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Structural relaxation kinetics defines embrittlement in metallic glasses

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ABSTRACT

Structural relaxation during isothermal annealing, quantified by enthalpy recovery of $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ towards its metastable equilibrium and correlation to embrittlement, quantified through fracture toughness, K_Q, is studied. Enthalpy relaxation over time obeys the Kohlrausch-William-Watts (KWW) stretch exponent with $\beta = 0.74$ and $\tau = 11{,}000$ s. Such β and τ are used to fit experimental $K_Q(t)$ with KWW, resulting in $R^2 = 0.79$. This finding combined with a controlled characterization of the glasses'K_Q versus temperature, fictive temperature, and their combination, revealed that embrittlement in metallic glasses is predominantly controlled by structural rearrangements, whereas volume changes from thermal expansion have negligible influence.

Structural relaxation, the evolution of a glass towards its metastable equilibrium of the supercooled liquid state is one of the most widely studied and richest topics in glasses. The kinetics and characteristics of structural relaxation are often described by the stretch exponent function, the Kohlrausch-William-Watts [1,2] (KWW) exponent which takes into account the plurality of relaxation processes that typically occurs simultaneously.

As structural relaxation reflects how the structure of a glass evolves towards the (metastable) equilibrium structure of the supercooled liquid, it reveals information about the structure, kinetics, and, when correlated with properties, generally reveals processing-structure-property relationships [3]. Due to the complexity of polymer or molecular glasses, relaxation characteristics in these glasses have been widely observed to obey KWW behavior [4–8]. For the seemingly "simple" metallic glasses (MG's) it is even more surprising that they also follow a KWW relaxation characteristics for their structure [9–12] and related properties such as free volume [13,14], density [15], and viscosity [16].

Annealing induced relaxation of a glass towards the supercooled liquid state in MGs has also been associated with the degradation of mechanical properties, so-called embrittlement, quantified in bending ductility [17–22], tension and compression plasticity [23,24], impact toughness [25,26], and fracture toughness [27–29]. Although previous investigations suggested a correlation between mechanical properties and relaxation process conceptualized as free volume [30,31], the specific correlation between the evolution and kinetics of relaxation and embrittlement were left inconclusive [27,32–35]. For example, it was inconclusive if the reduction of the free volume has been responsible for the embrittlement, and/or what contribution of annealing induced crystallization plays a role [36]. Even though free volume has been suggested widely as a key player in annealing induced embrittlement, previous discussions do not go past a general reduction in density as a free volume change. Isothermal relaxation kinetics of a glass towards its corresponding supercooled liquid, measured by enthalpy changes, has been identified to originate from structural rearrangements processes and not the thermal expansion contribution to the free volume [3,37–41]. Hence, identifying the correlation between enthalpy relaxation and embrittlement kinetics would constitute a powerful step to reveal the mechanism of embrittlement and beyond, fracture toughness in MG's in general.

One of the most direct measurements of embrittlement is fracture toughness measurements. However, until recently such measurements have been difficult and often overshadowed by extrinsic and possible intrinsic effects [42,43]. Since the main objective of this study is to understand how structural relaxation kinetics affect the MG's mechanical behavior, precise measurements are needed to reveal even small changes. We have developed a method that allows precise measurement of the conditional (notched) fracture toughness, K_Q, within 3% sample-to-sample variation once MGs undergo identical processing condition [44], and shown that K_{IC} can be extrapolated from K_Q [45]. This method has enabled to reveal complex processing-property relationships and extrinsic effects on K_Q [46–50].

We apply such method to study the K_Q of the glass and supercool liquid with i). the characterization temperature (T), ii). the fictive

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temperature (T_f), and iii). the relaxation kinetics of the glass towards the supercooled (equilibrium) liquid as a function of time. The fictive temperature, T_f, of a glass is the temperature where the glass had the same enthalpy with the liquid, which can also be viewed as the temperature where the glass falls out of the equilibrium (Fig. 1(c)). As the absolute temperature of the glass is changed, enthalpy of the glass changes due to thermal contraction which is an affine expansion of the glass. On the fictive temperature scale, the structure of the glass changes in a non-affine manner. As a consequence, the response of a glass to temperature variations involves only thermal contraction. This is in contrast to a glass's responses to changes in T_f (characterized at the same T) where only structural changes occur. These two contributions can be quantified from experimental results on thermal expansion of BMG alloys in their glass state and supercooled liquid state. The overall free volume contributes of both terms, which are approximately comparable in their magnitude [51]. We probe such changes through K_Q and enthalpy measurements. We revealed that embrittlement quantified by K_Q measurements follows the same KWW kinetics to enthalpy relaxation kinetics.Comparison between $K_Q(T_f)$ and K_Q (T) reveals that annealing induced embrittlement is controlled predominantly by the structural rearrangement contribution of the free volume. Volumetric thermal contractions contribution occurring on the temperature scale have a negligible effect on K_Q. This implies that overall enthalpy (free volume), which comprises of both, the structural rearrangement and thermal expansion counterparts, is insufficient to quantify the fracture toughness of a glass.

$Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ was used to study the relationship between enthalpy relaxation and K_Q upon isothermal annealing. To understand the effect of structural relaxation on K_Q, appropriate relaxation timescales were estimated using the Vogel-Fulcher-Tammann (VFT) relation, $\tau = \tau_0 \ \exp(\frac{D^*T}{T-T_0})$, where D^* is the fragility parameter, T_0 is the temperature at which $\tau \to \infty$, and τ_0 the relaxation time in the limit as $1/T \to 0$ and is estimated to be ~2.5×10^{-13} s for Zr-BMG systems [52]. D^* and T_0 are fitting parameters which are obtained by calorimetry as explained elsewhere [32]. We estimated D^* to be 28 and T_0 to be 344 K, giving τ of approximately 20,000 s. To study the relaxation time-dependent K_Q response towards metastable equilibrium, we selected various annealing times including $t = 0, 0.1\tau, 0.5\tau, 1\tau, 2\tau, 4\tau$ at a constant temperature below the calorimetry glass transition temperature, T_g.

Single edge notched tension (SENT) samples with geometry of 25 × 5 × 0.3 mm (length x width x thickness) with precisely controlled notch root radius $\rho = 10$ μm and notch length of 2.5 mm ($a/W = 0.5$) were prepared as described in Fig. 1(a)–(b). As previously shown that the considered MG exhibit a flaw tolerance behavior, the considered notch radius is below the critical notch radius, hence result in approximately the same K_Q as for the sample with an infinitely sharp notch radius [53]. MGs were thermoplastically formed into the as-prepared mold under pressure of 20 MPa at 698 K ($T_g = 623$ K), for 100 s, followed by rapid quenching. This procedure results in uniform and fully amorphous test samples. Samples were then subjected to sub-T_g annealing, which was chosen to avoid decomposition and crystallization, in a temperature-calibrated salt bath system at 593 K for various times (Fig. 1(c) path 3), followed by rapid quenching to prevent further relaxation upon cooling. To reveal the importance of free volume contributions due to thermal contraction, we characterized glasses at different temperatures (Fig. 1(c) path 2) and glasses with different T_f's, which was characterized at the room temperature (superimposed by the change in T). Enthalpy relaxation (ΔH_{rel}) due to annealing was quantified by Differential Scanning Calorimetry (Perkin Elmer Diamond DSC) upon heating with 20 K/min. K_Q tests were conducted by uniaxial tension under a quasi-static displacement controlled mode with a strain rate of 10^{-4} s^{-1} by Instron 5543. Qimaging CCD camera was utilized to observe in-situ plastic zone development during experiment (Fig. 1(d)).

Structural relaxation of $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ quantified by ΔH_{rel} for various relaxation times is shown in Fig. 2. Relaxation follows a

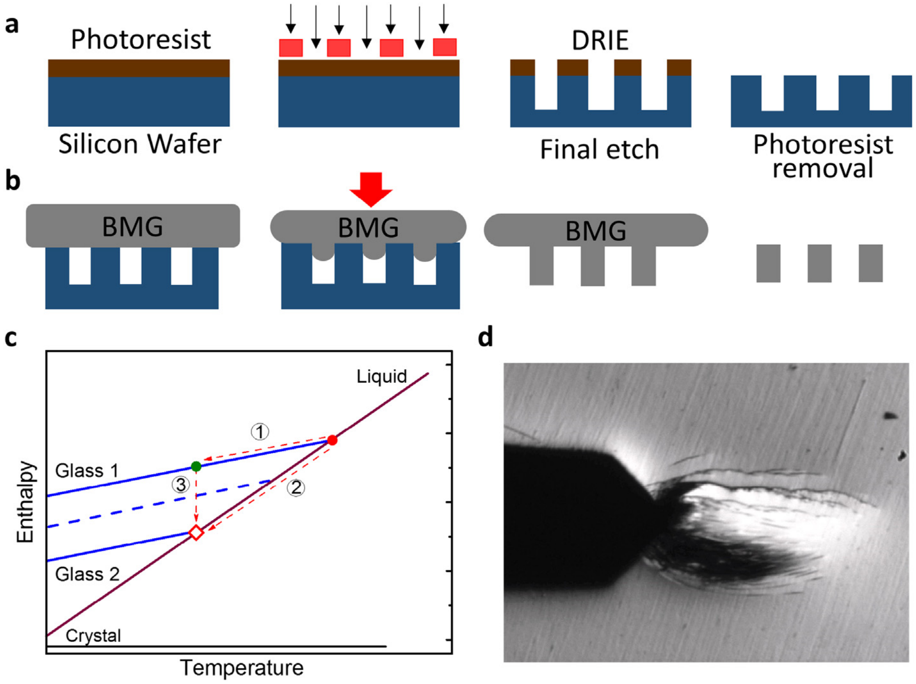

Fig. 1. Single edge notched tension (SENT) specimen fabrication method. (a) Silicon molds were prepared by a photolithography and deep reaction ion etching technique. (b) Thermoplastic forming of $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ MG into as-prepared silicon mold by compression under a temperature above the material's T_g. Samples were released from the silicon molds by 20% KOH etchant, followed by sanding and polishing procedure. (c) Possible paths for enthalpy changes, Path 1:liquid taken out of equilibrium to form a glass by cooling faster than the internal relaxation rate to maintain equilibrium which results in thermal contraction. Path 2: Cooling is carried out such that the liquid remains in metastable equilibrium. The liquid undergoes rearrangements and thermal contraction. Path 3, a glass is isothermally annealed to allow structural relaxation from its unstable glass state to the metastable equilibrium liquid state. (d) shows typical plastic zone region of $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_2$ SENT sample before fracture.