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Thermal and mechanical activation of inelastic events in metallic glasses

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ABSTRACT

The activation-relaxation technique is used to explore the potential energy landscape of a $Cu_{64}Zr_{36}$ metallic glass and to investigate how heating and elastic deformation affect the energy distribution of potential activations. It is shown that heating involves only a few low-energy activations, whereas stress-induced mechanisms are enabled by elastic deformation induce inelastic events over a broader energy range. Observed inelastic events exhibit features similar to those of STZs, which suggests a link between β relaxation and plastic deformation processes.

The physics of glasses is one of the unresolved issues in condensed matter physics [1]. This can be ascribed to their metastable amorphous structure, difficult to resolve and to relate to properties [2,3]. It also results in a complex relaxation dynamics, which includes collective inelastic processes not yet unambiguously characterized [4,5]. Referred to as β relaxation, these processes affect the behavior of glasses [4,5]. Thus, understanding their nature is required to advance fundamental knowledge in the field, particularly from an atomic scale perspective.

Atomic structure and tunable chemical composition make metallic glasses (MGs) ideal model systems to study β relaxation [4,5]. Lacking intra-molecular degrees of freedom, their β relaxation is the analog of Johari–Goldstein β relaxation in non-metallic glasses [4,5]. In addition, metallic bonding enables relatively low energy paths for the inelastic events mediating β relaxation, which consist of persistent changes in the positions of atoms that intermittently show correlated displacements [4–6]. For the same reasons, metallic bonding allows readily accommodating atomic level strains in deformed MGs by inelastic distortions of STZs (STZs) [7–11]. Since the activation of STZs is the fundamental process underlying MG plasticity [12–21], a common structural origin for β relaxation and mechanical properties can be envisaged [22,23].

In this respect, it is worth noting that inelastic events mediating β relaxation and deformation share common features. In particular, their spatial occurrence is sparse, it matches structural heterogeneities [4–6, 24–29], and it is governed by similar activation energies [4,5,22,30]. This suggests that they involve approximately the same regions prone to rearrangement. Therefore, estimating the degree of stability of local structures, and investigating their thermal and mechanical activation, can throw new light on both β relaxation and deformation processes.

The present study aims exactly at measuring the degree of stability of local structures in a model MG, and at showing how heating and mechanical deformation can affect it. To this aim, the potential energy landscape (PEL) of the model MG is explored by classical atomistic simulation methods. Since β relaxation corresponds to fast hopping across inherent structures within a PEL mega-basin, the energies associated with transitions between neighboring local minima provide a measure of local stability [4,5,22,30]. The way the distribution of such energies varies upon heating and elastic deformation provides, instead, information on the thermal and mechanical activation of inelastic events.

The work focuses on a $Cu_{64}Zr_{36}$ MG of about 4100 atoms occupying a 65 nm^3 cubic volume. The initial MG configuration was prepared by quenching the corresponding melt from 2000 to 50 K at 2 K ps^{-1}, and zero pressure. A second configuration was quenched at 0.2 K ps^{-1} to detect possible cooling rate effects on MG properties. Interactions were described by the embedded-atom method [31]. Molecular dynamics calculations were performed in the isobaric-isothermal ensemble [32], with periodic boundary conditions along Cartesian directions. Equations of motion were solved with a fifth-order predictor-corrector algorithm [32] and a time step of 2 fs. The Wendt–Abraham method was used to estimate the glass transition temperature T_g [33]. In agreement with previous work [12,34,35], T_g was found equal to about 730 K. Obtained MGs were relaxed at 50 K for 0.5 ns.

The MG equilibrated at 50 K was heated at 100 K ns^{-1} to generate configurations at temperatures differing by 50 K in the range between 50 and 400 K. The selected MGs were relaxed for 0.5 ns, and, then, subjected to elastic deformation cycles to simulate dynamic mechanical analysis experiments [36,37]. Deformation cycles on short time scales reproduce, indeed, the fundamental features of the MG viscoelastic

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response [38,39]. For MGs loaded elastically, this consists of local processes contributing to residual strain [38,39]. Hereafter, the term β relaxation designates such events.

Elastic deformation cycles consisted of three stages. First, the MG was subjected to a uniaxial stress increasing at 0.01 GPa ps^{-1} up to 0.8 GPa, which is well below the 1.8 GPa yield strength of $Cu_{64}Zr_{36}$ MGs [12,35]. Then, the stress was kept constant at 0.8 GPa for 20 ps. Finally, the load was suddenly removed and the MG relaxed for 100 ps, although stress vanishes already after 60 ps. MGs were subjected to 30 cycles. However, most structural changes occur already after 10 cycles [38]. According to the structural analyses performed, the sudden load removal does not generate shock waves able to affect the MG structure.

Inelastic events activated by heating and deformation were identified by the activation-relaxation technique [40–42]. The technique allows exploring the PEL topology at constant volume searching for saddle points separating local minima [40–42], and has been successfully used to study diffusion in amorphous Si [43], and inelastic events in undeformed and highly driven MGs [44,45]. In the present work, connected clusters formed by a central atom and its nearest neighbors, i.e. the atoms within the distance r_{nn} of the first minimum in the pair distribution function, were perturbed by displacing each atom by a given length along random directions [40–42]. After each displacement, five relaxation steps were taken perpendicularly to the direction of motion to prevent any uncontrolled rise of potential energy [44]. Displacement lengths were increased by 0.05 nm until the PEL curvature became negative and less than -1 eV nm^{-2} [44]. Then, twenty iterations of the Lanczos algorithm per step were performed using a conjugate gradient algorithm [46] to relax the system to the saddle point [40–42]. This was considered reached for maximum atomic force component values equal to 10^{-3} eV nm^{-1} or less [44]. The energy difference between the initial local minimum and the saddle point represents the activation energy, E_a, associated with the inelastic event.

For any selected temperature, the activation-relaxation technique was applied to relaxed MG configurations before and after deformation cycles, hereafter referred to, respectively, as undeformed and deformed. For each configuration, non-redundant activations were determined by allowing ART search for a fixed time interval. Within such time interval, 4296 non-redundant activations were identified in the initial undeformed MG configuration equilibrated at 50 K. This number, and those for MG configurations equilibrated at different temperatures, are sufficiently large to sample the physics of inelastic events and to capture the shape of the activation energy distributions, ensuring good statistics. Initial conditions do not affect distributions, being quenching rate effects negligible and limited to small differences in the number of activations.

Following previous work [8,47], only atoms displaced more than $0.35\,r_{nn}$ by their initial position at the end of activations are considered involved in inelastic events. Atomic positions were used to identify activations in different MG configurations. In this respect, two MG configurations generated from different initial configurations and equilibrated at the same temperature can be expected to exhibit equivalent activation energy distributions, but different activations. This can be readily pointed out by dividing the volumes of the two MG configurations into corresponding sub-volumes defined by the same set of Cartesian co-ordinates. Any given sub-volume in the two configurations can be expected to include atoms with different positions, and, therefore, different possible activations. This means that the atoms participating in activations in corresponding sub-volumes have different initial and final average positions. For simplicity, such activations are referred to as non-coincident.

Conversely, if one of the two MG configurations is generated starting from the other, for example by annealing for a certain time interval, the generated MG configuration can be expected to retain memory of the parent one. In this case, any given sub-volume can include atoms with the same positions and susceptible of the same activation, i.e. of reaching the same final positions in the two MG configurations. These activations are referred to as coincident, and their number provides a measure of parenthood between the two MG configurations.

Equilibrating the generated MG configuration at a temperature higher than the parent one, or subjecting it to mechanical deformation, can be expected to decrease the number of coincident activations. The number of coincident and non-coincident activations was evaluated for any given pair of related MG configurations, and non-coincident activations divided into lost and generated ones. Lost activations correspond to activations present in the parent MG configuration, but not in the generated one. Conversely, generated activations are present in the generated MG configuration, and not in the parent one.

The number of activations identified in undeformed MG configurations, N_a^u, varies from 4296 to 4126 as the temperature rises from 50 to 400 K. The distributions $p(E_a^u)$ of activation energies E_a^u in undeformed MGs are shown in Fig. 1a. Similar in shape to analogous distributions obtained by experimental and numerical methods [43,44,48–50], the curves show that activations cover a relatively wide energy spectrum. Offset for clarity, the distributions exhibit only few differences concentrated in the E_a^u range between 0 and 0.5 eV.

Differences stem from the heating-induced loss of activations. The number of lost activations, $\Delta N_{a,lost}^u$, was calculated by subtracting the number of activations at higher temperatures from those at 50 K. For undeformed MGs at 100, 150 and 200 K, $\Delta N_{a,lost}^u$ is equal to only 1, 2, and 2 respectively, which indicates a poor statistics. As shown in Fig. 1b, $\Delta N_{a,lost}^u$ markedly increases between 200 and 400 K, and its logarithm decreases linearly with the reciprocal of temperature T. If data at 100 and 150 K are neglected, an Arrhenius-like dependence of $\Delta N_{a,lost}^u$ on T emerges. Therefore, $\Delta N_{a,lost}^u$ can be written as $\Delta N_{a,lost,0}^u \exp(-E_{a,lost}^u/kT)$, where $\Delta N_{a,lost,0}^u$ is a pre-exponential factor, k is the Boltzmann's constant and $E_{a,lost}^u \approx 0.15$ eV is the apparent energy barrier associated with lost activations. Implicitly, $E_{a,lost}^u$ takes into account the thermal processes responsible for the activation of inelastic events. Therefore, it is different from the energy barriers

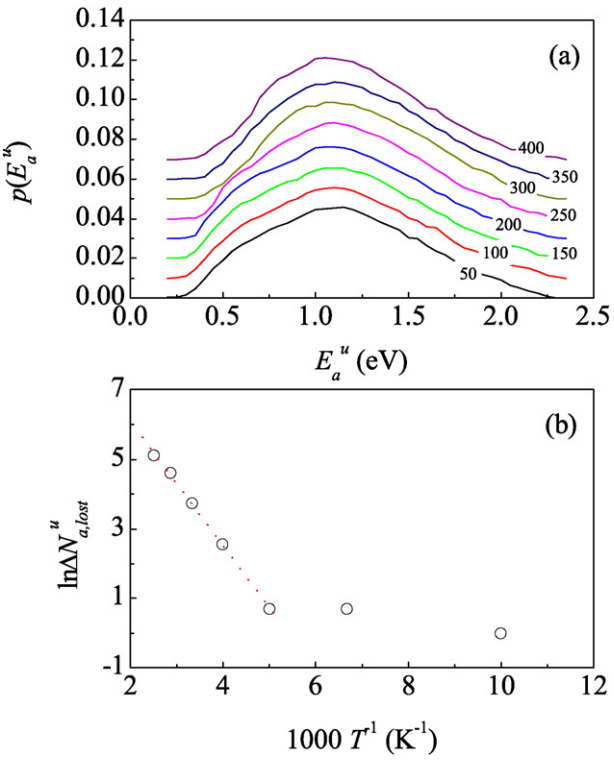

Fig. 1. (a) The statistical distributions $p(E_a^u)$ of the energy E_a^u of activations in undeformed MGs. Curves are offset for clarity and identified by temperature. (b) The logarithm of the total number of lost activations, $\ln\Delta N_{a,lost}^u$, as a function of the reciprocal of temperature, T^{-1}. The line best-fitted to data between 200 and 400 K is shown.