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Linking macroscopic rejuvenation to nano-elastic fluctuations in a metallic glass

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ABSTRACT

Metallic glasses are structurally heterogeneous below a certain length scale. Here we demonstrate how elastic heterogeneities change in response to a macroscopic cyclic, but elastic, loading protocol. Fluctuations in local elastic properties are spatially resolved across the surface of a bulk sample by evaluating nano-scale contact resonances of an atomic force microscope. The findings indicate a significant increase in nano-elastic fluctuations due to loading. The distribution of these fluctuations broadens symmetrically and almost three fold, revealing how the atomically disordered structure is driven further out of equilibrium at the nano-scale. Macroscopically, the stress-driven elastic heterogeneities lead to a rejuvenation and therefore a new structural state of the bulk metallic glass, characterized by a higher energy release during heating and mechanical softening. These results show how macroscopic energy storage in metallic glasses may be linked to the development of nano-scale elastic fluctuations.

1. Introduction

A long-standing problem in the science of disordered materials is to unravel structural dynamics and structural evolution introduced by either temperature or stress. This is of particular importance for relaxation [1,2] (aging) and rejuvenation [3,4] of metallic glasses (MGs), since these atomistic processes allow one to engineer the glassy state, and therefore the material's macroscopic response. After quenching from the melt, a MG ages naturally thereby deteriorating a number of its advantageous properties. How to reverse age, that is how to rejuvenate the glass, remains a challenge, and urges the establishment of a structure-property relation between the nano- and macro-scale.

At low homologous temperatures, there is virtually no experimental method which allows to trace local atomic structure-evolution of a MG. Investigating a glass as a function temperature, and in particular towards the glass transition and into the undercooled liquid regime, offers pathways to assess signatures of structural mechanisms, examples of which are α-, β- and γ-relaxation dynamics [5–7], viscous flow parameters [8,9], and crystallization [10]. In the glassy state, we continue to rely primarily on atomistic simulations or flow models that are based on a specific mechanism or physical variable(s), such as the well-known free-volume [11], shear transformation [12], or effective temperature theories [13]. To test these models on the atomic scale requires tracing atomistic reconfigurations resulting from an external bias, such as temperature or stress.

Early theoretical work has given insights into how the underlying atomically-disordered structure may evolve under the application of a load [14]. It was predicted that the internal stress distribution initially broadens symmetrically, and later skews due to strain localization. In more contemporary theoretical work that investigates thermally activated flow, a broadening of the underlying energy-barrier distribution due to stress has also been used [15,16]. This is compatible with results emerging from potential-energy-landscape exploration methods that directly probe activation-barrier energies and their evolution upon loading [17,18]. These modelling works indicate a broadening of experimentally

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measured quantities, such as local elastic properties or local yield stresses, both of which need to be resolved on the nano-scale in order to avoid averaging of the disordered solid at too coarse length scales. Successfully conducted, nanoindentation and atomic force microscopy have revealed both long [19] and short range [20–22] structural fluctuations of different glassy states, but the stress-induced evolution of such structural heterogeneities, both locally and statistically, remains until today unexplored. Here we show how the glassy structure evolves at the nano-scale in response to stress.

Using atomic force acoustic microscopy (AFAM) [21,23], we report on how strong elastic fluctuations develop in a Zr-based bulk MG as a result of a sinusoidal elastic load (fatigue experiment). We find that the initial as-cast atomic structure is characterized by local elastic fluctuations that rarely exceed ±2%, whereas the elastically-cycled material experienced an almost 3-fold symmetric broadening of local elastic properties. Furthermore, spatial fluctuations of ~11% were revealed at the scale of 10 nm, clearly indicating the formation of local high-energy states. The formation of these stress-driven elastic fluctuations are found to mechanically soften the MG and to induce an excess enthalpy storage of 920 ± 245 J/mol.

2. Experimental details

Atomic force acoustic microscopy (AFAM) measurements were performed on an as-cast and fatigued $Zr_{50}Cu_{40}Al_{10}$ MG using a Veeco-Metrology AFM and an ultrasonic transducer with a center frequency of 2.25 MHz. The fatigued glass was subjected to 10^6 compressive load cycles at a rate of 10 Hz with a maximum stress of 752 MPa (43% of the yield stress, elastic regime) and an R-ratio of 0.1 [24]. The sample ends were polished plane parallel prior to testing. After the fatigue experiment, scanning electron microscopy (SEM) was conducted to study the surface of the sample. No shear bands could be found. The total length of the sample did not change within the error of the caliper measurement (7.69 ± 0.1 mm). The absence of shear bands and the constant sample length support the nominally elastic loading, with potential viscoelastic effects that can at most amount to 1.3%, which is the error of the length measurement. A Zerodur glass composite served as a reference sample for the AFAM measurements. Si cantilevers (Budget Sensors) with the two first free resonance frequencies of 183 kHz and 1125 kHz, and a stiffness, k_c, of 42 Nm^{-1} were used to record contact resonances across square arrays [two dimensional (2D) maps] of 200 × 200 nm^2 at 20 × 20 different positions. The data of 13 such arrays is presented, and the arrays were positioned randomly on the surface along the 7.69 mm long sample. Longitudinal waves of frequencies in the range from 160 to 1600 kHz were injected into the sample from the bottom. They cause out-of-plane oscillations of the sample surface with the contacting cantilever tip. In this way both the first and second contact-resonances of the cantilever are detected by the optical detection system of the AFM. The obtained resonances were fitted with a Lorentzian to determine the contact-resonance frequency, f_c^n, where n indicates the n-th mode. This arrangement allows to calculate the real part of the tip-sample contact stiffness, k^*. Further details on the AFAM method and its data analysis are outlined in Refs. [21,23]. Differential scanning calorimetry (DSC) measurements were performed using a Perkin Elmer DSC 8000 at a heating rate of 100 K/min. Nanoindentation was conducted with a Hysitron TI-950 indenter in displacement-controlled mode, using a standard Berkovich probe. The indentation data was not corrected for pile-up. AFM topography scans were done across indents with an Asylum Research Cypher AFM in tapping mode to investigate the pile-up behavior. The yield pressure p_y of the initial pop-in was determined via $p_y = F/A$, whereas F indicates the load at the first pop-in and A corresponds to the contact area at the pop-in. The tip-area function was determined on a fused quartz sample prior to testing. Pop-ins were identified by using a difference between consecutive data points method [25], where values above a threshold of 2.6 standard deviations resulted in a detection of a pop-in.

3. Results and discussion

3.1. Spatial distribution of elastic heterogeneities at the nanoscale

Three different materials were investigated: a reference Zerodur oxide glass, an as-cast Zr-based bulk MG, and the same Zr-based MG subjected to compressive fatigue at 43% of the yield stress. In comparison to other cyclic loading studies conducted at higher peak stresses [24,26], no signature of shear banding could be resolved after elastic cycling. Using the AFAM-technique, we measure the contact-resonance frequencies of the cantilever in contact with the sample surface. Fig. 1 shows two contact-resonance peaks of $n = 2$ (second cantilever mode) for each of the three investigated materials measured at different locations on the sample surfaces. The curves have been shifted along the ordinate to facilitate readability. The peak positions of the as-cast MG and the Zerodur are slightly offset due to their different Young's moduli ($E_{MG} = 89$ GPa; $E_Z = 91$ GPa), and for both materials the two contact resonances are practically identical. In contrast, the two individual curves from the fatigued MG display a clear difference in the contact resonance frequency, f_c^2, where the superscript 2 refers to the second mode. This difference in f_c^2 indicates a much more pronounced position-dependent elastic signature of the elastic contact than observed for the as-cast MG and the Zerodur reference. In the following, 5200 measurement points distributed in 13 different 2D arrays across the sample surface shall be investigated.

Since f_c^n is directly related to real part of the tip-sample contact stiffness, k^*, which itself translates to values of an indentation modulus [21,23], any shifts in the resonance peak position resolved across a 2D map with 20 × 20 measurement points provide insight into the spatial fluctuation of nanoscale elastic properties. In the

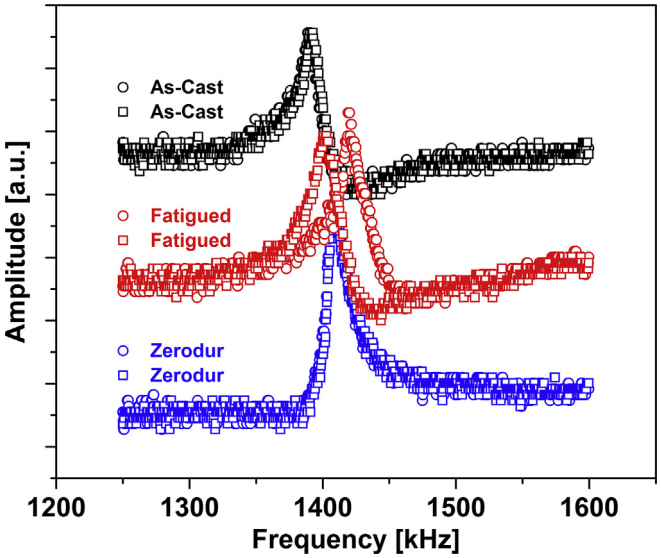

Fig. 1. Contact resonance curves for the second cantilever mode measured at two different locations on the as-cast $Zr_{50}Cu_{40}Al_{10}$ metallic glass, the compressively-fatigued $Zr_{50}Cu_{40}Al_{10}$, and the reference Zerodur glass.