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Shear stress induced reduction of glass transition temperature in a bulk metallic glass

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Abstract

In contrast to previous observations of a slight increase in glass transition temperature (T_g) under hydrostatic pressure, we report, for the first time, a drastic reduction of T_g (40 K/500 MPa) induced by shear stress in a $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$ bulk metallic glass, which gives rise to the experimental observation of the drastic decrease in flow temperature while a compressive stress was applied. The significant T_g reduction is attributed to a large activation volume of relaxation ΔV_τ under shear stress (126 Å^3), and can be quantitatively interpreted in terms of the free volume model.

Keywords: Metallic glasses; Enthalpy recovery; Glass transition; Pressure; Stress; Free volume; Activation volume

1. Introduction

In many theoretical approaches, when a liquid is supercooled to a critical temperature where entropies of the liquid and the crystalline solid are identical, i.e., the isentropic temperature or Kauzmann temperature (T_k), a phase transition will take place from the supercooled liquid to a glassy phase if crystallization is suppressed, namely a glass transition [1–3]. However, such an "ideal glass transition" at T_k has never been observed experimentally. Glass transition, in either inorganic or metallic glasses, is always observed at a characteristic temperature (glass transition temperature, T_g), which is well above the Kauzmann temperature. Hence, it would be of great interest to experimentally lower T_g to approach T_k so that the glass transition can be studied at temperatures around the isentropic temperature. Moreover, reducing of T_g would enlarge the supercooled liquid region ($\Delta T_x = T_x - T_g$, T_x is the crystallization temperature), which may profit the superplastic deformation of the metallic glasses, and consolidation of glassy ribbons or powders in this temperature interval.

Nevertheless, reducing T_g of a glass seems to be rather difficult experimentally. Previous investigations showed that T_g is weakly sensitive to the composition and the thermal histories of glasses. Reducing the cooling rate of the melt or the heating rate of the glass may lower T_g and the $T_g - T_k$ gap diminishes to some extent. But T_g tends to be unchanged at a low heating/cooling rate (<1 K/s) [4,5]. Therefore, reducing T_g to T_k by lowering the heating rate seems to be inaccessible on lab time scale. When a hydrostatic high pressure is applied to metallic glasses, a rather small enhancement in T_g is observed (3–6 K/GPa) [6–8].

In terms of a free volume model suggested by Sietsma and co-worker [9], the glass transition is regarded as a kinetic phenomenon depending on competition between the creation and annihilation of the free volume in glasses. Previous studies showed that when metallic glasses were deformed below T_g [10–14], strain softening

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could be observed. This phenomenon was interpreted as an enhancement of free volume in the glass while applying a (shear) stress below T_g [10,13,15–18], which may result from the relatively enhanced creation rate or reduced annihilation rate of free volume. It hints that the applied stress may have an effect on the relaxation rate, enhancement of which, in principle, would lead to a reduction in T_g. Our previous studies [19] revealed that for a bulk metallic glass, the flow temperature decreases drastically with the increasing compressive stress by 50 K/1.4 GPa. However, direct evidence is still lacking to clarify if and how much the T_g was reduced under this circumstance.

The objective of this work is to identify the effect of a shear stress on the structure relaxation and glass transition in a bulk metallic glass $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$ (Vit 4) by using an enthalpy recovery method (ERM). For the sake of simplicity, a compression experiment was applied in this study to provide a shear loading. The variation of T_g induced by compression stress can be totally contributed to its shear component, since the contribution of the hydrostatic component is negligible (T_g increases slightly under a hydrostatic pressure [6–8]). Details will be discussed later in this study.

2. Enthalpy recovery method

While a compression stress is applied to the glassy sample, difficulties arise in determination of T_g by using thermal analysis or viscosity measurements. An ERM, of which the details have been described in [7], was applied in this study to measure the glass transition temperature indirectly.

Structural relaxation and enthalpy recovery phenomenon have been widely investigated in many metallic glasses for decades [20–23]. It was found that the structural relaxation, which was usually characterized by thermal analysis (differential scanning calorimeter, DSC), was strongly dependent on the initial state of the glassy sample before the measurement, as schematically illustrated in Fig. 1. The effect of initial state of glass on the relaxation and glass transition upon heating can be summarized as follows:

(a) The glass transition temperature is not sensitive to the initial glassy state.
(b) The shape of the DSC curve around T_g depends on the initial glassy state. For a glassy sample with high enthalpy state (sample 3 in Fig. 1), there is a broad exothermic peak on its DSC curve before glass transition; For the glassy sample with low enthalpy state (sample 1), there is a sudden increase in the enthalpy state during glass transition upon heating, which gives rise to the well known irreversible "overshoot" peak overlapped on the thermal signal of the glass transition (a step in the specific heat) in the DSC trace; for sample 2 with a medium enthalpy state, both the exothermic peak before glass transition and the endothermic overshoot peak during glass transition can be observed. But both of them are not very evident.
(c) The difference in the initial enthalpy state can be reflected by the width (or area) of the exothermic relaxation peak before glass transition for a glassy sample with high enthalpy state, or by the height (or area) of the endothermic overshoot peak during glass transition for samples with low enthalpy state. Because the overshoot peak is much sharper than the exothermic relaxation peak, the difference in the initial state of low enthalpy glasses is easier to characterize than that of the high enthalpy samples. A higher overshoot peak (of low enthalpy glasses) usually refers to a lower enthalpy state and a smaller amount of the free volume. The enthalpy state of a glassy specimen (with low enthalpy state) can be quantitatively measured via DSC measurements.

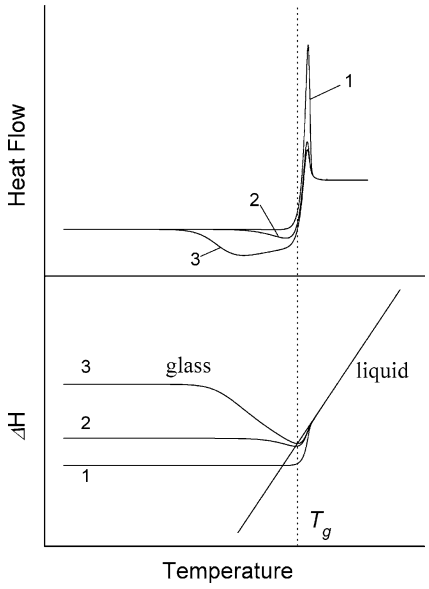

Fig. 1. A schematic illustration of the enthalpy changes (lower) and DSC traces (upper) during continuous heating for low enthalpy (sample 1), medium enthalpy (sample 2), and high enthalpy (sample 3) glassy samples.

While a low enthalpy glass sample was heated up, the glass transition and the sudden increase in the enthalpy take place simultaneously. Therefore, in principle, the glass temperature can be determined alternatively by measuring such an enthalpy change upon heating, based on which, the ERM was developed to measure T_g indirectly [7,8]. This method includes four steps: