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Liquid structure and long range diffusion: Their impact on glass formation and nanoscale devitrification

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Abstract

The importance of liquid structure on phase formation is illustrated by recent high-energy X-ray diffraction studies of metastable liquids in the deeply supercooled state, and of transient solid phases that form during solidification. In addition, these results confirm a half-century-old hypothesis made by Frank and call into question the capability of the classical theory of nucleation to accurately describe such complex coupled nucleation processes. The addition of as little as 0.5 at.% of Ti in AlFeY alloys radically alters glass formation and crystallization. This microalloying effect is argued to arise from subtle changes in the structure of the liquid/glass with the addition of Ti. Long-range diffusion is often key in the crystallization of glasses that form nanostructures. A novel mechanism for nanoscale devitrification is discussed that is based on a nucleation model that couples the interfacial and long-range diffusion stochastic processes.

Keywords: B. Glasses, metallic; B. Microalloying; C. Nanocrystals; F. Calorimetry; F. X-ray diffraction

1. Introduction

Light-weight Al-based and highly processible Zr-based metallic glasses are under intense study for potential structural applications. Many of these glasses crystallize (devitrify) to an amorphous/nanocrystal composite (nano-composite). The nanostructures observed have grain densities ranging from 10^{20} to $10^{23}/\mathrm{m}^3$, with grain sizes between 5 and 20 nm, indicating an extremely high nucleation rate with a low growth velocity. Typically grain growth is initially rapid, but abruptly slows down when the grain size exceeds a few nanometer [1]. Many of these nano-composites are even more interesting and have greater technological potential than the glass precursors [2,3]. It is clearly desirable to optimize the microstructure evolution, but the reasons for nanoscale crystallization in particular glasses remain unclear.

Several possible mechanisms have been proposed, including icosahedral short-range order in the glass [4–6], quenched-in nuclei [7], heterogeneous precipitate formation [8], phase separation [9], and the influence of composition [10,11] and diffusion-controlled nucleation [12]. Which of these is responsible generally depends on the chemical composition of the glass and the processing conditions. In many cases, several mechanisms may be in competition. A key feature of all glasses that form nanostructures is a different composition of the primary crystallizing phase from the glass, making long-range diffusion effects important for nucleation and growth. This is particularly true for the Al–transition metal–rare earth (Al–TM–RE) glasses, where the primary crystallization kinetics of α-Al are primarily determined by the slow diffusion of the RE atoms.

In this article, three case studies are presented. The impact of icosahedral short-range order in the liquid or glass on the nucleation barrier of ordered phases is discussed, based on recent structural studies of undercooled TiZrNi liquids. Second, the effects of microalloying on glass formation and stability are illustrated by the substitution of small amounts of Ti for Al in AlYFe glasses. Finally, a diffusion-based model for nucleation during glass formation and subsequent crystallization is presented and shown to predict a high nuclei density when long-range diffusion effects are dominant. These three cases point to emerging evidence for the importance of coupled processes in nucleation.

2. Ordering in liquids

To explain the ability of metals to be cooled far below their equilibrium melting temperatures without crystallization, Frank proposed that the liquid structure is dominated by an

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Table 1
Reduced undercooling ($\Delta T_r = \Delta T/T_l$) and interfacial free energy for quasicrystals and crystal approximants in Al-transition metal alloys

Quasicrystal				Crystal approximant			
Alloy	Phase	ΔT_r	$\sigma(T_N)$ (J/m^2)	Alloy	Phase	ΔT_r	$\sigma(T_N)$ (J/m^2)
$Al_{58}Cu_{34}Fe_8$	i-phase	0.09	0.09 ± 0.01	$Al_{13}Fe_4$	λ-phase	0.12	0.16 ± 0.01
$Al_{30}Cu_{34}Fe_6$	i-phase	0.09	0.09 ± 0.01	$Al_{62}Cu_{25.5}Fe_{12.5}$	λ-phase	0.14	0.15 ± 0.01
$Al_{72}Pd_{21}Mn_{17}$	i-phase	0.11	0.10 ± 0.01	Al_5Fe_2	μ-phase	0.14	0.18 ± 0.01
$Ti_{37}Zr_{42}Ni_{21}$	i-phase	0.09	0.06 ± 0.01	$Ti_{37}Zr_{38}Ni_{25}$	C-14 Laves	0.14	0.10 ± 0.01

Data for Al-based alloys from Ref. [15]; data for Ti–Zr–Ni from Refs. [17,18].

icosahedral short-range order (ISRO) that is incompatible with crystallographic structures [13]. As first demonstrated by Holzer and Kelton [14] the interfacial free energy between an icosahedral quasicrystal phase (i-phase) and a metallic glass of the same composition is extremely small, supporting Frank's hypothesis. Similar results were obtained for containerlessly processed undercooled metallic liquids that form quasicrystals (Table 1). Liquids in which the i-phase is the nucleating phase show the least undercooling, consistent with a low barrier due to ISRO in the liquid. The crystal approximant phases (λ-, μ-phase and C14 Laves phase) show larger undercooling, reflecting greater differences between their icosahedral and tetrahedral structures and the liquid structure. Simple crystal phases, such as β(Ti/Zr) and β(AlCuCo) show the greatest undercooling due to the incompatibility of the local structures in the crystal and liquid. Icosahedral order is often invoked to explain glass formation, since the ISRO raises the barrier for crystal nucleation during cooling. For a sufficiently large driving free energy, however, the ISRO in the glass may produce a very high nucleation rate for the i-phase, leading to nanocrystal formation. In support of this, the i-phase is frequently reported as the primary devitrification phase, particularly for the Zr- and Hf-based bulk metallic glasses [5,16].

It might be argued that since the interfacial free energies were derived from the classical theory of nucleation, which is known to be suspect for small cluster sizes [19], care should be exercised in comparing the magnitudes. Further, the results of the undercooling studies reported in Table 1 support, but do not prove, Frank's hypothesis, since the nucleation barrier is not directly correlated with the structure of the liquid. Recently, we unambiguously demonstrated this link in a Ti–Zr–Ni alloy [17]. In situ high energy synchrotron diffraction studies on an electrostatically-levitated $Ti_{37}Zr_{42}Ni_{21}$ liquid clearly showed that the i-phase was the primary nucleating phase from the undercooled liquid (Fig. 1b). However, the cooling data showed (Fig. 1a) that within one to two seconds after the temperature rise indicating the nucleation and growth of the i-phase (recalescence), a second recalescence event was observed (see arrows in Fig. 1a). X-ray diffraction data (Fig. 1b) demonstrated that this corresponded to the transformation of the metastable i-phase to a phase mixture of the C14 Laves phase and β(Ti/Zr), a bcc solid solution phase, the stable phase mixture at elevated temperatures. That the i-phase nucleated in preference to a stable phase, with a higher driving free energy indicates that the i-phase must have the lower nucleation barrier, independent of the model of nucleation assumed for the data analysis. As shown in Fig. 2a, a shoulder on the high *q* (momentum transfer) side of the second peak in *S*(*q*) becomes more prominent with undercooling. The peak intensity and location match those expected for icosahedral order [20], indicating that the lower nucleation barrier for the i-phase is due to a developing icosahedral short-range order—providing a direct experimental proof of Frank's hypothesis in this alloy.

Glass formation hinges on avoiding significant crystallization during cooling. An increasing ISRO in the liquid can have a dramatic impact on phase selection, increasing the barrier for the nucleation of crystal phases despite an increasing driving free energy for crystallization, thus suppressing the nucleation rate (Fig. 2b). More recent studies of pure transition metals have shown that with an increasing angular dependence

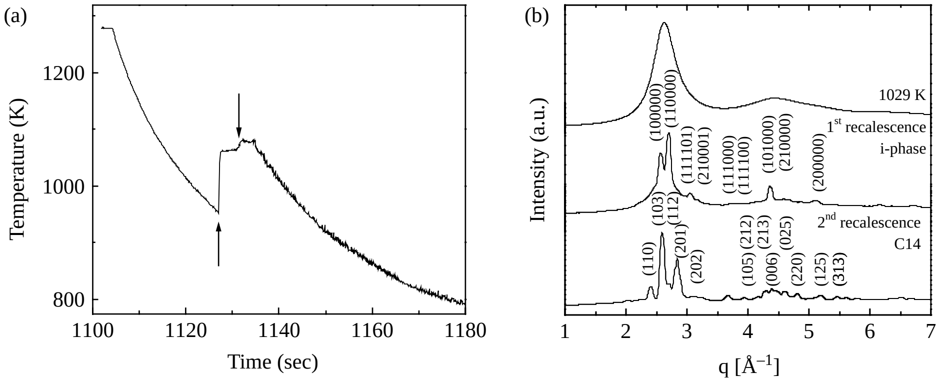

Fig. 1. (a) Cooling curve for electrostatically levitated 2.5 mm droplet of $Ti_{39.5}Zr_{39.5}Ni_{21}$ showing recalescence (indicated by arrows) as a function of temperature; (b) X-ray diffraction pattern as a function of momentum transfer, *q* ($=4\pi \sin \theta/\lambda$), for the undercooled liquid of Ti–Zr–Ni alloy at 1029 K, during the first recalescence to the i-phase, and during the second recalescence to the C14 phase. (from [17]).