Modeling of dissolution kinetics of rare earth crystals in a borosilicate glass melt

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ABSTRACT

The novelty of this work is the comparison of two methods to determine the dissolution kinetics in order to evaluate the applicability of the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model for the crystals dissolution in silicate melts. For this, this work focuses on the dissolution of rare earth (RE) silicates ($Ca_2RE_8(SiO_4)_6O_2$ where RE = Nd) with an apatite structure in a sodium-borosilicate glass melt. The first approach consists in the characterization of the dissolution kinetics by following the crystalline area fraction by image analysis as a function of time and temperature. Then, a model based on the generalized JMAK equation is proposed to fit the experimental data. This model enables to determine both the mechanism limiting the dissolution (i.e. the diffusion) and the activation energy of crystals dissolution in the studied glass system (496 kJ/mol). To support these results, a second and most common approach is the measure of the chemical profiles at the crystal/melt interfaces by microprobe. The conclusions obtained by this last method are in agreement with the conclusions based on JMAK model. All these results allowed to confirm that the JMAK model is well suited to model crystals dissolution in silicate melts.

1. Introduction

The knowledge of dissolution kinetics is a crucial issue in many scientific fields. For example in geology, the dissolution of crystals in silicate melts, mechanisms, kinetics and chemical evolution of the local environment during the dissolution process are often studied (among others [1–8]). In the domain of high level nuclear waste confinement, the dissolution kinetics of crystals in sodium-borosilicate glass melts has practical importance. Indeed, the radionuclides are confined in a borosilicate glass and the melting process capacity depends, among other, on crystals dissolution kinetics. During the melting process, different types of crystals are likely to precipitate [9–14]. Among these different phases, Rare Earth silicates (RE-silicates) $Ca_2RE_8(SiO_4)_6O_2$ are one of the most common crystallizations.

Two mechanisms can limit dissolution. The first corresponds to interface reactions which are the detachment of species at the crystal's surface. The second is related to diffusion, i.e. the mass transport of species within the melt. Because quasi-saturation is rapidly attained at the interface, diffusion is assumed as the mechanism limiting dissolution [2]. In this case, chemical profiles at the crystals/melt interfaces are constant whatever the experimental duration [1–3]. In more

complex cases, the dissolution rate can be influenced due to the density differences between (i) crystal and melt or (ii) melt formed by crystal dissolution and original melt [4].

The purpose of this paper is to evaluate the generalized Johnson-Mehl-Avrami-Kolmogorov (JMAK) model for the dissolution of crystals in silicate melts. This model has originally been developed for modeling phases transformations in metals and alloys [15–19]. Its application has been extended to the crystal growth in silicate melts [9,20–23]. Recently, this model has been applied to fit phase dissolution in metallic melts [24]. However, its applicability to crystal dissolution in silicate melts remains to be demonstrated. In this study, we propose to test this model in the case of RE-silicate crystals dissolution in a glass melt of nuclear interest.

In this objective, dissolution experiments are conducted on a sodium-borosilicate glass previously thermal-treated to precipitate RE-silicate crystals (about 2 suf. % of crystals). The obtained initial partially crystallized glass is then thermal treated at different durations in isothermal mode above the liquidus temperature (T_{liq}, i.e. the lowest temperature from which no more crystals are expected at the equilibrium) in order to follow the crystals dissolution. According to the literature, the expected limiting mechanism is the diffusion [2]. The

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originality of this work is based on the application of two approaches for the study of the dissolution kinetics of RE silicate crystals. On the one hand, the crystals area fraction in glass samples is followed as a function of time in isothermal mode by scanning electron microscopy (SEM) coupled with image analysis [11]. The so-acquired data allow testing the JMAK model in the case of crystals dissolution in a silicate melt. On the other hand, chemical profiles at the crystals/melt interfaces are measured by microprobe on samples previously heat-treated at different durations and temperatures. This method is a standard method to characterize the diffusion coefficients and the activation energy of crystals dissolution in silicate melts. Finally, the confrontation of results obtained with both approaches will allow concluding about the applicability of the adapted JMAK model to the case of crystals dissolution in silicate melts.

2. Theoretical model for crystals dissolution in silicate glass melt

2.1. JMAK model applied to crystallization in silicate glass melt

The generalized Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation, initially defined for isothermal solid-state transformations in metals or alloys [15–19,25], is used to describe the nucleation and crystals growth processes in silicate glass melt [9,20–23] and is given below:

$$f_v(t) = f_{veq} [1 - \exp(-(kt)^n)] \qquad (1)$$

where $f_v(t)$ is the volume fraction transformed at the time t, f_{veq} the volume fraction transformed at the equilibrium, k is the transformation constant (s^{-1}) and n the Avrami exponent. One way to obtain Eq. (1) in the case of crystallization is to consider non-crystallized volume fraction = 1 − crystallized volume fraction. In most cases, the transformation constant k follows an Arrhenius function:

$$k = k_0 \exp\left[-\frac{E_a}{RT}\right] \qquad (2)$$

where k_0 is the pre-exponential factor, E_a the activation energy of the transformation, R the gas constant and T the temperature in kelvin. The Avrami exponent n is a precious parameter which gives information on the mechanism controlling the phase transformation according to Christian [25]. An estimation of its behavior and value can be obtained by plotting $\ln(\ln(\,(f_v(t)/f_{veq}) - 1))$ vs. $\ln(t)$. If the trend formed by experimental data for a same temperature is linear, that means that the mechanism is continuous during the phase transformation [26]. In this case, the value of the slope, i.e. n value, indicates the mechanism controlling the phase transformation [25]. A n value between 0.5 and 1 can be associated to diffusion mechanism limiting the transformation.

2.2. Adaptation of JMAK model to crystals dissolution

In [24,27], the generalized JMAK equation is applied to model the dissolution kinetics of phases in metallic melts. However, the dissolution of crystals in melts is usually considered as the inverse of crystals growth, since diffusion can limit both crystals growth and dissolution [2]. Similarly, it can be considered that the undissolved volume fraction is equivalent to the crystallized volume fraction, and so the following expression can be proposed for modeling dissolution above the liquidus temperature of crystals (T_{liq}) [27] [24]:

$$f_v(t) = f_{v0} \exp(-(kt)^n) \qquad (3)$$

where f_v is the undissolved volume fraction at the time t, f_{v0} the initial crystallized volume fraction, k is the dissolution constant (s^{-1}) and the parameter n is linked to the mechanism controlling the dissolution.

Based on these considerations, we propose to apply this model for the first time to the dissolution kinetics of rare earth silicates in a partially crystallized sodium-borosilicate glass melt.

3. Experiments

3.1. Glass synthesis

A parental nine-oxide sodium-borosilicate glass is first prepared. The precursors used are powder samples of oxides (SiO_2, CaO, Nd_2O_3, Al_2O_3, ZnO, ZrO_2), carbonates (Na_2CO_3, Li_2CO_3) and boric acid (H_3BO_3). The powders are mixed in the right proportions according to the theoretical composition (49.18% SiO_2, 15.48% B_2O_3, 10.6% Na_2O, 4.32% CaO, 7.71% Nd_2O_3, 5.44% Al_2O_3, 2.49% ZrO_2, 2.66% ZnO, 2.11% Li_2O in wt%). This mixture is then put into a Pt-Rh crucible and heated at 1250 °C for 3 h in ambient air. A mechanical stirrer is used during the entire melting to ensure melt homogeneity. The melt is then quenched on a steel plate and 800 g of glass is finally obtained. Visually, this parental glass is pink-colored, transparent and its homogeneity is checked at SEM scale. 100 g of this parental glass is crushed to improve the heterogeneous nucleation during the nucleation-growth thermal treatment of 68 h at 820 °C and thus to promote the homogeneous spatial distribution of crystals in the final partially crystallized glass bulk. This temperature corresponds to the maximum of crystallization fraction in this glass composition [28]. The characterization of this initial partially crystallized glass is presented in Section 4.1.

3.2. Determination of T_{liq}

The liquidus temperature (T_{liq}) is defined in thermodynamic as the maximum temperature at which the last crystal is at thermodynamic equilibrium with the glass melt. Two methods validated in a Round Robin test approach and described by Riley et al. [29] are used to determine T_{liq} in the considered system. The first, called the Uniform Temperature (UT) furnace, is a dichotomic method based on 24 h thermal treatments at different temperatures. The temperatures are chosen according to successive dichotomies. This method rapidly enables a framing of the liquidus temperature. The second, called the Crystal Fraction (CF) extrapolation method is based on the linear evolution of the equilibrium crystallized fraction as a function of temperature for $T \leq T_{liq}$. The extrapolation of the equilibrium crystallized fraction to zero gives the liquidus temperature (for more details, see [29]). Both methods lead to the same liquidus temperature of RE-silicates in the sodium-borosilicate melt studied here: 905 °C ± 5 °C.

3.3. Thermal treatments for the study of dissolution kinetics

All the experiments to study dissolution kinetics of RE-silicates are performed using the initial partially crystallized glass. Thermal treatments are carried out in a tube furnace in isothermal mode at temperatures around and above the liquidus temperature. The small size of the furnace chamber (80 mm × 30 mm × 20 mm) ensures a good temperature precision with an absolute uncertainty of ± 10 °C and a relative uncertainty of ± 2 °C. In order to avoid the volatility of Na and B, thermal treatments are performed in closed systems. About 0.15 g of crushed initial crystallized glass is placed in a platinum capsule of 5 mm in diameter and 15 to 20 mm long. The capsules are closed by folding up them at each end. They are then placed into the hot-furnace and, after a given thermal treatment duration, they are quenched in water in order to avoid crystallizations during cooling. Specific experiments (not described here) allowed checking that no sedimentation of crystals and no convection take place during the dissolution thermal treatments. The experiments are run in isothermal mode at six temperatures around and above T_{liq} (900 °C, 910 °C, 915 °C, 925 °C, 930 °C and 935 °C) and for several durations (at least four) at each temperature. The final glass is retrieved by cutting the capsules, and pieces of glass are then put in epoxy resin and polished in order to be analyzed by microscopy.