H. Chopinet, E. Sondergard, L. Salvo, M. Suéry, M. Di Michiel, G. Varoquaux, In situ synchrotron microtomography reveals multiple reaction pathways during soda-Lime glass synthesis, *J. Am. Ceram. Soc.* 95[5] (2012) 1504-1507. <https://doi.org/10.1111/j.1551-2916.2012.05151.x>
- [4] I. M. Peterson, Y. Shi, D. Ma, J. L. Rygel, B. Wheaton, P. S. Whitfield, J. Wright, M. Carlineo, In situ measurements of reactions in a glass-forming batch by X-ray and neutron diffraction, *J. Am. Ceram. Soc.* 102 (2019) 1495-1506. <https://doi.org/10.1111/jace.15977>
- [5] R. Podor, G. I. Nkou Bouala, J. Ravoux, J. Lautru, N. Clavier, Working with the ESEM at high temperature, *Mater. Charact.* 151 (2019) 15-26. <https://doi.org/10.1016/j.matchar.2019.02.036>
- [6] R. Pokorný, M. Vernerová, J. Kloužek, P. Cincibusová, P. Ferkl, P. Hrma, R. Podor, S. Schuller, A. A. Kruger, Transient melt formation and its effect on conversion phenomena during nuclear waste vitrification – HT-ESEM analysis, *J. Am. Ceram. Soc. - Special Issue 2nd Century Trailblazers* 107 (2024) 1691-1705. <https://doi.org/10.1111/jace.19361>
- [7] T. Jin, D. Kim, A.A. Kruger, 2019. Effects of sulfate on rhenium incorporation into low-activity waste glass, *J. Non-Cryst. Solids* 521 119528. <https://doi.org/10.1016/j.jnoncrysol.2019.119528>