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Fast crystal growth in glass-forming liquids

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ABSTRACT

In liquids of high glass-forming ability, in which crystal growth rates are low, the rates can be measured over the full range of supercooling from the liquidus temperature down to the glass transition. For systems of low glass-forming ability, growth rates are readily measured at small supercooling and at very large supercooling around the glass-transition temperature, but it is difficult to acquire data over the full range of intermediate supercooling, especially at the maximum in growth rate. Data at intermediate supercoolings are however of considerable interest for understanding glass formation in such systems as pure metals and chalcogenides for phase-change data storage. We will review the methods emerging for making such measurements, and will note that the fragility of the liquid (including possible crossover from 'fragile' to 'strong' liquid behaviour on cooling) is an important part of understanding fast crystal growth. We also note that there are deficiencies in existing theories of fast crystal growth.

1. Introduction

Glass formation on cooling a liquid involves avoidance of crystallization, and analysing glass-forming ability (GFA) requires the kinetics of both crystal nucleation and growth to be taken into account. In this review, however, we focus only on the rates of crystal growth U. Furthermore, to avoid complications from solute partitioning, we restrict ourselves to systems that crystallize congruently (i.e. the liquid/glass and the single-phase crystal forming from it have identical compositions). High GFA is associated with sluggish crystallization, but there is much current interest in marginal glass-forming systems in which U can be high. Most liquids, including it now seems pure-metal melts [1,2], can form glasses if cooled sufficiently rapidly, at $>10^{10}$ K s^{-1}. For glass-forming systems, it is well accepted schematically, but rarely measured quantitatively, that U must exhibit a maximum in the temperature range between the melting point T_m (equivalent to the liquidus temperature when freezing is congruent) and the glass-transition temperature T_g. For classic glass-formers, such as silica and the oxide glasses, the values of U are low and can be measured (often by direct observation of the crystals) over the full range of supercooling from T_m down to T_g. Even for poor glass-formers, such as most metallic systems, large supercoolings can be achieved in levitated droplets, and there are now many measurements of rapid crystal growth [3]. But so far only one study (on $Cu_{50}Zr_{50}$ [4]) has reached supercoolings large enough to permit measurement of the maximum U_{max} in crystal growth rate. There are many measurements of U in the glass (Section 5) and supercooled-liquid states near T_g, but for poor glass-formers it is difficult to acquire data over the intermediate supercoolings relevant for U_{max}. Yet such data are not only of fundamental interest, for example in setting the ultimate limits to glass stability, but also of technological importance for the operation of phase-change memory (where the materials of current interest are chalcogenides).

Our focus is on the measurement and analysis of fast crystal growth, especially in the temperature range of U_{max}. We note that the mode of crystallization in this regime may well be different from that at small supercooling; in particular the high driving force permits fast congruent freezing to a metastable phase, favoured by the lack of the inhibiting factor of solute partitioning. Property changes in the liquid as a function of temperature are not of concern in conventional solidification studies, where the liquid supercooling is always small. But such changes are important over the wide range of supercooling relevant for glass-forming systems, and provide further points of interest. We will review the methods emerging for making measurements of U, emphasizing those relevant for fast growth in systems of low GFA, and will note that the fragility of the liquid (including possible crossover from 'fragile' to 'strong' liquid behaviour on cooling) can be an important part of understanding crystal growth rates.

2. Liquid and glassy states

It is familiar that different glassy states are formed by cooling the liquid at different rates. The range of states that can be achieved has been explored particularly intensively for metallic glass-forming systems [5]. We take such a system to show the range of enthalpies of interest: Fig. 1

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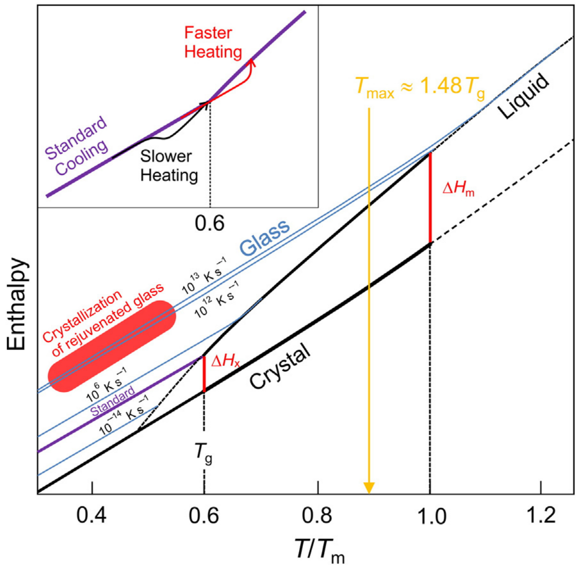

Fig. 1. Relative enthalpy as a function of reduced temperature for a bulk-metallic-glass forming system, showing representative scaling between the specific heats (dH/dT) and the heat of melting ΔH_m. T_{max} is the temperature at which the crystal growth rate reaches its maximum U_{max}. The inset shows the relaxation behaviour near T_g under differing heating rates. At a given temperature, the enthalpy range in potential glassy states is remarkably wide, up to ~0.9 ΔH_m.
Adapted from Ref. [5].

is schematic, but based on calorimetric data for the system $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10.0}Ti_{5.0}$ (composition in at.%) forming the bulk metallic glass Vitreloy 105 [6]. The T_g indicated in the figure is for the standard cooling rate of 0.33 K s^{-1}, and corresponds to the conventionally adopted value of viscosity $\eta = 10^{12}$ Pa s. The heat of crystallization ΔH_x of a relaxed glass, measured using conventional differential scanning calorimetry (DSC) at a typical heating rate of ~10^{-1} K s^{-1}, is ~0.4 ΔH_m (where ΔH_m is the latent heat of melting). The large difference between ΔH_x and ΔH_m indicates that there is considerable ordering in the liquid as it is supercooled. States of different order are retained in the glass by cooling at different rates. Fig. 1 shows rates from 10^{13} K s^{-1} (possibly achieved, or exceeded, experimentally in pure-metal nanobridges [1]) down to 10^{-14} K s^{-1} (the effective cooling rate that would correspond to ultrastable states obtainable by deposition with a glass-transition temperature at about 85% of the conventional value). For such a wide range of cooling rates, the range of enthalpy is very wide, up to ~0.9 ΔH_m [5]. In principle, analysis of crystal growth rates in glass-forming liquids should consider such a wide range of states. For any glassy state, the details of the transition to the liquid state on heating depend on the heating rate (inset in Fig. 1). On heating, usually the glass undergoes relaxation and goes through T_g before crystallization; the nature of the crystallization must then be unaffected by the prior glassy state. For glassy states of very high enthalpy (*rejuvenated* states), however, crystallization may occur below T_g [2].

Our interest is mostly in the maximum growth rate U_{max}, which occurs at a temperature T_{max} between T_g and T_m. It has been shown for a wide range of glass-forming systems (data for some of these are included in Fig. 2) that there is a good correlation between T_{max} and T_g, with $T_{max} = (1.48 \pm 0.15)T_g$ [7]. On that basis, T_{max} is indicated in Fig. 1, and we see that at this temperature, far above the standard T_g, only a small range of enthalpy would be relevant for the maximum in crystal growth rate. The value of U_{max} would be affected only by quenching at the very highest rates not relevant for our current interest (though relevant for molecular-dynamics simulations). While there can be non-equilibrium effects in supercooled liquids (e.g. analysed in terms of *retarded viscosity* [8]), we conclude that in the current work, with its focus near T_{max}, we can take the properties of the liquid to be characteristic of the actual temperature (i.e. independent of thermal history, cooling or heating rate).

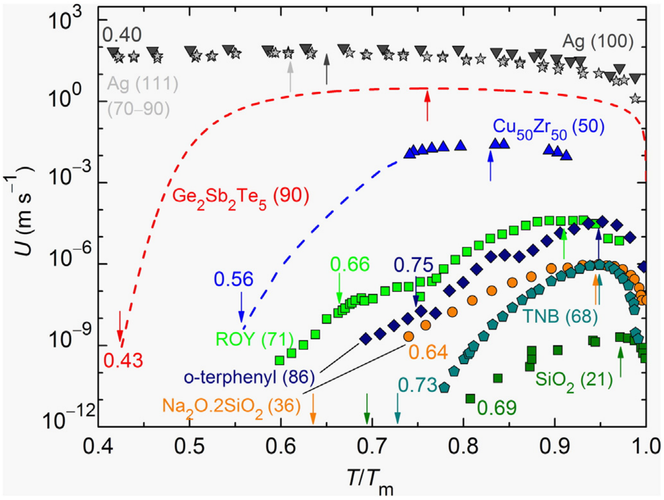

Fig. 2. Survey of crystal growth rates in variety of glass-forming liquids showing congruent freezing. The upward arrows indicate the maximum in the crystal growth rate; the downward arrows mark the reduced glass-transition temperature T_{rg}, and the values are given. The numbers in parentheses show values of the liquid fragility m.
Modified from Ref. [7].

3. Influence of reduced glass-transition temperature and fragility

Turnbull [9] noted that the *reduced glass-transition temperature*, T_{rg} ($= T_g / T_m$) is an important parameter governing GFA. He considered the rate, I, of homogeneous nucleation of crystals in the liquid, and showed that nucleation is effectively suppressed when $T_{rg} > 0.67$. As T_{rg} increases, the temperature at which I is maximum increases, and the maximum value of I decreases markedly. He also noted that the correlation of $I(T)$ with T_{rg} would be affected by different liquids having different temperature dependences of viscosity $\eta(T)$. In the current literature this is discussed in terms of the kinetic *fragility* of the liquid, defined as $m = [\mathrm{d}(\log_{10}\eta)/\mathrm{d}(T_g/T)]_{T=T_g}$ [10]. Senkov [11] has suggested that GFA can be correlated with a combination of the two independent parameters T_{rg}, and m, and he defined a dimensionless parameter, $F = 2[(m/16)(1/T_{rg} - 1) + 2]^{-1}$, with F varying from ~0.1 for very fragile liquids to ~0.8 for strong liquid SiO_2.

Our previous work [7] examined how T_{rg} and m might affect the temperature dependence of crystal growth rate $U(T)$ in supercooled liquids. The compilation of $U(T)$ data for diverse glass-forming systems (Fig. 2), remarkably resembles Turnbull's plot of $I(T)$ for different values of T_{rg}. Although there are relevant studies of polymeric crystallization [12], we exclude polymeric systems from the comparison in Fig. 2; as noted in earlier work [7,13], in such systems, factors such as chain length disrupt the usual correlation between crystal growth rate and viscosity. In Fig. 2, the values of the maximum growth rate U_{max} range over nearly 11 orders of magnitude, and, for a given span of T_{rg} values, this range is essentially the same as that of the maximum in I. Thus growth rates are also important in understanding GFA. For a high-GFA system, the value of U_{max} is low and occurs at high value of T_{max}/T_m (e.g. 0.97 for SiO_2). For a low-GFA system, $U(T)$ shows a much broader peak, U_{max} is high, and occurs at a low value of T_{max}/T_m (e.g. 0.61 for pure silver, obtained from molecular-dynamics simulations).

In Fig. 2, values of T_{rg} and m are given for each set of data. The values of U_{max} do not show good correlations with a single parameter T_{rg} or m. But this earlier work [7] established, adopting a strategy similar to that

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