Merging of the α and β relaxations and aging via the Johari–Goldstein modes in rapidly quenched metallic glasses

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This paper provides evidence that the physical aging of deeply and rapidly quenched metallic glasses is promoted by the Johari–Goldstein slow β relaxation, resulting in a significant irreversible increase in the mechanical modulus on initial heating. Dynamic mechanical analysis has been used to characterize relaxation phenomena of a strong and a fragile metallic glass. In addition, we can extrapolate the temperature dependence of β- and α-relaxation peaks to higher temperatures and calculate the merging temperature for both types of glasses. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2903697]

The kinetic feature of a liquid and a glass including the glass transition is of fundamental interest as well as essential for industrial applications, but not yet completely understood.[1,2] Regarding metallic glass-forming alloys, a quantitative description of how elasticity and viscosity correlate with the shear modulus of a glass or a liquid can now be quantitatively described.[3] It is now also understood that a single process, termed α relaxation or primary relaxation, is not sufficient to describe in general glassy dynamics.[4]

Metallic glasses are typically regarded as nearly ideal because their structure is thought to represent a mixture of hard spheres. A slow β relaxation, also termed Johari–Goldstein process,[5] has been identified in metallic glasses in experiments as well as simulations.[6–10] Consequently, the slow β relaxation is regarded as a universal feature of the glassy dynamics.[10] Recent evidence suggests that this β-relaxation or, more precisely, the local cooperate dynamics of several β relaxations, give rise to one shear transformation event, or one α relaxation,[11,12] and is thought to be the driving process for enhanced diffusion.[13]

In the literature, there is often an additional relaxational process discussed that occurs during the heating of an unannealed, as-quenched glass. This effect has been repeatedly observed as an increase in Young's modulus[14,15] or decrease of the free volume,[16] at temperatures at which irreversible aging of the macroscopic structure, the partial restoration of equilibrium structure below T_g, where complete equilibration is significantly longer than the experimental time window, is negligible on experimental timescales.[17] Already at temperatures of 100 K or more below the glass transition temperature, a change of the elastic constant indicates local relaxation events,[18] which are incompatible with the typical picture of physical aging regarding the structure of the glass. Depending on whether the material hardens or softens, the terms physical aging or rejuvenation are used.[19]

In this paper, evidence is provided that this aging process observed well below T_g can be associated with the slow Johari–Goldstein type β relaxation, in the following denoted as β relaxation. Furthermore, a Kissinger analysis[20] provides an estimate for the activation energy of this β relaxations. If the measured data are extrapolated to higher temperatures, a merging temperature of α and β relaxations can be assessed. That merging temperature is in close vicinity to the mode-coupling theory (MCT) temperature T_c.[27]

$Pd_{77}Cu_6Si_{17}$ (fragile, $m=52.8-77.0$) and $Zr_{65}Al_{7.5}Cu_{27.5}$ (strong, $m=36.4-38.4$)[7,10,21,22] have been prealloyed by arc melting the pure elements in argon atmosphere. The crushed lumps have been inductively molten and melt spun onto a rotating copper wheel in argon atmosphere, quenching the sample at approximately 10^5 K/s.[23] The resulting metallic glass bands are 20–30 μm thick and have been cut into strips, 10–15 mm long, and 1–2 mm wide. Composition and amorphicity have been verified using energy-dispersive x-ray spectroscopy, wide angle x-ray scattering, and differential scanning calorimetry.

Mechanical spectroscopy has been performed using a Perkin Elmer dynamic mechanical analyzer (DMA) 7. All experiments are carried out in the extensional mode at a constant frequency of $\nu=5$ Hz and at constant heating rates of 0.5–20 K/min in nitrogen atmosphere. The data shown in Fig. 1 has been measured using a liquid nitrogen cooling and initial stresses of 7.5 MPa of static stress, onto which a dynamic stress of 4.6 MPa is superimposed. All following measurements have been carried out with a constant glycol cooling, providing more stable conditions at higher temperatures and less disturbing mechanical vibrations. The initial values have been increased to typically 11 MPa of static stress plus 9 MPa of dynamic stress. All samples except the one of Fig. 1 are from the same melt-spinning run. More experimental details are found in Ref. 10.

Figure 1 shows a typical curve of a PdCuSi sample repeatedly heated at 10 K/min. The real part of the Young's modulus, also called storage modulus E', shows a nearly constant regime below 400 K with a shallow minimum around 260 ± 20 K. Toward higher temperatures, a strong increase in storage modulus is observed with an onset at 460 ± 20 K and a turning point at 515 ± 10 K. The heating was stopped at 609 K at the first indications of a decrease of E'. The storage modulus at this maximum is about 40 GPa. The sample is then cooled down, starting with a cooling rate

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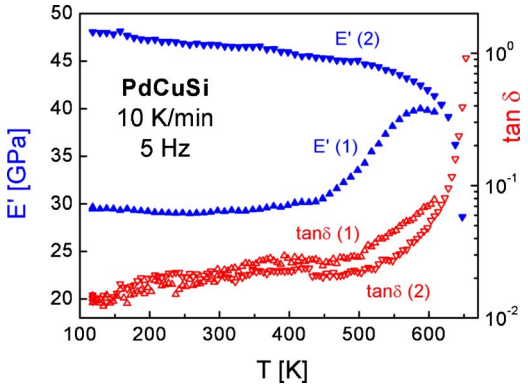

FIG. 1. (Color online) Storage modulus E' and tangents of phase angle tan δ vs temperature for an as-quenched (1) and an annealed (2) PdCuSi sample, measured by DMA in extensional spectroscopy mode.

of 30 K/min (not shown). The storage modulus during the second run shows the behavior expected from aging well below T_g behavior. A linear decrease of initially 48 GPa with a small slope of 0.0045 GPa/K is followed by a strong decrease of tens of gigapascal above 550 K.

The changes in tan δ between first and second heating are less pronounced than the changes in storage modulus E'. Below 500 K, the average slope during the second run is smaller. Above 500 K, tan δ bends over in a steeper increase and the values of the second run are decreased compared to the first heating scan.

To determine the heating-rate dependence, as-quenched PdCuSi and ZrAlCu samples have been investigated by DMA above room temperature. Figure 2 only shows the results of the smallest (0.5 K/min) and highest (20 K/min) heating rates used. In both types of glasses, a clear temperature shift of the onset of the increase and the final decrease in storage modulus E' is observed. On the other hand, the onset of the bending over of tan δ is only weakly affected by a change in heating rate.

The determined positions of the onset and turning points of E' are plotted in Fig. 3 using a Kissinger-type plot[20] and fitted with a straight line. In addition, the onset points of the

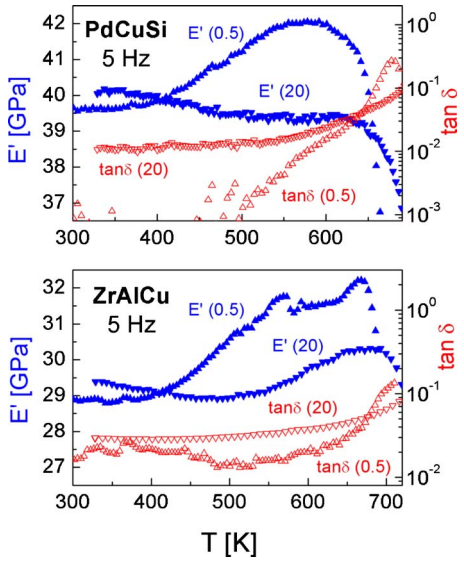

FIG. 2. (Color online) Storage modulus E' and tangents of phase angle tan δ vs temperature at heating rates of 0.5 K/min (0.5) and 20 K/min (20) for as-quenched samples of PdCuSi and ZrAlCu as labeled.

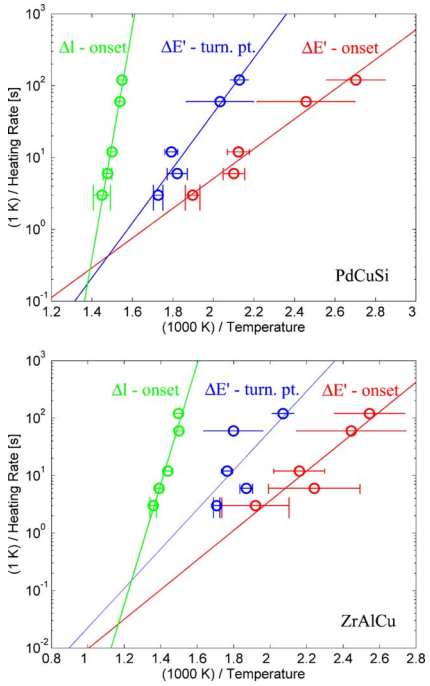

FIG. 3. (Color online) Kissinger-type plots, summarizing the temperatures of the discussed events at all investigated heating rates for PdCuSi and ZrAlCu, including linear fits of the data. The quantities considered are the onset of length change (Δl—onset), the onset ($\Delta E'$—onset) and turning point ($\Delta E'$—turn.pt.) of the change in storage modulus E'.

change in sample length l, which is measured in the DMA (Ref. 10) and is an indication for viscous flow or irreversible configurational changes termed α-relaxation of the sample, are plotted and fitted linearly.

As shown in Fig. 1 the as-quenched sample shows a change in slope and a clear increase in storage modulus that is missing during the second run. It is a result of a pronounced physical aging, relaxing internal stresses that originate from the rapid quench at a rate of $\approx 10^5$ K/s. The onset temperature the resulting increase in the instantaneous modulus E_0 appears at around 450 K. The total irreversible change in E_0 between the initial and subsequent runs is considerable and exceeds 60%. At higher temperatures (550 K) the E_0 values reach the values of the second run equivalent to that temperature and heating rate before the strong drop of both curves occur due to viscous-plastic flow. As in molecular glasses,[24] the amplitude of this β process itself is considerably decreased by aging. This feature is seen here for PdCuSi in Fig. 1 as change of tan δ between first and second heating run in the temperature range between 500 and 600 K.

Both types of metallic glasses (strong and fragile) clearly show that the onset of physical aging is highly dependent upon heating rate (see Fig. 2). Observing a high heating-rate dependence at temperatures far below the α-relaxation activity indicates that this aging is governed by relatively fast modes compared with the so called primary structural relaxation. The increase in E' is consequently attributed to β-relaxation steps within a megabasin of the potential energy landscape.[2] Such an assignment is consistent with the substantial increase in E' because the curvature of the potential energy increases when the system moves toward a local minimum of the metabasin.[3] It is also supported by the low stretching exponents observed for isothermal aging of alloys well below T_g,[16] with values around $\beta=0.3$ being typical for

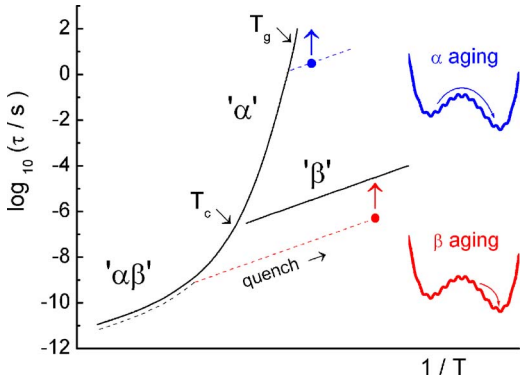

FIG. 4. (Color online) Schematic illustration of the conjecture that a sufficiently fast quench can relax regarding its slow β-relaxation modes at temperatures well below T_g. By contrast, the more common aging after a mild departure from equilibrium near T_g requires more than very local events within the landscape and, thus, higher temperatures.

slow β processes. In terms of energy landscape and activation pictures, the current aging process that starts from a highly excited potential energy state is compared with regular aging of the α-dynamics in Fig. 4.

Figure 3 summarizes the results of all measured heating rates in terms of a Kissinger-type plot.[20] The onset points of viscous flow are interpreted as the start of the α-relaxation on timescales corresponding to the heating rate. In this experimentally limited regime of accessible heating rates, the data points are linearly fitted instead of using a curved Vogel–Fulcher–Tammann fit.[25] For high temperatures, all curves tend to merge together, consistent with the β relaxation no longer distinguishable from the α relaxation at very short timescales in the $T > T_c$ regime (see also Fig. 4).[13,26] If linearly extrapolated, the fitted lines of the onsets of α and β relaxations intersect at 720 ± 110 K for the fragile PdCuSi system and at 870 ± 290 K for the strong ZrAlCu system. These values are close by the reported values for the critical temperatures T_c (710 K for PdNiCuP and 875 K for ZrTiCuNiBe) of the idealized MCT.[13,27] This is due to the fact that the curve of the α relaxation is bent more strongly than those of the β relaxation, as already established for organic glass formers.[26] An activation energy of the β relaxation can be estimated from the slope of the turning points, plotted in the Kissinger plots. The values are 0.67 ± 0.11 eV for PdCuSi and 0.59 ± 0.39 eV for ZrAlCu. These energies are quite similar for the two glasses and much bigger than $k_B T$, which can be attributed to the cooperative nature of the β relaxation.[9,13,27]

In summary, the present aging and the excess wing can be attributed to common degrees of freedom: the slow β-relaxation process. This can be regarded as a universal feature of glass dynamics, because it occurs for both, strong and fragile, metallic glasses. Furthermore, the estimated activation energy is calculated within a Kissinger analysis.[20] Recalling the conjecture that several β relaxations give rise to an α relaxation and that the β relaxation might be the driving process of diffusion, the fundamental character of the β relaxation becomes apparent. The phenomenon of physical aging at very high levels of the energy landscape and the slow β relaxation can be interpreted as a β process alone while several of them cause an α relaxation, which eventually leads to viscous flow. In addition we can also determine the merging temperature of both processes which is close to the T_c of the MCT. This temperature is seen as critical for the entire low-frequency relaxation spectrum of a simple, quenched-in system of hard spheres.

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