LETTER TO THE EDITOR

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Letter to the Editor

Correlation between kinetic strength, volumetric properties, and glass forming ability in metallic liquids

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A B S T R A C T

A systematic study of the viscosity in the equilibrium and supercooled states is reported for $Cu_{100-x}Zr_x$ $(30 \leq x \leq 55)$ liquids. While no correlation between the magnitude of the viscosity at $T = T_g/0.6$ with the glass forming ability is observed, peaks in the kinetic strength are observed at the best glass forming compositions. This not only confirms the rule that strong metallic liquids are better glass formers, but also sheds light on recent correlations reported between volumetric properties and glass forming ability.

1. Introduction

Since the discovery that metallic alloys could be cooled and held below their equilibrium melting temperature (supercooled) [1,2], volume and atomic packing have played central roles in the theories used to describe these systems. From Frank's hypothesis [3], to Turnbull, Cohen and Grest's free volume models [4,5] and more recently Miracle's packing model [6], dense packing has been identified as a key reason for greater thermodynamic stability and slower kinetics in liquids. Although atomic packing in amorphous phases has been correlated with critical casting thickness [7], an empirical connection to the dynamics of the liquid and volume has not been reported previously. Here, we present a systematic study of the viscosity of $Cu_{100-x}Zr_x$ $(30 \leq x \leq 55)$ liquids, establishing relationships between the volumetric properties of the liquid, the kinetic fragility, and the glass forming ability (GFA).

The unifying concept of strength/fragility, first proposed by Angell [8], has played an important role in understanding the thermodynamic and dynamical properties of glass forming liquids for many diverse materials classes (organic and inorganic compounds, metallic alloys, colloids). Liquids are kinetically “strong” when the temperature dependence of the response functions (viscosity, diffusivity, relaxation time etc.) follows an Arrhenius behavior. They are “fragile” when these quantities show a non-Arrhenius (or super Arrhenius) behavior with temperature. The degree of non-Arrhenius behavior of the viscosity, η, can be parameterized by fits to the Vogel–Fulcher–Tammann (VFT) equation,

$$\eta = \eta_0 \exp\left[D^* T_0/(T - T_0)\right], \tag{1}$$

where η_0 is the viscosity in the infinite temperature limit, T_0 is the temperature at which the viscosity becomes infinite, and D^* is a measure of the fragility of the liquid, called here the kinetic strength, to differentiate it from the commonly-used fragility index, which is defined near the glass transition temperature. As D^* increases the VFT equation becomes more Arrhenius, consistent with a stronger (less fragile) liquid [9].

The empirical rule, for metallic liquids, that strength correlates with glass formability is reasonable, since stronger glasses have higher viscosities at high temperatures, which inhibit the nucleation and growth kinetics [10]. There are, however, exceptions to this rule. For example, $Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}Nb_5$ (Vitreloy 106) requires a higher cooling rate to form a metallic glass than $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ (Vitreloy 106a) [11,12] despite being the kinetically stronger of the two liquids [13]. This occurs because, the local order in the liquid in the former case is more similar to that of the primary crystal phase [14], which decreases the nucleation barrier and promotes crystallization.

Density provides a measure of the degree of local or medium range order in a liquid because of the positive correlation between energy and volume in metallic systems. Maxima in the density of the glass [7] and the thermal expansion coefficients of the liquid [15] at the best glass forming compositions in Cu–Zr alloys (*i.e.*, $Cu_{50}Zr_{50}$, $Cu_{54}Zr_{44}$ and $Cu_{64}Zr_{36}$ [16–20,7,21]), corresponding to presumed minima in the internal energy of the glasses, were therefore interpreted as manifestations of strong liquid behavior. However, in the absence of experimental data for viscosity and diffusivity, this could not be verified. The viscosity data

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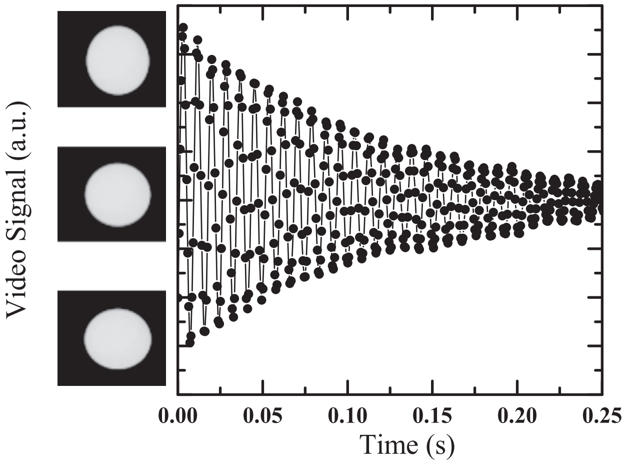

Fig. 1. Viscous damped surface oscillations recorded for a $Cu_{56.5}Zr_{43.5}$ liquid at 1200 K.

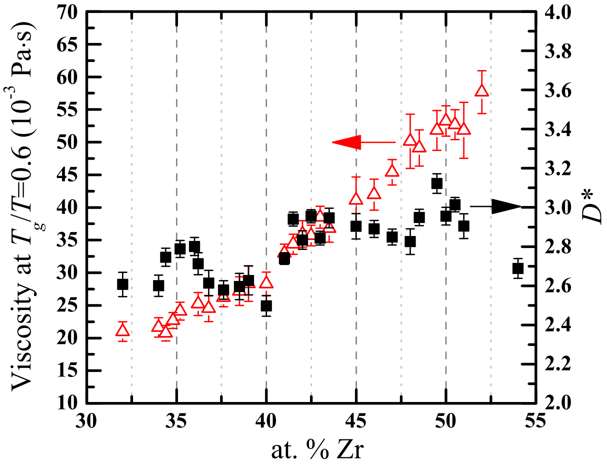

Fig. 3. The viscosity (red △) and D^* (■) for $Cu_{100-x}Zr_x$ liquids at $T_g/T = 0.6$.

reported here for 30 $Cu_{100-x}Zr_x$ ($30 \leq x \leq 55$) equilibrium and supercooled liquid alloys provide a direct verification of that interpretation. Peaks in kinetic strength are observed for the best glass forming compositions, confirming the inverse correlation between fragility and GFA.

2. Experimental

Master ingots of approximately 1 g for each composition were prepared by arc-melting high-purity Cu (99.995%) and Zr (99.9+% with nominal 3% Hf) in stoichiometric quantities. The arc-melting was performed in a high-purity Ar gas atmosphere (99.998%) after at least three cycles of evacuation (to less than 13 Pa) and Ar gas backfilling of the chamber. Samples of mass 70–90 mg were prepared from portions of the master ingots by additional arc-melting. These samples were levitated and melted in an electrostatic levitation facility under high vacuum (~ 10^{-5} Pa) [22]. By levitating the sample in vacuum, heterogeneous nucleation catalyzed by contact with air and/or the container is avoided, allowing for data be to acquired in the supercooled liquid [23,22]. The temperature was measured using a Metis MQ22 two-color ratio pyrometer (Process Sensors Corp.), operating at 1.40 and 1.64 µm wavelengths. The viscosity at each temperature was measured by the oscillating drop technique [24,25].

In brief, the oscillating drop technique was used to determine the viscosity by modulating the levitation electric field near the $l = 2$ resonant frequency (120–140 Hz) of the liquid to induce surface vibrations. The surface deformation was captured by high speed (1560 frames per seconds) video of the sample's silhouette. Intensity integration of each video frame varied in proportion to the amplitude of the second harmonic. After the perturbation was removed, the amplitude of the surface harmonic oscillations damped exponentially, with a time constant inversely proportional to the viscosity [26]. A representative intensity signal, decaying due to viscous damping, is shown in Fig. 1.

The viscosity was measured as a function of temperature and liquid composition during slow cooling, Fig. 2. Since the oscillating drop technique only allows the viscosity to be measured over a limited, low viscosity range, fits to the VFT equation (Eq. (1)) are over parameterized. This results in unphysical T_0 values (*i.e.*, $T_0 > T_g$) and artificially reduces D^*. Because Cu–Zr liquids are fragile, since $T_0 \rightarrow T_g$ with increasing fragility [27], and since the measurements were made at high temperatures, an approximate form of the VFT was used to mitigate the problems with unphysical values of T_0,

$$\eta \sim \eta_0 \exp\left[D^* T_g / \left(T - T_g\right)\right] \quad \text{as} \quad \left(T_g - T_0\right)/T \rightarrow 0. \tag{2}$$

Fits to Eq. (2) gave the D^* values discussed in this paper.

The modified VFT fit now has the same number of free parameters as an Arrhenius fit, but with lower residuals. Due to this approximation, however, the values of D^* are expected to be systematically lower than those obtained from fits over a wider viscosity range,

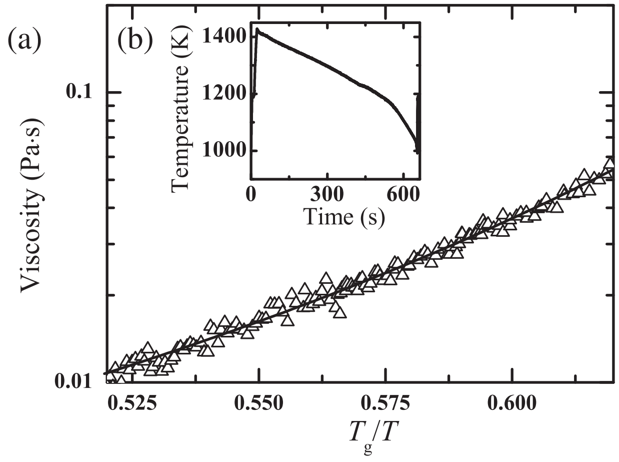

Fig. 2. (a) The viscosity (△) of $Cu_{56.5}Zr_{43.5}$ as a function of T_g/T, $T_g = 696$ K and a fit to Eq. (2) (line); (b) the cooling curve during which damping time measurements were made.

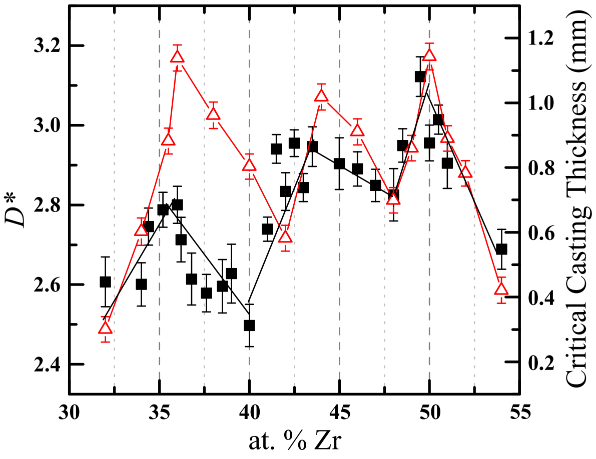

Fig. 4. The kinetic strength, parametrized by D^*, from the present measurements (■, lines inserted to guide the eye) and the critical casting thickness (red △, taken from Ref. [7]) for Cu–Zr liquids.