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Hierarchical aging pathways and reversible fragile-to-strong transition upon annealing of a metallic glass former

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ABSTRACT

The change of physical properties during aging and the associated microscopic dynamics of the $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$ bulk metallic glass are investigated using a broad collection of laboratory and synchrotron-based techniques, such as differential- and fast-scanning calorimetry, thermomechanical testing, and x-ray photon correlation spectroscopy. We observe multiple decays in the enthalpy change during aging. This is reflected by a microscopic ordering consisting of distinct stationary dynamical regimes interconnected by abrupt aging processes. The stationary regimes are representative of states of local and transient equilibrium with increasingly higher activation energies. Furthermore, the aging study is conducted with the kinetically *fragile* frozen-in structure and the underlying fragile-to-strong transition is accessed by the ultra-viscous liquid state during annealing on a long-time scale and corresponds to the last observed enthalpy equilibration decay. The experimental work verifies, for the first time, that in a metallic glass forming system, the fragile-to-strong transition can also occur below the conventional glass transition temperature. Upon reheating, the reverse transformation, i.e. the strong-to-fragile transition, is observed with an entropy change of 0.19 J/(g-atom K), which is 2.4% of the entropy of fusion.

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1. Introduction

At temperatures below the glass transition temperature, T_g, physical properties of glasses, such as density or enthalpy, as well as viscosity or electrical resistivity, slowly evolve in time [1]. This physical aging process occurs in all classes of glasses and leads to significant structural changes at the microscopic level. Even though the aging pathways are ruled by the thermodynamics as the unstable state attempts to re-attain thermodynamic equilibrium, they are steered by sluggish atomic dynamics [1]. In the case of bulk metallic glasses (BMG), sluggish liquid kinetics that impedes the nucleation and growth of crystals during solidification [2] reflects sluggish atomic mobility during the annealing of the glass. In contrast to conventional crystalline metals and alloys, BMG-forming liquids are multi-component liquids with highly dense random-packed structures that involve a large size distribution of different atomic species and a negative heat of mixing between most of the species [3]. These factors contribute to considerable local microscopic order and to a hierarchy of relaxation processes with distinct timescales and activation energies [4–10], representative of a complex system of energy wells involving the activated motion of atoms or groups of atoms. Especially at low temperatures where it is expected to encounter weakly coupled frozen-in relaxation processes, the concept of a local equilibrium within a restricted energy range can be used [7]. In addition, for systems that were slowly frozen, the distributions of the structural relaxation processes are expected to be sparse and yield higher activation

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barriers [11].

In this work, we have studied the activation energy spectrum for enthalpy relaxation of a slowly frozen $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ BMG. The initial state was obtained by a heat treatment, prior to annealing, that cooled the supercooled liquid state with a constant slow cooling rate. The annealing treatments were selected for times from less than 1 s up to several days at temperatures 50 to 20 K below T_g. The selected composition is robust against crystallization [12] and the melting point is low enough that the glass can be obtained from the stable melt upon solidification using fast scanning calorimetry (FSC) [13]. Thermodynamic and kinetic analyses are performed using FSC, conventional power-heat compensated differential scanning calorimetry (DSC), and thermomechanical analyses (TMA). The results from these laboratory experiments are compared with detailed microscopic information on the collective atomic motion obtained using the X-ray Photon Correlation Spectroscopy (XPCS) synchrotron technique [14].

Our results reveal distinct multiple decays in the enthalpy recovery behavior, representative of states of local and transient equilibrium with increasingly higher activation energies. This hierarchical relaxation behavior is confirmed at the atomic level, where we observe different regimes of stationary dynamics separated by intermittent temporary aging processes. In the framework of the potential energy landscape approach [15], we ascribe the observed relaxation process to transitions from a high-energy local minimum to energetically lower, more deeply relaxed states [8,9,16–18].

In this work, we find also the direct thermodynamic and kinetic evidence of a fragile-to-strong fragility crossover connected to a polyamorphic liquid-liquid transition (LLT) in the ultra-viscous liquid state where the viscosity is greater than 10^{12} Pa s and relaxation times greater than 100 s, as a consequence of the physical aging process of a frozen-in fragile structure. The observation of a LLT during annealing is, to our knowledge, the first of this type for BMGs and it is in agreement with some anomalous behaviors in sub-T_g enthalpy relaxation studies of BMGs [19–23]. In Ref. [24] we have observed the microscopic signature of the LLT of this glass former upon cooling. The transition was observed at a temperature slightly below the conventional T_g and it was revealed by applying a quasi-static cooling protocol that shifted T_g to lower values [24]. The transition resulted in a dramatic change of the kinetic fragility of the glass-forming liquid, which we define in the following. The kinetic fragility is described with the empirical Vogel-Fulcher-Tammann (VFT) equation,

$$f(T) = f_0 \exp\left(\frac{T_0 D^*}{T - T_0}\right), \quad (1)$$

where the quantity f is either viscosity η or relaxation time τ. The pre-exponential factor f_0 is the infinite-temperature limit. In terms of viscosity it is 4.0×10^{-5} Pa s and in terms of relaxation time of the liquid it is approximately equal to 10^{-14} s. T_0 is the putative temperature, at which the barrier to viscous flow would become infinite. The combined parameters T_0 and D^* model the temperature dependence of the liquid relaxation kinetics. The larger the D^*, the 'stronger' the liquid, which more closely obeys the Arrhenius law. At high temperatures most BMG-forming liquids display fragile liquid behavior ($D^*<12$) above T_m and stronger liquid behavior ($D^*>20$) when equilibrated below T_g [25–27]. Upon cooling the studied BMG forming liquid was seen to transform spontaneously into a more ordered, kinetically stronger structure without changing chemical composition and density [24], thereby leading to a fragile-to-strong LLT, similar to the LLT observed in other glass-forming systems [2,26–35].

In this work, we observe not only the occurrence of a fragile-to-strong LLT upon long time annealing below the conventional glass transition, but we observe also the reverse transition (strong-to-fragile) upon re-heating. Such reversibility was recently observed for the first time for a molecular liquid [35], but never before in a metallic glass-former.

2. Materials and methods

2.1. Materials preparation

To prepare $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$ glassy specimens, the mixture of elements (purity 99.995%) were melted and homogenized at a temperature of ~1100 K in an alumina crucible in an Indutherm MC15 casting apparatus and tilt-cast into their glassy state in a water-cooled Cu-mold. A few rods of 5 mm diameter and length of 34 mm and plates of 3 × 13 × 34 mm dimension were produced by applying identical tilt-casting procedures. Some of the rods were re-melted in a quartz tube and injected onto a rotating copper well under argon atmosphere conditions to obtain glassy ribbons of approximately 8 μm of thickness. Prior to all experiments, the specimens were shown to be x-ray amorphous by x-ray diffraction. To prevent room temperature aging, the material was stored in a freezer at roughly 290 K.

2.2. Calorimetry

Conventional differential scanning calorimetry (DSC) was carried out under a constant argon flow in a power-heat compensated Perkin Elmer Hyper-DSC8500, equipped with an intracooler and calibrated according to the melting transitions of n-decane ($C_{10}H_{22}$), indium and tin. Approximately 200 mg of material was used for each DSC experiment. Fast scanning calorimetry (FSC) measurements were carried out in a Mettler Toledo Flash-DSC1. This was coupled with a temperature controller based on a two-stage intracooler. The calibration of the FSC was carried out according to the melting of indium at different rates. The conventional glass transition temperature is defined as the onset value of the calorimetric glass transition signal during a scan with a heating rate of $q_h = 0.333$ K s^{-1}. For both the bulk specimens (rods and plates as described above) and the melt spun ribbons the conventional T_g is observed at 396 K.

2.3. Standard treatment and annealing protocol

Prior to the enthalpy relaxation experiments, a standard treatment was applied to the sample by heating up with a rate of $q_h = 0.333$ K s^{-1} to a temperature of 418 K, which is above the end of the calorimetric glass transition and then cooling to 273 K with a rate of $q_c = 0.333$ K s^{-1}. This assured the same enthalpic state for each specimen. After completion of annealing, the sample was first cooled to 273 K and then re-heated with $q_h = 0.333$ K s^{-1} to the end of the crystallization process for the detection of the enthalpy recovery. Matching cooling and heating rates were applied in order to produce a realistic measurement of fragility and, therefore, of activation energy as discussed elsewhere [36]. The crystalline baselines were produced by repeating the measurement in a second up-scan of the reacted material under identical conditions without removing the sample.

The enthalpy recovery data at 378 K and all those corresponding to $t_a \leq 100$ s for the other temperatures indicated in Fig. 1 are measured with the FSC using one sample for each annealing set. Each FSC specimen was directly placed onto the chip and the mass was estimated by comparing the heat of fusion value detected in FSC to that obtained with the conventional DSC with a known mass. A typical mass was in the range of 0.001–0.005 mg. Conventional

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