Brief Introduction to Glass Crystallization

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Research on glass systems, including oxide, non-oxide, polymer and even metallic glasses is one of the red-hot areas in the field of Materials Science because of the great scientific and technological importance of these prominent materials.

In the design of novel materials, properly predicting glass-forming ability — i.e., how easily a material can form glass — for various glassy systems, is extremely crucial and urgently needed.
Any material can vitrify if cooled from the molten state to the glass transition temperature, $T_g$, at a rate fast enough to prevent crystallization.

It is thus desirable to know how one can estimate the glass forming ability (GFA).
Experimental Classical Procedures

- Traditional procedures in heat-treated glasses to obtain kinetic information

Number of crystals per volume (or surface)

Crystal Size

Fraction crystallized

\( N_V \)

\( N_S \)

\( U_1 \)

\( U_2 \)

\( I_{st} \)

\( \tau \)

time
Nucleation Definition

Terms

- **Homogeneous**: spontaneous formation from the melt; composition of the melt and crystal are the same.

- **Heterogeneous**: nuclei form on some 'foreign' surface: impurities, crucible wall, bubbles, seeds, etc.

If could be possible do not form nuclei (and if there are no heterogeneities), crystallization can be avoided.
Nucleation & Crystal Growth Rates

$I_{\text{max}}$ homogenous

\[ \text{Li}_2\text{O.2SiO}_2 \]

- Nucleation
- Crystal Growth

- $U_{\text{max}}$

\[ T_g, T(K), T_m \]

Nucleation Rate $I$ (m$^{-3}$s$^{-1}$)

Crystal Growth Rate $U$ (m/s)
Observation of number of crystals per volume unity $n_V (1/m^3)$:

Fixed Temperature

$tangent = n_V / t = I$

$I = number of crystals per volume per time (1/m^3s)$
Optical Micrographies

Glass 28.8BaO-71.2SiO$_2$ mol%:
9.5h at 752°C + 22min at 815°C

Glass 33.2BaO-66.8SiO$_2$ mol%:
40min at 765°C + 14min at 815°C

Optical Micrographies

Glass 28.3BaO-71.7SiO₂ mol%:
6.5h at 760°C + 22min at 815°C

Glass 28.3BaO-71.7SiO₂ mol%:
8.0h at 760°C + 22min at 815°C

Optical Micrographies

Glass 28.3BaO-71.7SiO$_2$ mol%: 1.5h at 800$^\circ$C

Glass 29.9BaO-70.1SiO$_2$ mol%: 1.5h at 800$^\circ$C

Transmitted Light

Number of crystals per volume unity \( (n_v) \) vs. time for glasses 28.3BaO-71.7SiO\(_2\) and 29.7BaO-70.3SiO\(_2\) mol % nucleated at 718\(^\circ\)C.

\[ n_v \times \text{time} \]
Glass-forming ability (GFA) is the easiness to vitrify a liquid on cooling. It is possible to calculate GFA via critical cooling rate, $q_{cr}$:

$$q_{cr} = \frac{\Delta T}{\Delta t} \approx \frac{T_m - T}{t}$$

Glass stability (GS) is the glass resistance against devitrification on heating. GS could be defined by at least fourteen different combinations of $T_g$, $T_x$, $T_c$ and $T_m$.

$$K = K(T_g, T_x, T_c \text{ or } T_m)$$
Glass stability (GS) involves up to four characteristic temperatures: $T_g$, $T_x$ and/or $T_c$ plus $T_m$.

- $T_g = 454^\circ C$
- $T_x = 608^\circ C$
- $T_c = 625^\circ C$
- $T_m = 1042^\circ C$

**Li$_2$O.2SiO$_2$**
Objective

- To correlate glass-forming ability (GFA):

\[ q_{cr} = \frac{\Delta T}{\Delta t} \approx \frac{T_m - T}{t} \]

with glass stability (GS) in volume and surface crystallizations:

\[ K = K(T_g, T_x, T_c \text{ or } T_m) \]

- But is quite difficult to accurately measure \( q_{cr} \). On the other hand, once a glass is made, its stability against crystallization can be easily investigated.
1. Glass Forming Ability

A) UHLMANN’S NOSE METHOD
Uhlmann was one of the first to use the idea of crystallization kinetics controlling glass formation.

To vitrify a liquid by cooling, the crystallized volume fraction $X_c$ is assumed to be $10^{-2}-10^{-6}$.

A ‘nose’ arises in TTT diagram at $T_n$. Thus:

$$q_{cr}^n = \frac{\Delta T}{\Delta t} \approx \frac{T_m - T_n}{t_n}$$

This method gives values near one order higher than experimental results.

Donald Robert Uhlmann, American physicist (b. 1935)
A KINETIC TREATMENT OF GLASS FORMATION

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A kinetic treatment of glass formation is presented. This treatment is based on the construction of time-temperature-transformation curves corresponding to some barely detectable degree of crystallinity. From such curves, the minimum cooling rates required to form glasses of various materials are estimated. The most important factors determining the glass-forming abilities of different materials are suggested to be the magnitude of the viscosity at the melting point and the rate of increase in viscosity with falling temperature below the melting point.

1. Introduction

In the past decades there have been several treatments of the conditions for glass formation based on considerations of crystallization kinetics (refs. 1–3, e.g.). The first of these treatments led to the conclusion that a pure liquid in bulk form, free of nucleating heterogeneities, would not crystallize if the kinetic barrier to either nucleation or crystal growth exceeds 30kT/m (where R is the gas constant and T is the melting point.)

Subsequent discussion has directed attention to the possible importance of transients on the frequency of nucleation. It was noted that the times required to build up the steady-state concentrations of subcritical embryos can be quite long (estimated in the range 10⁶–10⁷ sec) as the glass transition is approached. These times can thus be longer than the usual experimental times, and can effectively preclude the reliable determination of nucleation kinetics in many systems.

A parallel series of developments based on kinetic and statistical mechanical treatments of transport and molecular rearrangement in liquids have suggested that the existence of a glass transition may be a universal feature of liquid behavior – provided that the liquid can be cooled to a sufficiently low temperature without the occurrence of crystallization.

More recently, Turnbull has reassessed his attention to the conditions under which glasses may be formed. He noted that there are at least some
Fig. 1. *TTT* curves for salol corresponding to different volume crystallized fractions.


\[ A: X_c = 10^{-6} \]
\[ B: X_c = 10^{-8} \]
Fig. 2. TTT curves for SiO$_2$ corresponding to a volume crystallized fraction of $10^{-6}$.


1. Glass Forming Ability

B) JOHNSON-MEHL-AVRAMI KOLMOGOROV THEORY applied in the volume

Andrey Nikolaevich Kolmogorov (1903 – 1987), Soviet mathematician
Reaction Kinetics in Processes of Nucleation and Growth

BY WILLIAM A. JOHNSON* AND ROBERT F. MEHL† MEMBER A.I.M.E.
(NEW YORK MEETING, FEBRUARY, 1939)

It is now recognized that several important types of reactions in metallic systems proceed by the formation of nuclei and the growth of these nuclei. The process of freezing is a simple example of this, as Tammann pointed out years ago. Tammann held that the rate of freezing is determined by a rate of nucleation, expressed as the number of nuclei formed per unit volume of unfrozen liquid per second, and a rate of growth of these nuclei, expressed as the linear rate of radial growth in units of length per second. For isothermal freezing the conception is simple; for ordinary freezing, extending over a range of temperature, it is not as simple, for the values of the two constants must change with change in temperature. There is ample evidence that the postulated mechanism is correct even though a quantitative derivation of the rate of isothermal or of ordinary freezing in terms of the two constants has been lacking.

In recent years other reactions have been found to proceed in a similar fashion. It has been well established, particularly by Bain, that the formation of pearlite from the eutectoid decomposition of the solid solution austenite proceeds in such a way, and Polanyi and Schmidt, Tammann and Cron, Carnop and Sachs, and others have shown that the process of recrystallization proceeds in a similar way.

Isothermal reaction rates have been determined for eutectoid decomposition by a number of investigators. Bain’s work on the formation of pearlite from austenite is especially valuable in this respect—the type of isothermal reaction curve obtained, as illustrated in Fig. 13, showed an initial slow rate, accelerating to an intermediate maximum rate which then decelerated to the completion of the reaction; similar curves have been obtained by Weyer and his collaborators. Other eutectoid decompositions show similar behavior: for example, the decomposition of the beta eutectoid in the copper-aluminum system, studied by Smith.

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References are at the end of the paper.
Glass-forming ability (GFA): definition from JMAK (Johnson – Mehl – Avrami – Kolmogorov) theory:

\[
X_c = \frac{\text{Number of crystals } \times \text{ volume of one crystal}}{\text{total volume}} = \frac{4\pi I t r^3}{3} = \frac{4\pi I t (ut)^3}{3}
\]

Procedure:

1) Shape factor: \(4\pi/3\) as circular;
2) Counting the number of crystals per volume per time \(I\);
3) Volume of each crystal \(v = v(r)\) from growth kinetics \(r = ut\);
Assuming small $X_c$:

$$X_c \approx \frac{4\pi I u^3 t^4}{3}$$

JMAK Theory

where $I$ is the nucleation rate, (considering spherical crystals), and $u$ is the crystal growth rate for each $T$.

In general, $X_c$ could be treated as:

$$X_c(T) = 1 - \exp \left[-\frac{4\pi I(T)u(T)^3 t^4}{3}\right]$$

If $q_{cr}$ is defined as:

$$q_{cr} \approx \frac{dT}{t}$$

and

$$\ln[1 - X_c(T)] = -\frac{4\pi I(T)u(T)^3 t^4}{3}$$

(for a fixed temperature $T$)
Thus, if: 

\[ q_{cr} = \frac{dT}{t} \]

\[ \ln[1 - X_c(T)] = -\frac{4\pi I(T)u(T)^3 t^4}{3} \]

The critical cooling rate necessary to crystallize a fraction \( X_c \) is:

\[
q_{cr}(X_c) = \left\{ \begin{array}{c}
\frac{4\pi}{3} \int_{T_m}^{T'} \left[ \int_{T''}^{T'} u(T'')dT'' \right]^3 dT' \\
\frac{1}{4} \ln[1 - X_c(T)]
\end{array} \right. \]
Experimental nucleation and crystal growth rate curves from many authors.

Glass formation is a competing process between liquid phase and the resulting crystalline phases.

From a historical point of view, Tammann was the first to assess GFA from nucleation and crystal growth rate curves.

Gustav Heinrich Johann Apollon Tammann (1861 – 1938)
Russian physicist and chemist
JMAK Deduction

Eduardo Belline Ferreira, Brazilian materials science engineer

Volume Crystallization
To model transformation it is obviously necessary to calculate the nucleation and growth rates, but an estimation of the volume fraction requires impingement between particles to be taken into account.

Two precipitate particles have nucleated together and grown to a finite size in time $t$. New regions $c$ and $d$ are formed as the original particles grow, but $a$ & $b$ are new particles, of which $b$ has formed in a region which is already transformed.
Suppose that two particles exist at time $t$; a small interval $\Delta t$ later, new regions marked $a, b, c$ & $d$ are formed assuming that they are able to grow unrestricted in extended space whether or not the region into which they grow is already transformed. However, only those components of $a, b, c$ & $d$ which lie in previously untransformed matrix can contribute to a change in the real volume of the product phase ($\alpha$):

$$
\frac{dV^\alpha}{dV_e^\alpha} = \frac{V - V^\alpha}{V} = 1 - \frac{V^\alpha}{V}
$$

The subscript $e$ refers to extended volume, $V^\alpha$ is the volume of $\alpha$ and $V$ is the total volume.

Mael Avrami Melvin (1913 - 2014), Palestinian-American physicist
Multiplying the change in extended volume by the probability of finding untransformed regions has the effect of excluding regions such as $b$, which clearly cannot contribute to the real change in volume of the product. For a random distribution of precipitated particles, this equation can easily be integrated to obtain the real volume fraction:

$$\frac{V^\alpha}{V} = 1 - \exp\left( -\frac{V_e^\alpha}{V} \right)$$

which is equal to $X_c$, as demonstrated before. The extended volume $V_e^\alpha$ is straightforward to calculate using nucleation and growth models and neglecting completely any impingement effects.
Consider a simple case where the $\alpha$ grows isotropically at a constant rate $u$ and where the nucleation rate per unit volume, $I$. The volume of a particle nucleated at time $t = \tau$ is:

$$v_\tau = \frac{4\pi}{3} u^3 (t - \tau)^3$$

The change in extended volume over the interval $\tau$ and $\tau + d\tau$ is:

$$dV_e^\alpha = \frac{4\pi}{3} u^3 (t - \tau)^3 \times I \times V \times d\tau$$

Writing $\varepsilon = V^\alpha/V \Rightarrow$
JMAK Deduction\(^6\)

Overall Transformation Kinetics

\[
dV^\alpha = \left(1 - \frac{V^\alpha}{V}\right) \frac{4\pi}{3} u^3(t - \tau)^3 \times I \times V \times d\tau
\]

considering \(\varepsilon = \frac{V^\alpha}{V}\):

\[
-\ln[1 - \xi] = \frac{4\pi}{3} I u^3 \int_0^t (t - \tau)^3 \, d\tau
\]

so that:

\[
\xi = 1 - \exp\left(-\frac{4\pi}{3} I u^3 t^4\right)
\]
JMAK Deduction\textsuperscript{7}

Overall Transformation Kinetics

This equation has been derived for the specific assumptions of random nucleation, a constant nucleation rate and a constant growth rate. There are different possibilities but they often reduce to the general form:

$$\xi = 1 - \exp(-kt^n)$$

where $k$ and $n$ characterize the reaction as a function of time, temperature and other variables. The values of $k$ and $n$ can be obtained from experimental data by plotting $\ln (-\ln [1 - \xi])$ versus $\ln t$. The specific values of $k$ and $n$ depend on the nature of nucleation and growth. Clearly, a constant nucleation and growth rate leads to a time exponent $n = 4$, but if it is assumed that the particles all begin growth instantaneously from a fixed number density of sites (i.e. nucleation is not needed) the $n = 3$. 

1. Glass Forming Ability

C) JOHNSON-MEHL-AVRAMI KOLMOGOROV THEORY applied in the surface
Glass-forming ability (GFA): definition from JMAK theory:

\[ X_c = \frac{\text{Number of crystals} \times \text{area of one crystal}}{\text{total area}} = N_s gr^2 = N_s g (ut)^2 \]

Procedure:

1) Shape factor \( g \) (circular as \( \pi \), squared as 1, etc.);
2) Counting the number of crystals per unit area (\( N_s \));
3) Area of each crystal from growth kinetics (\( r = ut \));
Surface crystallized fraction ($X_c < 0.1\%$): 

$$X_c = N_s g [u(T) t]^2$$

where $g$ is the crystal shape factor ($\pi$ for circular crystals), $u$ the crystal growth rate and $N_s$ is the number density of crystals per unit area ($10^4$ crystals/m$^2$).

The critical cooling rate necessary to crystallize a fraction $X_c$ is:

$$q_{cr} = \frac{dT}{t} \Rightarrow q_{cr} \approx \frac{u(T) dT}{\sqrt{\frac{X_c}{gN_s}}} \Rightarrow q_{cr} = \sqrt{\frac{gN_s}{X_c}} \int_{T_m}^{T_g} u(T) dT$$

RESULTS IN THE FINAL PART OF THIS PRESENTATION
1. Glass Forming Ability

D) BARANDIARÁN & COLMENERO METHOD
CONTINUOUS COOLING APPROXIMATION FOR THE FORMATION OF A GLASS

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Non-isothermal equations describing the liquid-crystal transformation are derived using the isothermal Avrami equations. A theoretical expression for the critical cooling rate for the formation of a glass is found. Calculations based on this expression are in better agreement with experimental values than those derived from TTT (time-temperature-transformation) curves. A study performed on typical glass forming materials enables the glass forming ability (GFA) to be determined by experimentally measuring crystallization temperatures at different cooling rates, which are easily accessible with commonly available technology. The behaviour of the rate constant for crystallization is also obtained from the same data in the experimental range considered. In both cases no previous knowledge of the parameters involved is needed.

With some assumptions the values of the viscosity in the crystallization temperature range can be estimated.

Although the study was performed for an Avrami index of 4 an extension to other values of n is made under some restricted conditions and a more general treatment is outlined.

1. Introduction

In the past few years much work has been done in an attempt to estimate the glass forming ability by means of the isothermal equations for the nucleation and growth of the crystalline phase during liquid cooling.

The present method allows the critical cooling rate, $R^*$, for the formation of a glass to be determined, and it is found that the calculated values agree with the experimental ones although the former are somewhat higher than the latter [1-4].

The most common procedure is to derive the time-temperature-transformation (TTT) curves for a crystallized fraction ($\xi$) of $10^{-4}$, for which the solid is considered to be amorphous, by means of the approximate Avrami equations for small transformed amounts:

$$\xi = (Kr)^4$$

where $K$ is a rate constant found by combining the homogeneous nucleation and growth rates $I$ and $\alpha$ in the following manner:

$$K = \frac{\pi}{3}(I/\alpha)^{1/4}u^{1/4}$$

Continuous Cooling Approximation$^{1/3}$

- The critical cooling rate could be described as a function of stability parameters:

\[
\ln q_{cr} = A - \frac{B}{(T_m - T_c)^2}
\]

where $A$ and $B$ are constants, $T_m$ the melting point and $T_c$ the crystallization peak.
Fig. 3. Fitting of crystallization temperatures in Au-Ge-Si (a) and metglass (b).

\[ \ln q_{cr} = A - \frac{B}{(T_m - T_c)^2} \]

Cabral et al. suggested a modification of Barandiáran & Colmenero (BC) proposal:

\[ \ln q_{cr} = A - \frac{B}{(T_m - T_c)^2} \Rightarrow \ln q_{cr} = A - \frac{B}{T_m^2} \]

According to BC, when \( T_c \) increases to infinity, no crystallization occurs. However, this could not be applied because the difference \( T_m - T_c \) is always finite.

Both approaches could be viewed as proposals that try to relate GFA with GS.

2. Glass Stability

A) CARACTERISTICS TEMPERATURES
Glass Stability Models

- Up to now the only two models that reasonably explains glass stability criteria are due to Hrubý and Chain & Liu.

- As will be show, Hrubý gives a more physical interpretation to characteristics temperatures $T_g$, $T_x$ (or $T_c$) and $T_m$. Lu & Liu used the TTT diagrams to explain crystallization kinetics.
From Hrubý, a glass with short interval \( T_x - T_g \) indicates high crystallization tendency. A short interval \( T_m - T_x \) indicates that the crystalline phase formed at \( T_x \) is ready to melt.

\[
K_H = \frac{T_x - T_g}{T_m - T_x}
\]

(Hrubý)
EVALUATION OF GLASS-FORMING TENDENCY BY MEANS OF DTA

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A simple method is described that makes possible fast evaluation of glass-forming tendency on the basis of relative position of the recrystallization, transformation and melting temperatures. These temperatures are determined by means of DTA. One assumes that the glass-forming tendency is proportional to the thermal stability of glass. The glass-forming tendency is expressed numerically, thus enabling one to compare different kinds of glasses and the influence of various admixtures. The validity of the model is experimentally verified on the CdAs₂ and As₂Te₃ systems containing different admixtures.

I. INTRODUCTION

Determination and/or evaluation of the glass-forming tendency of melts has been the focus of attention and study for a long time. This attention has been particularly renewed several years ago, when glassy semiconducting materials entered the stage. Here appeared several papers that attempt to define the problem in such a way as to enable one to estimate or predict the glass-forming tendency of a melt on the basis of structural or kinetical factors [1, 2, 3, 4]. Several rules have also been worked out, which can serve as a good guide for preparation of new materials in the lab [4, 5]. All these views, approaches and models are summarized in a review paper by Holze [6]. Some of these papers have good theoretical basis but have to employ rather crude estimates and approximations if concrete cases are to be considered. Other studies are of semiempirical character and their validity is verified only in narrow region. This situation is due to the difficulties in obtaining reliable thermodynamical data, especially for non-stoichiometric melts, which — in fact — most of the materials used in practice are prepared from. Let us now mention some unclear points in the models proposed for the glass-forming tendency.

Dietzel [5] defines “glassiness” G (Gläserigkeit) as reciprocal rate of crystallization of the melt. Sarjeant and Roy [4] have made a systematic attempt to use critical rate of cooling as a criterion of glass-forming tendency. Haverman, Stein and Stevels [7] have compared Dietzel’s criterion G with the critical rate of cooling in the rim of sodium and lithium silicate and they have found that no definite relation between these two criteria exists, even for stoichiometric composition M₂O . 2 SiO₂ (M = Li, Na) with the lowest critical rate of cooling. Hence, there is disagreement between both approaches.

In another model, Kautzmann [8] gives a criterion of good glass-forming tendency,

\[ T_c \geq 2/3 \]

\[ ^{a)} \text{Cukrovarněcká 10, Praha 6, Czechoslovakia.} \]

The minimum cooling rate required to form a glass (i.e., critical cooling rate) is the cooling rate needed to bypass the nose of the TTT curve.

\[ K_{LL} = \frac{T_x}{T_g + T_m} \]

(Lu & Liu)
Therefore, the GFA of a liquid is directly related to the location of the TTT curve in the time-temperature coordinates.

In fact, the average position of the TTT curve along the temperature scale can be indicated by the line of $\frac{1}{2} (T_g + T_m)$.

Crystallization occurs between $T_m$ and $T_g$, and can be avoided by sufficiently cooling of the liquid ($q_{cr}$); when the glasses are isochronally heated at a constant heating rate, the sample starts to crystallize at an onset temperature denoted as $T_x$.

Liquid phase stability for glass-forming liquids should include two aspects: (i) the stability of the liquid at the equilibrium state (i.e., stable state), and (ii) the stability of the liquid during undercooling (i.e., metastable state).
When two glassforming liquids have the same $T_g$ but different $T_m$, their relative liquid phase stability is then dominated by the stability of their stable states (i.e., the values of $T_m$). The lower the value of $T_m$, the higher the liquid phase stability.

In the case that two liquids have the same $T_m$ but different $T_g$, their relative liquid phase stability is then dominated by the stability of their metastable states (i.e., the $T_g$ values). The lower the $T_g$, the higher will be the liquid phase stability.

Thus, if two liquids have different $T_m$ and $T_g$, then their liquid phase stability has to be measured by:

$$\frac{1}{2} \frac{T_x}{T_g + T_m}$$

which is the average of the stability of the liquids at equilibrium and metastable states.
If all liquids have the same liquid phase stability, then the glass-forming ability of a liquid can be reflected by the quantity of $T_x$ alone.

The materials with a higher $T_x$ likely have longer onset times and a higher resistance to crystallization. Compared with liquid “a,” liquid “b” has a larger onset crystallization temperature $bT_x$ ($aT_x < bT_x$) and longer onset times, thus consequently a lower critical cooling rate $bq_{cr}$ ($bq_{cr} < aq_{cr}$).

Therefore, the onset crystallization temperature $T_x$ measured upon continuous reheating alone can assess the GFA under the special condition that the liquids have the same liquid phase stability.
Lu & Liu’s Glass Stability Model\textsuperscript{5}

The correlation between the critical cooling rate and the parameter $K_{LL}$ for 49 metallic glasses.


$$K_{LL} = \frac{T_x}{T_g + T_m}$$
Other GS


\[ K_T = \frac{T_g}{T_m} \]  
(Turnbull)

\[ K_W = \frac{T_x - T_g}{T_m} \]  
(Weinberg)

\[ K_{SP} = \frac{(T_x - T_g)(T_c - T_x)}{T_g} \]  
(Saad & Poulain)
An assessment of glass stability criteria

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Several of the commonly used criteria for gauging glass stability are examined for the case of bulk crystallization of relatively unstable compositions. The qualitative and quantitative usefulness of these criteria are assessed by comparisons with the computed values of the actual thermal treatments required to crystallize a specified volume fraction for a thermal history appropriate for fibre drawing. The stability indices are altered by changing the physical parameters which control the crystal nucleation and growth processes. It is found that the standard treatment of glass stability is often, but not always, qualitatively useful. However, they are not quantitatively reliable, and generally no single criterion is especially superior to the others.

Recently we have considered the relationship between glass forming ability and stability towards devitrification. It was observed that these are related, but independent concepts. Glass forming ability pertains to the intrinsic tendency for a composition to be formed as a glass when cooled from the melt. A quantitative measure of glass forming ability can be provided, in many cases, by the critical cooling rate needed to produce a glass.

Stability towards devitrification (hereafter termed glass stability or stability) is a more elusive concept. We have defined glass stability as the resistance of glasses towards devitrification upon reheating. All quantitative measures of stability are somewhat arbitrary since the devitrification behaviour of a glass is a function of the thermal history to which it is subjected. Therefore, some stability criteria are more appropriate for certain thermal paths than others. On the other hand, one can distinguish the more useful criteria by identifying those thermal histories which might be of importance in processing glass products and for which glass stability issues are significant. For example, in the present work a thermal history is considered which might be used for the drawing of optical fibres from preforms. Stability criteria are shown evaluated within the framework of this particular choice of thermal history.

In the past, several measures of glass stability have been proposed to gauge the resistance of relatively unstable glass to devitrification upon reheating.\(^\text{1-4}\) The most commonly used measure of glass stability is given by \(T_d - T_r\), where \(T_d\) is the temperature where the crystallization rate is maximum in a non-isothermal DTA/ DSC measurement and \(T_r\) is the glass transition temperature. Other criteria which have been used are the following: \(T_d - T_c - T_r\); \(T_d - T_c\); \(T_c - T_r\); \(T_r - T_c\); or \(T_d - T_c\) or \(T_r - T_c\), where \(T_c\) is the lowest temperature where crystallization can first be detected in a non-isothermal DTA/DSC experiment.

The purpose of the present work is to assess and compare the above stability criteria. In particular, the following three questions are addressed:

1. Which of the above are qualitatively and/or quantitatively accurate?
2. Is there a 'best' stability indicator?
3. For which physical situations would one expect the above criteria to be most meaningful?

The criteria indices are computed as a function of several of the physical parameters which control the crystal nucleation and growth rates. These functional behaviours are compared with the variations in times required to crystallize a specified volume fraction for a given thermal history.

Assumptions and evaluation method

As discussed previously,\(^\text{1-4}\) for surface initiated crystallization processes the crystallization rate will depend upon sample size, shape and surface condition. Thus, only bulk crystallization will be considered here. Also, for reasons of simplicity, the epitaxial layer on substrates is assumed to be single component (or pseudo single component).

The temperature dependence of the nucleation rate, \(J(T)\), is assumed to be given by classical nucleation theory (CNT). In nearly all cases this assumption has been verified experimentally.\(^\text{1-4}\) For reasons discussed previously,\(^\text{1-4}\) some dissolution growth\(^\text{3-4}\) is chosen as the growth model.

In fibre drawing from a preform, the glass experiences a two step heating history. In the first step the glass is heated from room temperature to the draw temperature. The second step consists of an isothermal heating for a specified time period which depends upon the draw rate. For relatively unstable glass compositions, one wants to draw at the highest practical glass temperature, \(T_g\), in order to minimize the danger of crystallization. For the standard treatments described above, the following are obvious:

Glass forming ability criterion

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INTRODUCTION

In a given multicomponent system, there is an obvious correlation between composition and glass forming ability. However, no simple way still exists in order to find easily the best composition. The search for "stable" glasses becomes predominant for various applications, and promising glasses will remain laboratory materials as long as they could not be prepared in large and homogeneous bulk samples.

The concept of glass stability itself is somewhat impressionable as it may refer to crystallization rate at cooling or at reheating, to relaxation processes near glass transition or even to chemical durability. From a technological point of view, it is of prime importance that glass could be manufactured in the required shape and that its physical characteristics do not change with time. In practice, this means that glass melt could be cooled slow enough and that glass samples could be reheated without devitrification in the viscosity range \(10^4-10^5\) poises. In this paper, we will deal only with this content of the stability concept.

GLASS STABILITY EVALUATION

While only direct experimentation -e.g. fibre drawing- can demonstrate that a glass exhibits the required stability, it is necessary to use a quantitative scale for comparing different glasses or assessing the level of stability. Various methods have been used for this purpose. With classical optical glasses, it has been possible to draw the two characteristic curves of nucleation rate and crystal growth versus temperature.

This was made possible because nucleation rate during cooling could be neglected; but this is not the case of most exotic glasses. Moreover, these determinations require a lot of time and experiments. Another rigorous approach to the problem lies in the establishment of TTT curves (Time-Temperature-Transformation). They apply to most behaviour in an isothermal stage, and critical cooling rates in agreement with the required optical quality may be deduced from such curves. However, this method also requires numerous measurements: at least one D.S.C. scan per point. Most commercially available D.T.A. or D.S.C. apparatus make the measurement uneasy. Finally, it is often difficult to keep heterogeneous nucleation factors at a level low enough to make the TTT curve fully significant.

In practice, glass scientists usually base their glass stability evaluation upon the D.T.A. or D.S.C.\(^\text{5-10}\) scan on reheating. For it is a matter of current observation that unstable glasses show a crystallization exotherm close to glass transition temperature, while this exotherm is closer to melting temperature for stable glasses. In best cases,
3. Glass Forming Ability × Glass Stability

RESULTS USING JMAK THEORY CONSIDERING HOMOGENEOUS & HETEROGENEOUS SYSTEMS

Main Problem: Which GS?

- To assess the best glass forming values ($q_{cr}$) we used the same experimental glass stability parameters ($K$’s) presented.

- Proceeding in this way, some $K$ parameters showed better correlation with $q_{cr}$ than others.

- These test evolved homogeneous and also heterogeneous systems, but we used the JMAK approximation for surface only.
Glass stability (GS) using $T_x$:

JMAK Theory

\[ K_T = \frac{T_g}{T_m} \quad \text{(Turnbull)} \]

\[ K_W = \frac{T_x - T_g}{T_m} \quad \text{(Weinberg)} \]

\[ K_H = \frac{T_x - T_g}{T_m - T_x} \quad \text{(Hrubý)} \]

\[ K_{SP} = \frac{(T_x - T_g)(T_c - T_x)}{T_g} \quad \text{(Saad & Poulin)} \]

\[ K_{LL} = \frac{T_x}{T_g + T_m} \quad \text{(Lu & Liu)} \]

\[ K_1 = T_m - T_g \]

\[ K_2 = T_x - T_g \]

\[ K_3 = \frac{T_x}{T_m} \]

\[ K_4 = \frac{(T_x - T_g)(T_c - T_x)}{T_m} \]
Glass stability (GS) using $T_c$: JMAK Theory

$$K_T = \frac{T_g}{T_m} \quad \text{(Turnbull)}$$

$$K_W = \frac{T_x - T_g}{T_m} \quad \text{(Weinberg)}$$

$$K_H = \frac{T_x - T_g}{T_m - T_x} \quad \text{(Hrubý)}$$

$$K_{SP} = \frac{(T_x - T_g)(T_c - T_x)}{T_g} \quad \text{(Saad & Poulin)}$$

$$K_{LL} = \frac{T_x}{T_g + T_m} \quad \text{(Lu & Liu)}$$

$$K_1 = T_m - T_g$$

$$K_2 = T_x - T_g$$

$$K_3 = \frac{T_x}{T_m}$$

$$K_4 = \frac{(T_x - T_g)(T_c - T_x)}{T_m}$$
Thus, there are fourteen characteristic GS parameters. Which are the best ones?
Results

JMAK Theory

Full symbols: heterogeneous nucleation

\[ \log_{10} u \text{ (m/s)} \]

\[ T/T_m \text{ (K/K)} \]

**Fig. 1**: Crystal growth rates \( u(T) \)
Knowing the crystal growth rate of each glass is possible to assess the glass-forming ability (GFA) by means of $q_{cr}$:

$$q_{cr} = \sqrt{\frac{gN_s}{X_c}} \left| \int_{T_m}^{T_g} u(T) dT \right|$$

10^4 crystals/m² (pristine surface)

Thus, let's correlate $q_{cr}$ with each GS parameters $K=K(T_g, T_x, T_c$ or $T_m)$ using FINE or COARSE powders in the next figures…
Results

Fig. 2: GFA ($q_{cr}$) vs. GS ($K$):

- $q_{cr} \text{ (K/s)}$
- $K_T = T_g / T_m$
- $K_W = (T_x - T_g) / T_m$

**JMAK Theory**

**SURFACE**
Results

Fig. 3: GFA ($q_{cr}$) vs. GS (K):

\[ K_H = \frac{(T_x - T_g)}{(T_m - T_x)} \]

\[ K_{LL} = \frac{T_x}{T_g + T_m} \]
Results

Fig. 4: GFA ($q_{cr}$) vs. GS ($K$):

\[ K_1 = T_m - T_g \]

\[ K_2 = T_x - T_g \]
Results

Fig. 5: GFA ($q_{cr}$) vs. GS ($K$):

$K_3 = T_x^h/T_m$

$K_4 = T_x^h/T_g$
Results

Fig. 6: GFA ($q_{cr}$) vs. GS ($K_K$):

\[ K_5 = \frac{(T_x^h - T_y)(T_x^h - T_y)}{T_{m}} \]

\[ K_{SP} = \frac{(T_x^h - T_y)(T_c^h - T_y)}{T_g} \]
Results

Fig. 7: GFA ($q_{cr}$) vs. GS ($K$): JMAK Theory

\[ K_W = \frac{(T_c - T_g)}{T_m} \]

\[ K_H = \frac{(T_c - T_g)}{(T_m - T_c)} \]
Results

Fig. 8: GFA ($q_{cr}$) vs. GS ($K$):

\[ q_{cr} (K/s) \]

\[ K_{LL} = \frac{T_c}{(T_g + T_m)} \]

\[ K_2 = T_c - T_g \]
Results

Fig. 9: GFA ($q_{cr}$) vs. GS ($K$):

- $q_{cr}$ (K/s)
- $K_3 = T_c/T_m$

- $q_{cr}$ (K/s)
- $K_4 = T_c/T_g$

JMAK Theory

SURFACE
Discussion

JMAK Theory

- \( N_s \) equal to 10^4 crystals/m^2 corresponds to the smallest value reported for fractured surfaces.

- We use a surface fraction crystallized \( X_c = 0.1\% \) as minimum surface crystallized fraction detectable by X-ray diffraction experiments.

- It is difficult to directly measure critical cooling rates (\( q_{cr} \)). But some measurements done in Li_2O.2SiO_2 and Na_2O.2SiO_2 near corresponds to present calculations. Comparison with TTT method also presented good results.
The resulting GFA decreases in the following sequence: \( \text{Li}_2\text{O}.2\text{B}_2\text{O}_3 \), \( \text{CaO}.\text{Al}_2\text{O}_3.2\text{SiO}_2 \), \( \text{CaO}.\text{MgO}.2\text{SiO}_2 \), \( \text{Li}_2\text{O}.2\text{SiO}_2 \), \( 2\text{MgO}.2\text{Al}_2\text{O}_3.5\text{SiO}_2 \), \( \text{Na}_2\text{O}.2\text{SiO}_2 \), \( \text{PbO}.\text{SiO}_2 \), e \( \text{GeO}_2 \). Thus, according to these results, compositions \( \text{GeO}_2 \), \( \text{PbO}.\text{SiO}_2 \) and \( \text{Na}_2\text{O}.2\text{SiO}_2 \) are the easiest to vitrify on cooling, while \( \text{Li}_2\text{O}.2\text{B}_2\text{O}_3 \) is the most difficult to be obtained as a glass. These findings agree with our practice in laboratory observations of glass formation.

There were no significant differences between the results for fine (22 - 38 µm) and coarse (150 - 177 µm) particles.

Most of the GS parameters that consist of three characteristic DSC temperatures show excellent correlation with GFA.

We thus demonstrated that certain, but not all GS parameters can be used to infer GFA. The best GS are \( K_W \), \( K_H \) and \( K_{LL} \).
Acknowledgments