A test of the Hrubÿ parameter to estimate glass-forming ability

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Abstract

Experimental nucleation and growth rates for some glasses that nucleate in the bulk were used to calculate critical cooling rates for glass formation (R_c) by the TTT method. Resulting critical cooling rates were consistent with laboratory melting and quenching and also with experimental data of critical cooling rates for lithium disilicate glass. Strong correlation between the Hrubÿ parameter of glass stability (K_{gl}) and the glass-forming ability, evaluated by R_c, was found. Therefore, K_{gl} can be used to estimate the glass-forming ability for glasses that exhibit volume nucleation. © 1997 Published by Elsevier Science B.V.

1. Introduction

Any substance can be vitrified provided the required cooling rate can be attained experimentally. The cooling rate which produces the lowest detectable crystallization degree, X_c (usually assumed to be 10^{-6}), is called the critical cooling rate for glass formation, R_c [1]. This parameter is a measure of the glass-forming *ability* of the substance.

Several methods have been formulated to evaluate R_c [2–5]. Nevertheless, three kinetic parameters should be accounted for to correlate glass-forming ability and crystallization characteristics in a quantitative way: (i) the steady-state crystal nucleation rate I; (ii) the rate of crystal growth, U; and (iii) the non-stationary time-lag for nucleation, τ [6]. Assuming that the period necessary to reach X_c is substantially higher than the time lag, non-steady state effects can be neglected. The kinetic criterion formulated by Uhlmann [1] to estimate R_c can then be used. Uhlmann's model is based on the Johnson–Mehl, Avrami, Kolmogorov (JMAK) theory of overall-crystallization and is formulated in terms of, time–temperature–transformation (TTT), diagrams. These curves define the relationship between the temperature and the time interval required to reach a given degree of transformation, $t(X_c)$. Thus, the critical or minimum cooling rate for glass formation corresponds to the tangent from the melting temperature which intercepts the $t(X_c)$-curve at the 'nose' temperature of the TTT diagram.

Calculations of R_c for any system depend either on the availability of an experimental TTT curve or on the knowledge of crystal nucleation and growth rates, in a wide temperature region, between the transformation range and the melting temperatures, T_g and T_m, respectively. As these data are seldom available, most reported research has used *theoretical* calculations of nucleation or growth rates to estimate R_c [1,2,7]. However, that procedure is not recommended because reliable experimental tests of classical nucleation theory indicate a large discrepancy between the calculated and experimental nucle-

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ation rates.

Conversely, some empirical criteria have been formulated to correlate critical cooling rates (*glass-forming ability*) with *glass stability* (on a given heating path) using more easily measured quantities [8,9]. One of the most popular is the Hrubý parameter, K_{gl} [9]. Thus, it is argued that K_{gl} can be used as a quick measure of glass-forming tendencies of materials. That parameter relies upon the measurement of the relative positions of the crystallization (T_{cr}), glass transition (T_g), and melting (T_m) temperatures in DTA or DSC experiments. Good glass formers are characterized by high values of K_{gl} and vice-versa. However, closer examinations of K_{gl} reveal problems [2,10,11]. The main result was that the Hrubý parameter did not provide an absolute measure of glass-forming ability. Nevertheless it is normally assumed that K_{gl} can be used to compare the glass-forming tendency between different materials, provided the samples are prepared and quenched under similar conditions and the same heating rate is used. Weinberg [12] demonstrated theoretically that an increasing glass-forming ability is not always accompanied by enhanced stability as measured by the difference $T_{cr} - T_g$ of the same magnitude. However, it is not trivial to extend Weinberg's findings to the Hrubý parameter ($T_{cr} - T_g / T_m - T_{cr}$).

In this research we compute the critical cooling rates using *experimental* crystal nucleation (I) and growth rates (U) for some stoichiometric glasses that exhibit volume nucleation: $Li_2O \cdot 2SiO_2$ (LS_2), BaO $\cdot 2SiO_2$ (BS_2), $Na_2O \cdot 2CaO \cdot 3SiO_2$ (NC_2S_3), and $2Na_2O \cdot CaO \cdot 3SiO_2$ (N_2CS_3). We then calculate K_{gl} from careful DSC measurements and test its validity as an easy way to estimate glass-forming ability, by comparing that parameter with the values of R_c obtained from the TTT curves.

2. Calculations

The steady-state crystal nucleation rate $I(T)$ may be expressed by

$$I(T) = \left(\frac{KT}{\eta} \right) \exp \left(- \frac{K'\sigma^3}{T\Delta G^2} \right), \qquad (1)$$

where T is the absolute temperature, η the viscosity, ΔG the bulk free energy difference between liquid

and crystal, σ the liquid-crystal surface tension, and K and K' are constants [13].

The most common crystal growth mechanism, screw dislocation, will be used in the following calculations. The corresponding growth equation is [14]

$$U(T) = \frac{K''T\Delta T}{\eta} \left[1 - \exp \left(- \frac{\Delta G}{RT} \right) \right], \qquad (2)$$

where K'' is a constant.

The thermodynamic driving force for glass to crystal transformation (ΔG) is given by [13]

$$\Delta G = - \frac{\Delta H_m \Delta T}{T_m} - \int_T^{T_m} \Delta C_p dT' + T \int_T^{T_m} \left(\frac{\Delta C_p}{T'} \right) dT', \qquad (3)$$

where ΔH_m is the enthalpy of melting and ΔC_p (< 0) is the difference in specific heats between the crystalline and liquid phases at constant pressure at a temperature T.

For crystallization cases proceeding from homogeneous nucleation of spherical crystals, with a constant growth rate, TTT diagrams can be calculated by [15]

$$X_c = \frac{\pi}{3} I(T) U^3(T) t^4, \qquad (4)$$

where t is the time required to crystallize a small volume fraction X_c (usually taken as 10^{-6}) at a temperature T. If $I(T)$ and $U(T)$ are known, the construction of a TTT diagram is straightforward.

By definition, the critical cooling rate, R_{cn}, computed by the nose method is given by

$$R_{cn} = \frac{T_m - T_n}{t_n}, \qquad (5)$$

where T_n and t_n are the temperature and time at the nose temperature, respectively.

Table 1
Sources of experimental data used to compute R_c

Glass	ΔC_p	ΔH_m	η	I	U
LS_2	[16]	[13]	[17]	[17]	[17]
BS_2	[13]	[13]	[13]	[13]	[18]
NC_2S_3	[16]	[19]	[19]	[19]	[19]
N_2CS_3	[16]	[20]	[17]	[17]	[17]

Table 2
Critical cooling rates estimated by the TTT method

System	T_n (K)	R_{cn} (K/s)
LS$_2$	833	0.2–0.3
BS$_2$	1101	3.0
NC$_2$S$_3$	928–933	3.3–4.3
N$_2$CS$_3$	828	5.0–6.0

Table 3
Onset temperatures from DSC curves recorded at 20 K/min and K_{gl} parameter

	LS$_2$	BS$_2$	NC$_2$S$_3$	N$_2$CS$_3$
T_g (K)	738	974	849	759
T_{cr} (K)	899	1137	991	902
T_m (K)	1281	1605	1511	1442
K_{gl}	0.422	0.348	0.272	0.266

Critical cooling rate estimates were performed for some stoichiometric glass-forming systems. We selected LS$_2$, BS$_2$, NC$_2$S$_3$, and N$_2$CS$_3$ for computing R_{cn} because these glasses exhibit volume nucleation, and experimental data of crystal nucleation and growth rates, viscosity and thermodynamic quantities are available in the literature (Table 1).

Although the determinations of I and U had not been made in identical temperature ranges, the nose temperatures, T_n (Table 2), include the temperature region in which the crystal growth rates were measured. Regarding the crystal nucleation rates, T_n is somewhat higher than the upper temperature where I was determined. Therefore, the crystal nucleation rates were extrapolated to T_n through Eq. (1).
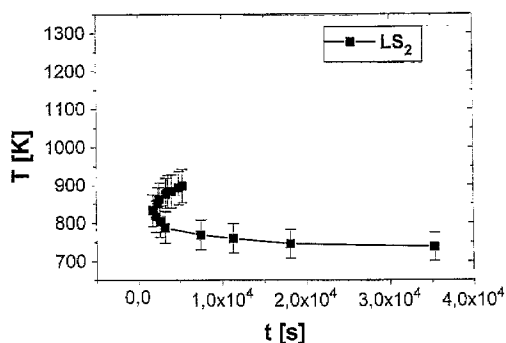

Fig. 1. Calculated TTT diagram of LS$_2$ glass. The bar indicates the uncertainty in the experimental values of I and U.
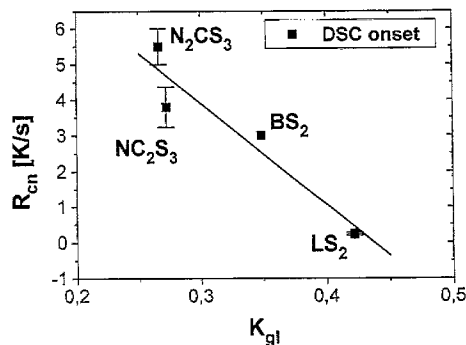

Fig. 2. Critical cooling rate versus Hrubý parameter of glass stability, calculated from the *onset* temperatures in a DSC scan of 20 K/min. The bar in the data points indicates the uncertainty in the calculations (Table 2).

Supposedly, *glass stability* can be estimated by the Hrubý parameter [9]:

$$K_{gl} = \frac{T_{cr} - T_g}{T_m - T_{cr}}, \tag{6}$$

where T_g, T_{cr} and T_m are taken as the onset temperatures of the corresponding DSC peaks.

3. Experimental procedure

Stoichiometric compositions of the chosen glasses were prepared. The chemicals and glass melting technique used are described in detail in [21].

The specimens were heated in a Netzsch DSC apparatus, type STA 409 with a heating rate of 20 K
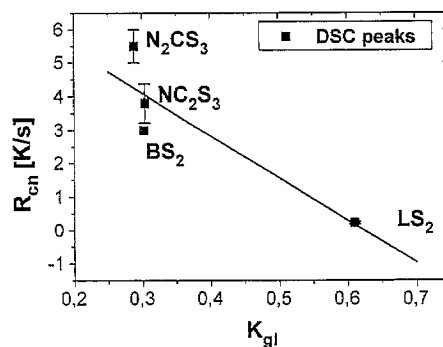

Fig. 3. Critical cooling rate versus Hrubý parameter of glass stability, calculated from the *peak* temperatures in a DSC scan of 20 K/min. The bar in the data points indicates the uncertainty in the calculations (Table 2).

Table 4
Peak temperatures from DSC curves and K_{gl} parameter

	LS$_2$	BS$_2$	NC$_2$S$_3$	N$_2$CS$_3$
T_g (K)	766	1002	883	805
T_{cr} (K)	983.2	1161.5	1035.1	957
T_m (K)	1339	1690	1537	1484
K_{gl}	0.610	0.303	0.304	0.288

min^{-1} to determine T_g, T_{cr} and T_m. To minimize surface nucleation, monolithic glass, was placed in a platinum crucible, where a small amount of high purity Al$_2$O$_3$ powder had been deposited to avoid contact with the crucible walls.

4. Results

The TTT diagrams obtained for each glass are reported in Ref. [21]. One of them is shown in Fig. 1. Critical cooling rate computations are reported in Table 2.

The uncertainty in the calculated values of R_c are shown in Table 2 for LS$_2$, NC$_2$S$_3$ and N$_2$CS$_3$ for which several sources of data were used. These values were used to construct Figs. 2 and 3.

The K_{gl} values obtained from the onset and peak temperatures of T_g, T_{cr}, and T_m are reported in Tables 3 and 4, respectively. The typical measurement errors were about 5%.

5. Discussion

The data of Table 2 indicate that the glass-forming tendency (decreasing R_c) increases in order: N$_2$CS$_3$, NC$_2$S$_3$, BS$_2$, LS$_2$. It should be stressed that the nose method systematically overestimates the critical cooling rates by approximately an order of magnitude [7], however, the data of Table 2 may be used for comparative purposes.

The critical cooling rate estimated by the nose method (R_{cn}) is an order of magnitude *smaller* than the experimental values obtained by Havermans et al. [22] and Ota et al. [23] for LS$_2$ glass. However, it should be stressed that in [22], a small amount of glass was put into contact with a *platinum* thermocouple, assuming that it did not influence the critical cooling rate. A similar problem occurred in [23],

where 10 g of glass were used in a *platinum* crucible. In both studies, the specimens were cooled with variable rates from T_m to room temperature. However, the nucleating power of platinum in lithium silicate glass is well known [24] and thus, R_c should increase with Pt concentration. It is therefore expected that the critical cooling rates measured by the experimental procedures of [22,23] are higher than those obtained in experiments in which the contact between the sample and Pt is avoided. Additionally, surface nucleation is always present and contributes to increase the minimum cooling rate for glass formation. Hence, as the values of R_{cn} computed by the TTT curves take into account only homogeneous volume nucleation, they should be smaller than the experimental values.

In respect to the Hruby parameter, Table 3 (onset temperatures) shows that the glass-forming ability increases in the following sequence: N$_2$CS$_3$, NC$_2$S$_3$, BS$_2$, LS$_2$. Values on Table 4 (peak temperatures) also indicate that LS$_2$ is the best glass-forming system, while N$_2$CS$_3$ is the most reluctant one, and BS$_2$ and NC$_2$S$_3$ have similar glass-forming ability. Then, in spite of the differences between the onset and peak values of K_{gl}, they show similar trends.

In order to test the validity of the Hruby parameter, we plotted $R_{cn} \times K_{gl}$ curves based on both onset and peak temperatures, Figs. 2 and 3, respectively. According to Fig. 2, the glass-forming tendencies predicted by K_{gl} are consistent with the R_{cn} results. We traced a straight line just to guide the eye, although there is no theoretical justification for this procedure. Further developments are needed to establish a theoretical relationship between the two quantities.

Regarding the peak temperatures, Fig. 3 indicates that the corresponding K_{gl} values show a more complex relation to R_{cn}. However, even in this case, there is a general correlation, i.e., the higher R_{cn} the smaller is K_{gl}.

6. Conclusions

There is significant correlation between the Hruby parameter and the glass-forming tendency, estimated by critical cooling rates, obtained by the TTT method, using *experimental* nucleation and growth rates. Calculated critical cooling rates are consistent with

laboratory practice for glasses studied and also with experimental measurements of R_c for LS_2 glass. The Hrubÿ glass stability parameter can be used to estimate glass-forming ability for glasses that exhibit volume nucleation.

Acknowledgements

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