In situ ESEM experiment applied to the description of chemical processes during glass elaboration

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Abstract

The HT-ESEM design and image acquisition conditions to perform in situ experiments are fully described. Two examples of applications in the nuclear glass field are reported.

Keywords: Environmental Scanning Electron Microscopy; reactivity; glass

1. Introduction

High Temperature Environmental Scanning Electron Microscopy (HT-ESEM) is a technique which has been developed in the late 90’s and that has been the subject of continuous developments. It is the combination between a scanning electron microscope of which capabilities in terms of image resolution and fast image acquisition are well-known, and a dedicated furnace which allows in situ heat treatment of a sample. This combination allows studying directly sample morphology modifications occurring during sample heat-treatment. It has been successfully used to study several phenomena such as the corrosion of metals (Jonsson et al., 2011), oxidation of metals (Oquab & Monceau (2001); Schmid et al. (2002); Reichmann et al. (2008); Mège-Revil et al. (2009); Quémarda et al. (2009); Delehouzé et al. (2011)), reactivity at high temperature (Maroni et al. (1999); Boucetta et al. (2012)), phase changes

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(Fischer et al. 2004; Hung et al. 2007; Beattie & McGrady 2009), hydrogen desorption (Beattie et al. 2009, 2011), redox reactions (Klemensø et al. 2006), microstructural modifications (Bestmann et al. 2005; Fielden 2005; Yang 2010), magnetic properties (Reichmann et al. 2011), sintering (Sample et al. 1996; Srinivasan 2002; Marzagui & Cutard 2004; Subramaniam 2006; Courtois et al. 2011; Joly-Pottuz et al. 2011; Goel et al. 2012; Podor et al. 2012), thermal decomposition (Gualtieri et al. 2008; Claparède et al. 2011; Hingant et al. 2011; Goodrich & Lattimer 2012), crystallisation (Gomez et al. 2009) in melts (Imaizumi et al. 2003; Hillers et al. 2007; Vigouroux et al. 2013) and the self-repairing – self-healing – properties of materials (Wilson & Case 1997; Coillot et al. 2010, 2011).

However, applications of this technique in the field of nuclear materials remains limited (Boucetta et al. 2012; Clavier et al. 2013) but it potentially offers new opportunities to study and describe complex chemical processes occurring during glass elaboration for the conditioning of radwastes. In this paper, we will report the basics of HT-ESEM and two examples of application in the nuclear field. This work was carried out on non-radioactive samples.

2. Basics of HT-ESEM

2.1. The Environmental Scanning Electron Microscope (ESEM)

The ESEM (or more generally the VP-ESEM family for Variable Pressure - Environmental Scanning Electron Microscope – as proposed by Stokes 2008)) has been commercialized in the late eighties. This microscope has been designed to work under a pressure limit of 4kPa of water vapor. The specific architecture of the column as well as adapted detectors allows working using different gazes (water vapor, air, He, O₂, CH₃COOH etc) and recording images of conductive or insulating, dry or wet materials. The versatility of this microscope, when combined with specific stages, offers the possibility to use the ESEM chamber as a “micro-laboratory” and to perform experiments by looking at the sample modifications occurring at the sub-millimeter scale up to the nanometer scale. This ability has been widely used to study the behavior of various objects or materials under wet conditions such as food, live organisms (Stabentheiner et al. 2010) or cells (McGregor et al. 2013), liquids (Jung and Bhushan 2008), clays (Carrier et al. 2013), Metal Organic Frameworks (Sievers et al. 2013) …

2.2. Heating stages – Temperature control – Sample

Specific heating stages have been developed since the seventies. The furnace that is adapted to the ESEM, and used in the present study, has been designed by Ralph and Knowles (1997). The heating element is a Pt wire and the temperature is monitored by an external thermocouple. Two specific furnaces have been built and dedicated to 25-1000°C and 200-1500°C applications (Figure 1a).

One problem encountered during the use of the 200-1500°C furnace is the accuracy of the temperature control. Indeed, the position of the thermocouple in the furnace, the position of the sample in the furnace, as well as the nature and pressure of the gas used in the ESEM chamber, yields to large variations of the temperature...
measurements. As an example, the temperature associated with gold melting point \( T_m = 1064°C \) which is measured with the as-received thermocouple from the supplier of the microscope ranges from 950 to 1179°C. This lack of accuracy led Podor et al. (2013) to develop a specific sample holder in which the measurement thermocouple is directly placed below the sample (Figure 1b). Using this new design, the measured temperature for gold melting point ranges from 1062 to 1069°C and is independent of the nature and pressure of the gases present in the ESEM chamber. This specific sample holder allows precise temperature measurements (±5°C accuracy) in the 200-1400°C temperature range.

The samples to be used during the HT-ESEM experiments can be in solid or liquid forms (silicate melts, molten salts, …). When solids are used, the sample size must be limited to allow the sample to be directly placed in the sample holder. Typical sample size is \( L \times l \times h = 1 \times 1 \times 0.5 \text{mm}^3 \). When liquids are used, the sample is placed in a platinum crucible and the sample size still remains limited: the objectives being to limit the chamber contamination by gazes that can be generated by the silicate melt or molten salt decomposition and to limit convection movements in the liquid. The sample preparation sequence for a HT-ESEM experiment is reported on Figure 2.

![Sample preparation sequence to perform a HT-ESEM experiment.](image)

Fig. 2. Sample preparation sequence to perform a HT-ESEM experiment.

2.3. Electron detection in the HT-ESEM

The electron collection and detection is ensured using a modified Gaseous Secondary Electron Detector (GSED) (Figure 1). The principle of the electronic emission amplification and collection is as follows (see Stokes (2008) for more details). An electric field is applied between the sample and the GSED detector. When an electron is emitted at the sample surface, it is accelerated and it ionizes the gas present in the chamber. Electrons are produced during this process and the cascade is propagated towards the anode and the secondary electron signal is amplified. The voltage measured in the GSED is proportional to the secondary electron signal and allows image construction of the sample surface. The positive ions formed during the ionization process are attracted by the negatively charged sample surface and compensate the surface charge. This allows direct observations of insulators (i.e., without a conductive coating).

Furthermore, a heat shield is placed between the sample (furnace) and the GSED. It is constituted by a metallic grid which can be polarized in order to specifically attract the secondary electrons (and filter the thermal electrons emitted at high temperature).

2.4. Image recording conditions

The images formed from a sample heated at high temperature require the adjustment of the microscope through 10 different parameters: gas pressure, nature of the gas, working distance, high voltage, spot size, diaphragm aperture, heat shield voltage, contrast, brightness and enhance. Increase of temperature enhances the thermal electron emission which becomes predominant compared to the secondary electron emission. Thus, advanced adjustments of these 10 parameters above 1150-1250°C are required to obtain both an acceptable secondary electron emission/thermal electronic emission ratio and stable images.

3. Applications in the field of nuclear glass elaboration

Both examples reported below mimic the reactivity between a simplified calcined solution of fission products and a glass frit.
3.1. Dissolution process during simplified glass elaboration

The reactivity of crystalline phases with a silicate melt has been studied using HT-ESEM up to 1200°C. An agglomerate of \( \text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O} \) particles was deposited at the surface of a bed of platelets of a simplified glass frit and the evolution of this system was recorded as a function of temperature. The image sequence reported in Figure 3 illustrates the different steps observed at several temperatures. The first phenomenon that is observed between 139°C and 225°C is the thermal decomposition of \( \text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O} \) into alumina. The size decrease of the particle is associated to the mass loss between the two compounds. The next step is melting of the glass. It occurs at \( T=800°C \). It is rapidly followed by the beginning of reactivity with the \( \text{Al}_2\text{O}_3 \) crystals which occurs in the 800-1000°C temperature range. This reaction can be explained by a partial dissolution of the \( \text{Al}_2\text{O}_3 \) particle that locally modifies the melt composition and generates its crystallization. The quantity of crystals increases with increasing temperature, up to 1087°C. At this temperature, the newly-formed crystals dissolve in the melt. Parallel, the remaining \( \text{Al}_2\text{O}_3 \) particles are also dissolved. This reaction process is completed at \( T=1189°C \).

3.2. Intermediary phase formation

Fig. 3. HT-ESEM image sequence illustrating the dissolution of \( \text{Al}_2\text{O}_3 \) crystals in a silicate melt

Fig. 4. HT-ESEM image sequence illustrating the formation and dissolution of \( \text{Na}_2\text{SiO}_3 \) intermediary phase (Boucetta et al. (2012))
The reaction between NaNO₃ and a simplified sodo-boro-silicate glass yields to the spreading of liquid NaNO₃ at the glass surface and to the formation of intermediary Na₂SiO₃ and “Na₂O-B₂O₃” phases above 306°C (see Boucetta et al (2012) for more details). The image sequence that illustrates the evolution of the intermediary phases (494-659°C) followed by their local melting in contact with the silicate melt (727-894°C) are reported in figure 4. These images clearly show how the chemical reactions occur. Coupling this morphological information with EDS analyses performed on samples cooled at room temperature allows a complete description of the reaction pathway.

4. Conclusions

The recent development of a new generation of scanning electron microscopes in which specific furnaces can be attached allows performing in situ experiments up to 1400°C, recording images with a sub-micrometer resolution and observing directly complex reaction pathways. The interest of this technique for the study of complex reactions occurring during the nuclear glass formation is obvious.

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