GLASS-FORMING ABILITY VERSUS STABILITY OF SILICATE GLASSES

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Abstract

We modified and used a method put forward by Colmenero and Barandiarán and measured the critical cooling rates, q_{cr}, of seven silicate glasses that show internal nucleation. The experiments were accomplished in two steps. In the first, monolithic pieces of each glass, obtained by splat cooling the melts, were heated in a Pt crucible, at the same heating rate, to estimate the glass transition, crystallization and melting temperatures. We then calculated the Hrubÿ parameter, K_H, based on these three quantities. In the second step, the same samples were melted, then cooled at different rates and the crystallization temperatures were used to estimate q_{cr}. A relationship between q_{cr} and K_H was experimentally demonstrated.

Introduction

All materials are vitrifiable if the cooling rates used to solidify their melts are fast enough to prevent the occurrence of a detectable fraction of crystals, usually assumed to lie between 10^{-2} to 10^{-6}. The cooling rate to produce that minimum crystallized fraction is denominated the *critical cooling rate*, q_{cr}. However, it is quite difficult to accurately measure the q_{cr}. We recently observed that the Hrubÿ parameter (K_H), which easily measures glass stability (GS) against devitrification on heating, can be used to estimate the glass-forming ability (GFA) on cooling [1]. In that research, the *calculated* critical cooling rates (q_{cr}') of four glasses were compared with K_H, demonstrating a correlation. However, our results contradicted Weinberg's [2] suggestion, which affirmed that, although GFA and GS are related concepts, they are ill-related quantities. Additionally, because we had analyzed only four systems in Ref. [1], in this research we test other three glasses to generalize (or not) our previous findings. Furthermore, we use an experimental rather than calculated q_{cr}.

Literature Review

Colmenero and Barandiáran [3] proposed an experimental method to measure critical cooling rates using thermal analysis techniques (DSC or DTA). This method will be dubbed the CB method. As far as we know, only a few researchers have tested this method to estimate q_{cr}. We will briefly review some of them in the following paragraphs. Wichard and Day [4] determined the critical cooling rates for five compositions in the Ga_2O_3-CaO system. Using a Pt-10% Rh thermocouple bead, they determined q_{cr} by repeated cooling and heating experiments. Each composition was melted between $150^{\circ}C$ and $250^{\circ}C$ above its respective *liquidus* and cooled at least 30 times at

various rates. As they expected, eutectic compositions displayed a greater tendency to vitrify. Another interesting study was conducted by Huang et al [5]. Using a glass of nominal composition 40Li$_2$O-60SiO$_2$ mole%, they showed that q$_{cr}$ increases with increasing Pt and Au additions. They used two methods for q$_{cr}$ measurements, the first being the one used by Wichard and Day [4], and the second the one proposed by Colmenero and Barandiárán [3]. An excellent agreement was found between these values. Finally, Ray and Day [6] measured the critical cooling rates for five compositions of the BaO-TiO$_2$-SiO$_2$ system, suggesting that the tendency for glass formation increases with increasing silica content, as expected. In the present paper, we report on our modification of the CB method [3] and determination of the critical cooling rates of seven "model" glasses (that show internal nucleation) having almost stoichiometric compositions: Li$_2$.2SiO$_2$ (LS$_2$), Na$_2$O.2CaO.3SiO$_2$ (NC$_2$S$_3$), 2Na$_2$O.CaO.3SiO$_2$ (N$_2$CS$_3$), BaO.2SiO$_2$ (BS$_2$), Li$_2$.2SiO$_2$ with 0.2% mole OH (LS$_2$OH), 2BaO.TiO$_2$.2SiO$_2$ (B$_2$TS$_2$) and 0.44Na$_2$O.0.56SiO$_2$ (NS). Our experiments were performed in two steps. In the first, monolithic pieces of each glass were heated in Pt crucibles (at the same heating rate) to estimate the Hrubý parameter. Then, the same samples were melted and cooled at variable cooling rates (from 1 to 50°C/min) and their crystallization temperatures on cooling used to estimate q$_{cr}$ by the modified CB method. An important effect of the crucible material on the crystallization temperatures of these glasses was detected. We confirm the relationship between q$_{cr}$ and K$_H$ proposed in [1] and discuss the relevance of these findings to the vitrification of reluctant glass-forming systems.

Theory

Methods to determine q$_{cr}$

Several methods have been proposed to calculate critical cooling rates, q$_{cr}$. One of the simplest is the so-called *nose method*, which refers to the nose of a TTT (time-temperature-transformation) diagram. According to this method, there is a corresponding time t$_n$ for the temperature T$_n$ of the "nose" of TTT diagrams. Thus, the critical cooling rate for glass formation, q$_{cr}^n$, is given by

$$q_{cr}^n = \frac{T_m - T_n}{t_n}$$

(1)

where T$_m$ is the melting point of the crystal phase or liquidus temperature.

The q$_{cr}$ determined by the *nose method* is typically less than an order of magnitude greater than the real q$_{cr}$ [7]. Thus, the nose method can be used to *estimate* critical cooling rates and to compare the vitrifiability of different materials [1]. Colmenero and Barandiárán (CB) [3] suggested another experimental method to determine q$_{cr}$. According to these authors, the cooling rates, which can be measured by DSC (Differential Scanning Calorimetry), are proportional to (ΔT_c^c)$^{-2}$. The expression proposed in [3] is:

$$Lnq = A - \frac{B}{(\Delta T_c^c)^2}$$

(2)

where $\Delta T_c^c = T_m - T_c^c$, T$_c^c$ is the peak crystallization temperature on cooling the sample at a cooling rate q.

By varying the cooling rate and plotting Ln(q) versus $1/(\Delta T_c^c)^2$, if the equation is correct, one should obtain a straight line. The constant A can be determined from the intercept of the straight line and B can be obtained from the curve slope. According to [3], when ΔT_c^c increases to infinity, no crystallization occurs, leading to:

$$Ln\ q_{cr} = A \tag{3}$$

Therefore, as the value of A is now known, it is possible to calculate q_{cr} from Eq. (3).

The Hrubÿ parameter of glass stability

Hrubÿ proposed that a different parameter, K_H, obtained by Differential Thermal Analysis (DTA) or DSC, indicates *glass stability* against crystallization on heating [8]. The Hrubÿ parameter is defined by:

$$K_H = \frac{T_c^h - T_g}{T_m^* - T_c^h} \tag{4}$$

where T_c^h, T_g and T_m^* are the onset crystallization temperature (on heating), glass transition and melting temperatures estimated by DSC, respectively. According to Hrubÿ, the higher the value of K_H of a certain glass, the higher its stability against crystallization on heating and, *presumably*, the higher its vitrifiability on cooling [8].

Experimental Procedures

We carried out several DSC experiments (Netzsch DSC equipment, with a controller model TASC 414/3, cell model DSC 404) using samples of seven glasses. These glasses were melted in Pt crucibles at temperatures approximately 50°C above the respective melting points of the isochemical crystals for a few hours, homogenized and quenched by pressing the liquid between two steel plates. Monolithic glass pieces weighing approximately 10 to 20 mg were placed in a Pt crucible and heated/cooled in the DSC. The same heating rate (20 K/min) was used for all the samples, but the cooling rates varied from 2 to 50 K/min to include the theoretical values of q_{cr} previously calculated by Cabral et al [1]. The samples were then reheated to 50°C above the liquidus temperatures and kept there for 5 minutes to ensure that the material had melted completely before each cooling run. We performed several experiments for each glass and found different values for K_H and q_{cr}, which were taken as a measure of the method's experimental errors. The same procedure was adopted for the other samples and Ln (q_{cr}) vs. K_H was plotted for all the glasses.

Results

Except for the NC_2S_3 glass, the cooling traces of all the glasses showed several crystallization peaks, a phenomenon typical of surface crystallization. To test the reproducibility of the crystallization temperatures during cooling, T_c^c, we successively heated/cooled a monolithic glass sample of LS_2 using a Platinum crucible. This procedure was repeated from three to five times for each cooling rate. For cooling rates of 10-20°C/min, the crystallization temperatures T_c^c varied by

approximately 50-60°C! For other cooling rates, variations of about 10-25°C were observed. These substantial variations are clearly outside the range of instrumental error and demonstrate the sensitivity of (heterogeneous) crystallization to the presence of solid impurities (from the atmosphere), mechanical vibrations, etc. Upon cooling through the region of high growth rates ($T/T_m \sim 0.9$), any solid impurity or mechanical perturbation can induce fast crystallization of the melt. In addition, it is well known that Platinum is an excellent catalyst for crystallization of LS_2, NC_2S_3 and probably of other glasses [5, 9]. Since there is surface contact between the melts and the DSC crucibles, these provide a favorable pathway for heterogeneous surface crystallization, leading to irreproducible crystallization temperatures. Fortunately, however, this phenomenon does not occur upon heating; thus, the crystallization temperatures are perfectly reproducible. In heating experiments, the glassy samples are (mostly) homogeneously nucleated before they reach a region of substantial growth and then fully crystallize. In order to take heterogeneous crystallization on the cooling path into account, we propose two modifications for the CB method. Using the same heating/cooling rates and different monolithic samples of each glass, we carried out at least three cooling experiments for each cooling rate. First, when more than one crystallization peak appeared on the cooling trace of a given DSC run, only the peak at the highest temperature (relating to the first phase to crystallize) was considered. We made this choice because, at lower temperatures, the sample already contained crystals. Second, considering all the tests with the same cooling rate, we took the lowest T_c^c peak (among the highest peak of each run) to favor volume (homogeneous) crystallization rather than heterogeneous crystallization. As an example, Fig. 1 shows some traces of a NC_2S_3 glass in which the crystallization temperatures varied significantly. From the resulting crystallization temperatures for each cooling rate, plots of $\text{Ln}(q) \times 1/(\Delta T_c^c)^2$ were obtained for each glass. Using the respective melting temperatures, the critical cooling rates estimated by Eq. (3).

Discussion

The q_{cr} obtained from Eq. (3) are qualitatively consistent with our experimental observations in melting and cooling these seven glasses in the laboratory. Additionally, they indicate the same trend of glass-forming ability. In other words, LS_2 is the easiest glass to make while the $Ba_2TSi_2O_8$ melt must be powerfully pressed to avoid crystallization during cooling. The present CB results for q_{cr} are about one order of magnitude greater than those previously calculated by the nose method [1]. However, it is known that the nose method overestimates q_{cr}. One could argue that these high q_{cr} differences result from the fact that the cooling rates used in this work are of the same order of magnitude as q_{cr}, in contrast with Colmenero and Barandiáran's [3] suggestion (the cooling rates employed must be at least two orders of magnitude lower than q_{cr}). We should emphasize, however, that the cooling rates used by Wichard and Day [4] and Huang et al. [5] to measure q_{cr} with the CB technique varied between 50 - 400°C/s, and 2 - 12°C/s, respectively. These values are of the same order of magnitude as the critical cooling rates obtained. Moreover, in the case of the $40Li_2O-60SiO_2$ glass, whose q_{cr} was measured both directly and by the CB method, the agreement between the CB and experimental value of q_{cr} was excellent. Therefore, Colmenero and Barandiáran's suggestion is apparently not required to ensure the accuracy of q_{cr} estimates. The

fact that the critical cooling rates calculated by the nose method are <u>lower</u> than those estimated by the CB method is probably due to heterogeneous nucleation of the melts on the Pt crucible walls.

Fig. 2 shows the critical cooling rates and the K_H obtained for each glass. This figure comprises a 2 o.m. range of q_{cr}, $0.5 < q_{cr} < 50$, and indicates that a relationship between q_{cr} and K_H exists: the higher the K_H the lower the q_{cr}. These results are contradictory to those of Ref. [2], however, in a forthcoming paper, Avramov et al. [10] theoretically demonstrate that glass-forming ability and glass stability are directly related concepts, reinforcing the present findings. Despite the crucible effect on q_{cr} the overall results of this research indicate that the K_H parameter, which is easy to measure, can be used to compare the relative vitrification tendency of good glass-forming systems. It is reasonable to assume that this technique can also be applied to reluctant glass formers, such as metallic and fluoride glasses. In this case, for instance, variations of K_H with the addition of certain compounds to the base glass could be used to optimize glass-forming compositions.

Conclusions

The experimental critical cooling rates obtained by the CB technique, modified in this work to favor bulk nucleation, were consistent with experimental observations on the melting and quenching of seven glass-forming liquids. The critical cooling rates obtained from experiments in Pt crucibles were one order of magnitude greater than those predicted from theoretical calculations using TTT curves. This result is due to heterogeneous nucleation on the Pt crucible walls. Despite this drawback, the CB method can be used to estimate the relative vitrification tendency and to compare different materials. However, the relationship between K_H and q_{cr} is only valid for glasses that nucleate internally (in addition to surface nucleation) and extreme care with the experimental procedures must be exercised. An empirical correlation between the Hrubý parameter of glass stability and the glass-forming tendency was demonstrated, in line with theoretical expectations.

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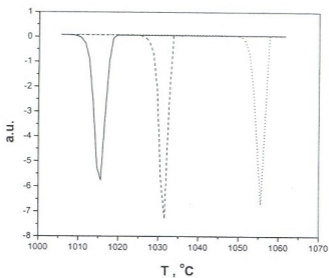
Fig. 1.   Different DSC runs obtained during cooling of the same sample of NC_2S_3 glass at 15K/min: (solid lines) first; (dashed line) second, and (dotted line) third run.
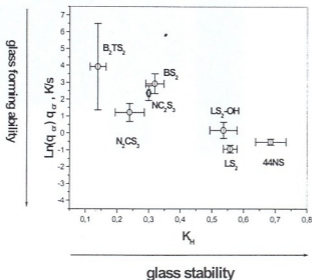

Fig. 2.   Ln (q_{cr}) x K_H for the glasses studied. The experimental variations of both parameters are also shown.