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Gamma relaxation in bulk metallic glasses

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Studying the primary α- and secondary β-relaxation process has contributed significantly to the understanding of the structure and rheology of metallic glasses. In this letter, we report on a third relaxation mechanism indicated by a maximum in the loss modulus at low temperatures, which we term γ-relaxation. Contrary to the α- and β-relaxation mechanisms, this irreversible, low energy excitation causes a macroscopic rejuvenation, which we assign to non-affine atomic rearrangements in the matrix that are driven by thermal stresses during cooling. Observed in three different glassy alloys, the low temperature relaxation is identified as a general process in metallic glasses.

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It has been long recognized that exciting a structural material with a small oscillatory stimulus may give rich insights into the details of fundamental relaxation mechanisms. Examples of such are momentary relaxation of dielectrics [1], internal friction measurements of dislocations in crystals [2], or viscoelastic properties of polymers [3], colloids [4], or metallic glasses [5]. In particular, the case of dynamical mechanical spectroscopy, DMA, has been a versatile tool to study different kinds of structural excitations in disordered systems, where distinct peaks in the loss modulus as a function of temperature reveal one, two or three structural relaxation processes when conducted at a given frequency.

The analysis of relaxation mechanisms has played an essential role in the understanding of glasses as they reveal fundamental structural differences to crystals [6,7]. In general, glassy systems universally exhibit two relaxations modes: the primary α- and the secondary β-process [8,9]. Primary excitations near the glass transition temperature, T_g, are associated with large cooperative atomic mobility leading to irreversible viscous flow. The secondary β-relaxation process below T_g is understood as a reversible cooperative rearrangement and reflects structural transitions on a much smaller energy scale [10–12]. In the particular case of metallic glasses, β-relaxations, also termed Johari-Goldstein relaxations [13], have been linked to reversible local transitions of small chain-like groups of atoms ([14,15]) that collectively are mediating α-transitions. Recently, evidence for a relaxation process observed at low temperatures (0.45 T_g) has been reported for a very particular La-based glass formers, which was sought to find its origin in the specific chemistry of the system [16,17].

Here we provide strong evidence for the existence of a general third structural relaxation mechanism in metallic glasses, which we observe in three glass forming alloys at around 0.2 T_g–0.3 T_g. This low temperature relaxation is very akin to the long known γ-relaxation in amorphous polymers, where it has been reported, for instance, in co-blockpolymers [18], epoxy resins [19,20] and substituted polystyrenes [21].

We find that γ-relaxation in the here studied bulk metallic glasses represents an irreversible structural excitation, causing a remarkable enthalpy storage that is recovered during reheating below the glass transition temperature. The barrier energy of the γ-relaxation was found to be of the order of a few tenth eV, being distinctly separated from the typical barrier energy scale of the α- and β-process.

Three different metallic glasses ($Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ (Vit106a, Liquidmetal Technologies), $Zr_{66.5}Cu_{33.5}$, $Pd_{77.5}Cu_6Si_{16.5}$) were prepared in ribbon form with a thickness of ca. 40–110 μm. X-ray measurements were conducted to verify a glassy structure. In the following we focus on the results for Vit106a, and data for the other two alloys can be found in the supplementary material (SM). Mechanical spectroscopy measurements were performed using a TA Q800 DMA in tensile geometry. The measurements were carried out in air and liquid nitrogen was used as a cooling agent. All samples were preloaded with a static stress below 13 MPa (which corresponds to 1% of the yield stress) and periodically excited either with a controlled strain of 0.03% or in a force controlled mode with a dynamic stress below 13 MPa. Differential scanning calorimetry (DSC) measurements were performed using a Perkin Elmer DSC 8000. After equilibration at 323 K, the samples were heated to 753 K in the supercooled liquid regime (T_g = 674 K, T_x = 782 K) with 40 K/min. After cooling with 80 K/min down to 323 K, where the temperature was held for 1 min, the samples were heated again with 40 K/min to 753 K.

Fig. 1 shows the loss modulus E'' as a function of temperature obtained by DMA measurements. Starting from room temperature the system was cooled to 116 K with a rate of 2 K/min while it was dynamically
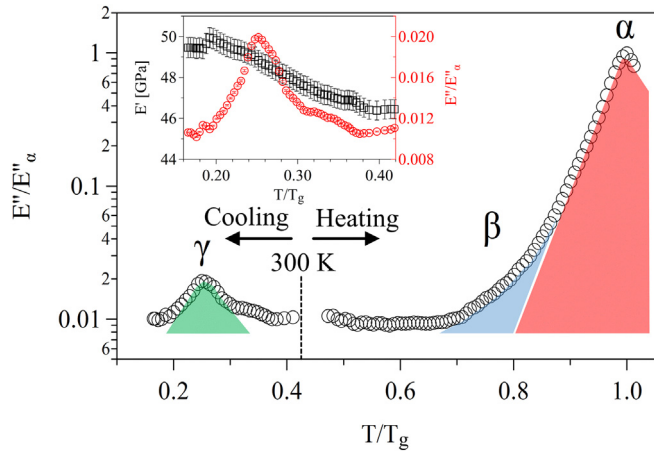
Fig. 1. Relaxation spectrum for the bulk metallic glass Vit106a between $0.15 \times T_g$ and T_g. Besides the well-known α- and β-process, a third relaxation process occurs around $0.26 \times T_g$ (γ-peak). The inset shows a magnification of the peak in the loss modulus E'' at low temperatures and the corresponding storage modulus E'. The error bars in the loss and storage modulus in the inset result from machine specific confidence intervals.

Fig. 2. Cyclic behaviour of the γ-peak during cooling with 5 K/min and 7 Hz. (a) The cooling is followed by reheating while the sample is still dynamically excited. (b) Two successive cooling runs with the same sample. During the intermediate heating the sample was not mechanically excited.

excited with a frequency of 5 Hz. Additionally, the sample was heated to 39 K above the glass transition temperature T_g with the same heating rate and dynamic excitation frequency. In the temperature regime between room temperature and T_g, the typical α-peak with the extensively investigated excess wing (β-relaxations) on the low-temperature side is seen. Conceptually visualized in a one-dimensional potential energy landscape (PEL), the α-transition is said to reflect transitions between meta-basins, where shear deformation can lower the effective transition barriers, therefore triggering the system to attain another nearby state. This viscous flow means configurational changes of all atoms in the system and requires a certain amount of thermal energy. At lower temperatures, the preceding local string-like excitation involves a significantly smaller maximum (β-transitions) that is partially merged with the α-peak and thus appears for the now discussed Zr-based alloy only as a low-temperature wing of the main α-peak.

Probing structural excitations upon cooling down from room temperature reveals a third distinct peak in the relaxation spectrum in Fig. 1. At around 177 K ($0.26 \times T_g$) we observe a maximum in E'', indicating that the structural relaxation dynamics of metallic glasses is far more complex than hereto believed. In addition to Vit106a, we observe the same behaviour in $Zr_{66.5}Cu_{33.5}$ and $Pd_{77.5}Cu_6Si_{16.5}$ (see SM, Fig. S1) with a third maximum in the mechanical loss spectrum at $0.26 \times T_g$ and $0.29 \times T_g$, respectively. This suggests that the third relaxation process is a general phenomenon in metallic glasses. In analogy to the low-temperature relaxation phenomenon of glassy polymers we term the low temperature mode γ-relaxation. The inset in Fig. 1 shows a zoom-in of the low-temperature peak in E''/E''_α and the storage modulus upon cooling. For the temperature range of the γ-peak, the storage modulus has an overall slope of $dE/dT = 26.4 \pm 0.4$ MPa/K, which is in good agreement with the typically reported temperature dependence of the Young's modulus [22,23].

To further quantify the nature and behaviour of this fast relaxation phenomena in metallic glasses, we conduct both a cooling-heating cycle, as well as two subsequent cooling cycles using the same cooling and heating rate and dynamical excitation frequency. The difference between both protocols is that in the latter mechanical excitation was only applied during cooling, whereas the sinusoidal dynamic strain amplitude was applied during cooling and heating in the former. It is found that the maximum in the loss modulus also occurs during reheating at 208 K ($0.31 \times T_g$), i.e. that there is a temperature difference of $\Delta T = 52$ K between the γ-peak position during cooling and during reheating (Fig. 2a), while in two subsequent cooling cycles, the γ-peak shifts from 174 K to 164 K (Fig. 2b). It is also noticed in Fig. 2 that the main loss peak
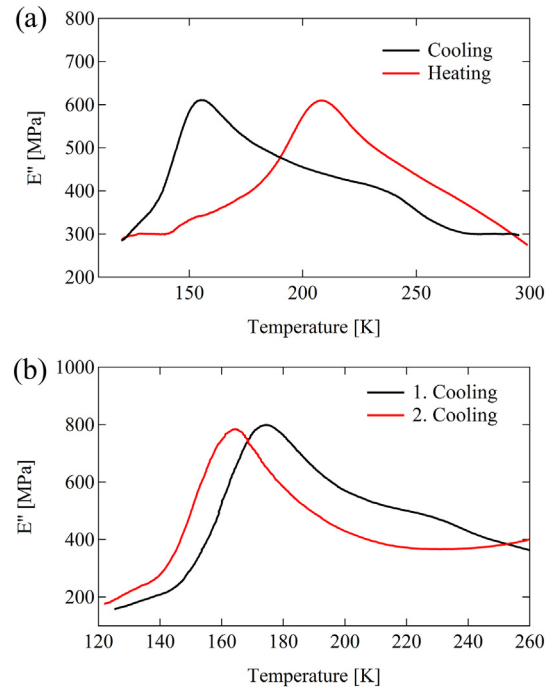
exhibits a high temperature shoulder, which suggests an additional underlying process partially merged with the main relaxation mode. At this point we cannot distinctly separate between these two parts of the relaxation spectrum and treat both processes as a single relaxation mode.

Probing the γ-relaxation as a function of heating rate and excitation frequency allows accessing the barrier energy of the associated structural transitions. Clearly, the onset and the peak position shift to lower temperatures upon decreasing the frequency from 100 Hz to 1 Hz at a constant cooling rate of 2 K/min (Fig. 3a). Evaluating the dependence of the γ-peak position on the frequency allows to derive the activation energy using the Kissinger method, as is shown as an inset in Fig. 3b. Irrespective of choosing the peak position or the onset of the peak, we find an Arrhenius behaviour with a slope that yields an activation energy of 0.32 ± 0.04 eV. Using the cooling rate Φ, an activation energy of 0.22 ± 0.08 eV was found (see SM, Fig. S3c). These values are distinctly lower than for β- (0.6–1.5 eV [10,24]) or α-relaxations (>5.0 eV [25]). Therefore the γ-relaxation in metallic glasses is a fast process involving transitions across barriers that are at least two times smaller than for the primary and secondary relaxation mechanism. Investigating the frequency dependence of the γ-relaxation with a sweep from 0.02 Hz to 200 Hz at a temperature of 173 K, reveals that E'' remains fairly constant in the lower frequency range, but there is a strong increase in the range from 10 Hz to 200 Hz (Fig. 3b). Here, the upper and lower frequency bounds are limited by the machine. This increase in E'' at higher frequencies is due a gradual shift of the γ-peak to higher temperatures: at each frequency the maximum is effectively at a different temperature while the frequency scan is performed at a constant temperature. Therefore, the data in Fig. 3b reflects a partial excitation of the relaxation dynamics at each frequency, with approximately the maximum being probed at the highest frequencies.

In order to quantify the structural modifications due to the transitions marked by the γ-mode, we performed DSC measurements on specimens excited at different frequencies but cooled to the same minimum temperature. This protocol is expected to tune the structural state by exciting different fractions of the γ-peak. To this end, four samples