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Structural relaxation and recovery of bulk and ribbon glassy Pd₄₀Cu₃₀Ni₁₀P₂₀ monitored by measurements of infralow-frequency internal friction

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Abstract

Internal friction (IF) measurements ($f = 0.05$ Hz) on bulk and ribbon glassy Pd₄₀Cu₃₀Ni₁₀P₂₀ samples (production quenching rates 200 and $\sim 10^6$ K s⁻¹, respectively) upon thermal cycling within $370 \text{ K} \leq T \leq T_g$ have been performed. It has been found that thermal cycling leads to a decrease of the IF and occurrence of related IF hysteresis as a result of (i) structural relaxation and (ii) relaxation of room-temperature plastic deformation arising upon preparation and handling of samples. Fast quenching (9–180 K s⁻¹) of relaxed samples from the supercooled liquid state results in the IF recovery, which is strongly different for bulk and ribbon specimens. For the latter the IF remains smaller than that in the as-cast state, while quenched bulk samples display IF which is two to three times *bigger* as compared with the as-cast state. Possible reasons for such unusual behaviour are discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Metallic glasses (MGs) are produced by fast melt quenching that defines excess Gibbs energy with respect to the crystalline state and, as a result, the presence of the thermodynamic stimulus for structural evolution towards higher order. This spontaneous evolution changes all properties of glasses and is generally referred to as structural relaxation. In particular, structural relaxation of MGs results in an increase of the viscosity by orders of magnitude [1], strongly restricting thus the capability of homogeneous viscous flow. Besides this, structural relaxation inhibits inhomogeneous (localized) plastic deformation, which normally occurs at $T \leq 400\text{--}450$ K [2]. The loss of deformation ability leads to severe embrittlement and is currently considered to be one of the main drawbacks of MGs that strongly restricts their application field.

It is commonly accepted that the change in physical properties of MGs upon annealing is mainly irreversible. However, several investigations show partial or even complete recovery of the properties of thermally aged MGs. For instance, differential scanning calorimetry reveals the recovery of the enthalpy lost during preceding annealing (so-called reversible enthalpy relaxation, e.g. [3, 4] and papers cited in [11]). Thermal cycling of preannealed metallic glass shows notable reversible relaxation of the shear modulus [5], while the capability of ‘irreversible’ relaxation of the shear modulus can be largely recovered by quenching from the supercooled liquid state [6, 7]. It is important to note a few reports indicating that high-temperature annealing results in partial [8, 9] or nearly complete [10] recovery of the bending ductility at room temperature. Finally, it was recently found that the capability of annealed metallic glass for homogeneous viscous flow as monitored by creep measurements can be

partially [11] or even completely [12] recovered by heat treatment above the glass transition temperature T_g . It can be assumed, therefore, that reversible property relaxation is rather common to MGs.

Currently, no adequate theory is available to describe all basic features of relaxations in MGs, including the aforementioned reversible relaxation phenomena. The free volume concept is used most often to understand different kinds of relaxations. The concept is based on the seemingly reasonable idea that molecular transport in glasses occurs via atomic rearrangements around high local free volume (low density) regions [13–15]. The aforementioned thermal embrittlement is normally ascribed to the loss of the free volume (see, e.g., [16]). Although very popular, the free volume concept has some evident difficulties. In particular, the free volume has no thermodynamic or even simple structural definition, as has been repeatedly mentioned in the literature (e.g. [17]). Qualitatively, the evolution of the free volume should be most directly estimated by density measurements. It is to be noted in this connection that novel so-called bulk MGs tend to display low density changes upon crystallization. For instance, the well known quaternary bulk $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ glass shows nearly zero density change upon crystallization into a structure close to the equilibrium one [18, 19], while ternary $\text{Pd}_{40}\text{Cu}_{40}\text{P}_{20}$ is even denser in the glassy state [18]. In the latter case, structural relaxation and related viscous flow through redistribution and annihilation of the free volume become especially questionable.

The production quenching rate of bulk MGs is several orders of magnitude smaller than that of ordinary ribbon MGs fabricated by conventional melt spinning that results in notable density difference. For instance, bulk $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ samples studied in the present investigation are by 0.48% denser than their ribbon analogues [20]. This is actually a big difference because structural relaxation of MGs normally leads to densification by about the same amount (for instance, bulk $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ shows a 0.5% density increase [21] upon structural relaxation³). Since structural relaxation leads to an increase of the shear viscosity by orders of magnitude, one should expect significantly lower viscosity of the ribbons with respect to bulk samples. However, this is not the case and the shear viscosities of bulk and ribbon $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ and $\text{Zr}_{52.5}\text{Ti}_5\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}$ directly derived from isochronal ($dT/dt = \text{const}$) creep measurements were found nearly equal at all temperatures $T < T_g$ [20, 22, 24] (see also papers cited in [20]). This basic fact evidently questions the widely assumed connection of the free volume with the ‘relaxation centres’ responsible for structural evolution and related Newtonian viscous flow of MGs below T_g .

Internal friction (IF) measurement is known to be a sensitive tool for monitoring different relaxations in solids. This especially concerns infralow-frequency ($f < 0.1$ Hz) IF measurements in MGs, which are known to reflect the viscoelasticity and related relaxation upon annealing [25, 26].

³ One should be not misled by nearly zero density change upon crystallization of bulk $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$, on the one hand, and by a 0.5% density increase upon structural relaxation of this glass, on the other. The crystallization of this glassy alloy first results in the densification which is next followed by a decrease of the density close to the value in the initial glassy state [19].

In view of the aforementioned, the purpose of the present paper was twofold: (i) an IF study of structural relaxation upon cyclic heat treatment of bulk and ribbon glassy $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ samples differing $\approx 10^4$ -fold in their production quenching rate and, consequently, significantly different in the density (free volume amount); (ii) an IF investigation of samples quenched from the supercooled liquid state in an attempt to recover the viscoelasticity, analogously to the case of aforementioned creep measurements [11, 12]. The obtained results clearly indicate that structural relaxation and recovery turn out to be complex processes, which cannot be reduced to the free volume evolution.

2. Experimental details

One of the best metallic glass formers, $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ (at.%), was used for the investigation. The initial master alloy was prepared by direct melting of the components (purity now worse than 99.95%) by a two-zone method in a thick-walled quartz vial under controlled phosphorus pressure. A part of this alloy was next melt jet quenched from $T_q = 923$ K into a copper mould with a $2 \times 5 \times 62$ mm³ cavity. The melt quenching rate was directly determined to be ≈ 200 K s⁻¹ near T_g by means of high speed measurements (50 kHz) of the signal of a thermocouple placed into the centre of the mould cavity [19]. The castings thus obtained were next cut by a diamond disc saw and mechanically ground to a thickness of 30–80 μm . The other part of the initial master alloy was used to prepare 30–40 μm ribbons by a conventional single roller melt spinning technique. The melt quenching rate in this method is usually estimated to be 10^6 K s⁻¹ and, therefore, the ratio of the production quenching rates of bulk and ribbon samples used in the present investigation can be accepted as $\approx 10^4$. The glass transition temperature was found by differential scanning calorimetry to be 559 ± 1 K for both bulk and ribbon specimens [20].

Samples for IF measurements (40–80 μm wide, 4–6 mm long) were prepared using a specially designed guillotine cutting-out press. The samples were gripped in the IF instrument using special clay-based glue. Test experiments showed that room-temperature exposure of the glue during 10–12 h upon vacuum pumping is quite sufficient to ensure rigid gripping of samples with a gauge length of 2–3 mm. After this exposure, no evidence of glue-related effects was detected in the IF scans. Internal friction was measured in a vacuum of about 10^{-3} Pa using torsion forced vibration mode [27] at a frequency $f = 0.05$ Hz. The sample’s vibrations were detected by an optical lever method using a high precision position sensitive detector driven by a laser beam. The internal friction was calculated as $Q^{-1} = \Delta W / 2\pi W$, where $\Delta W = \oint \varphi dM$ is the area of the ‘torsion angle φ –applied force moment M ’ hysteresis loop, $W = M_0\varphi_0/2$, with M_0 and φ_0 being the amplitudes of M and φ , respectively. It is to be noted that this method of IF calculation captures the whole inelastic response while the commonly used phase shift method (between M and φ) takes into account only linear viscoelasticity [28]. IF measurements were made during multiple thermocycling within the glassy state at subsequently

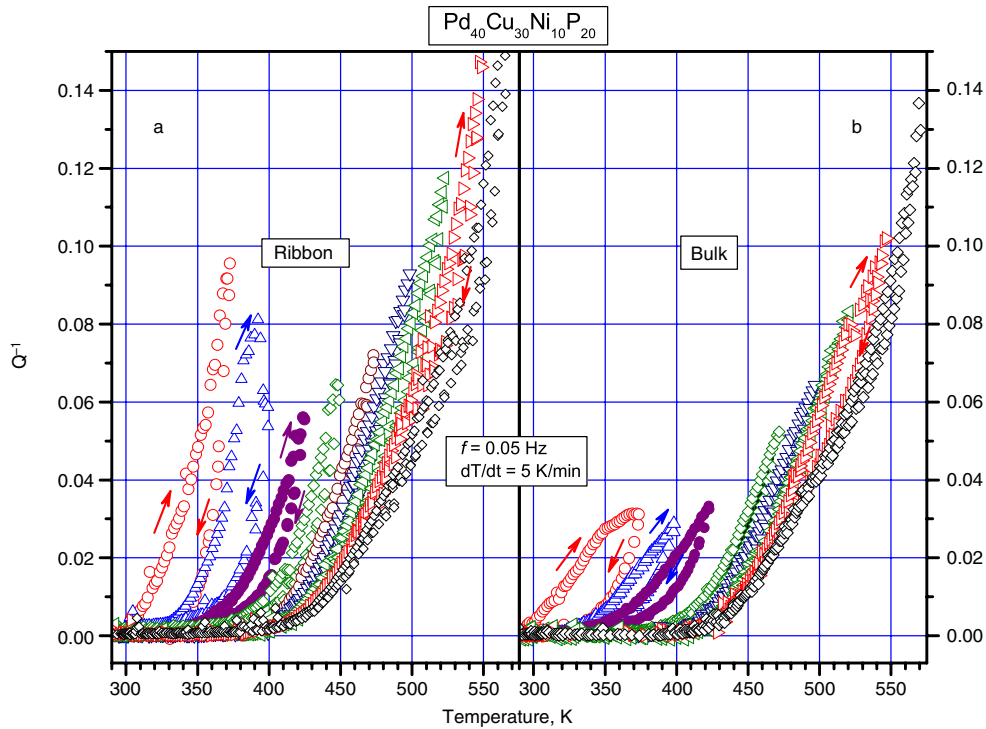


Figure 1. Changes of the internal friction in initial ribbon (a) and bulk (b) glassy $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ during thermal cycling. The arrows hereafter denote the sequence of heating/cooling.

increasing (with a step of 25 K) maximal heating temperature T_{\max} in the range $370 \text{ K} \leq T_{\max} \leq 570 \text{ K}$. A heating/cooling rate of 5 K min^{-1} was applied in all cases.

3. Results

3.1. Internal friction in as-cast ribbon and bulk samples

Figure 1 shows the results of IF measurements in initial ribbon and bulk samples upon multiple thermal cycling up to $T_{\max} = 570 \text{ K}$. The IF always increases with temperature and significant hysteresis is observed: the internal friction upon heating is bigger than that upon cooling. The hysteresis is most notable upon first two heating cycles, up to $T_{\max} = 370$ and 395 K . An increase of T_{\max} results in higher Q^{-1} and a tendency of decrease of the IF hysteresis is observed.

Generally, the IF value and hysteresis reflect the two relaxation components, (i) structural relaxation itself through the viscoelastic strain and its decrease upon thermal cycling [25], and (ii) inelastic relaxation due to room-temperature inhomogeneous plastic deformation introduced by cutting (ribbon and bulk specimens) and additional grinding (bulk samples) upon preparation of specimens and their handling. We believe that the second IF component in as-cast samples is fully annealed out after heating up to $\sim 500 \text{ K}$ as confirmed by the fact of rapid stress relaxation in the same bulk/ribbon glass in the range $400 \text{ K} < T < 450 \text{ K}$ upon linear heating at the same rate [23]. The disappearance of the deformation-induced IF peak (observed at $T \approx 250 \text{ K}$ in the Hz-frequency range) in the same bulk glass after annealing at about 450 K [7] is indicative of the same idea.

After heating up to $T_{\max} = 570 \text{ K}$ (i.e. slightly above calorimetric T_g), the $Q^{-1}(T)$ -dependences become fully reversible so that further thermal cycling of the same sample within $370 \text{ K} \leq T_{\max} \leq 570 \text{ K}$ does not reveal any IF hysteresis. This means that any irreversible structural relaxation is fully removed by this heat treatment.

Comparing parts (a) and (b) of figure 1, one has to note the significantly higher IF level and bigger hysteresis in the case of the ribbons at $T_{\max} \leq 450 \text{ K}$; at higher T_{\max} these differences are smaller. In general, this inequality can be attributed to at least two factors. First, as mentioned above, bulk samples are denser, that reflects their smaller initial free volume. The same follows from the fact that the ribbons display a 0.57% density increase upon structural relaxation while bulk samples reveal only 0.27% density augmentation [20] (this generally means that the starting free volume in the ribbons is about twice that in bulk samples). Therefore, higher IF level and bigger hysteresis of the ribbons could be in principle connected with their larger free volume. The second reason for the above difference can be envisioned in the amount of room-temperature inhomogeneous deformation of samples during their preparation and handling. It is known that MGs slightly deformed at room temperature display much more pronounced IF anomalies as compared with heavily deformed specimens [29, 30]. Since the ribbons were clearly subjected to smaller preliminary deformation (only cutting), the data shown in figure 1 seem to be on the whole insufficient to indicate the relaxation origin. It is also to be noted that a high IF level upon low-temperature cycling ($T_{\max} \leq 450 \text{ K}$) was not observed in all cases, indicating different preliminary plastic straining of specimens. However,

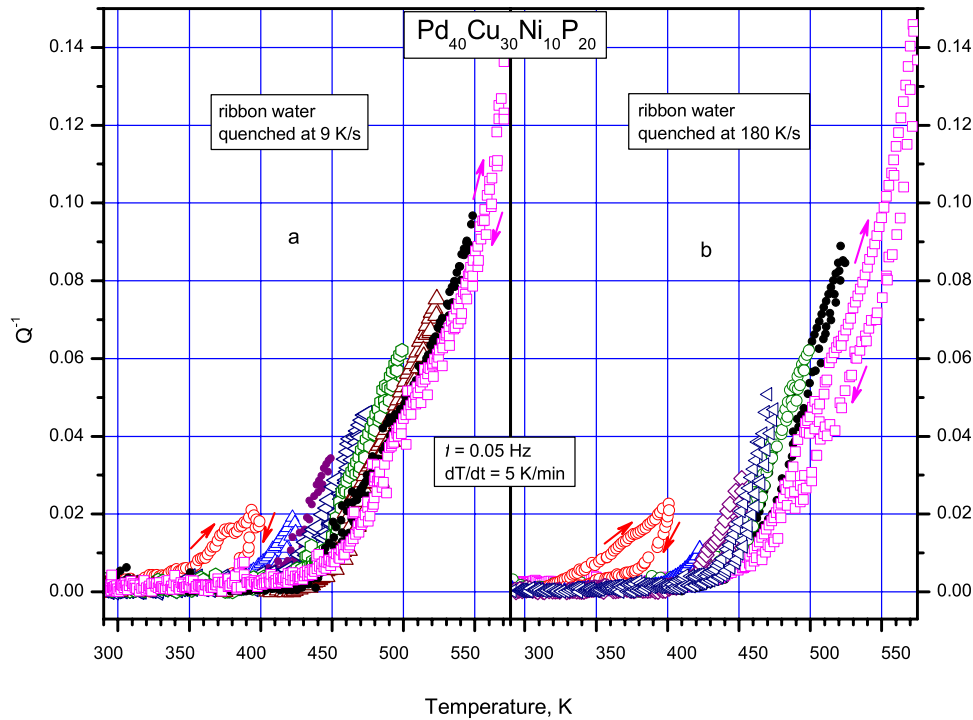


Figure 2. Changes of the internal friction during cyclic heating of annealed ribbon glassy $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ after water quenching from the supercooled liquid state at 9 (a) and 180 (b) K s^{-1} .

the IF at higher temperatures was always somewhat bigger for the ribbons.

3.2. Relaxation behaviour of annealed ribbon and bulk samples quenched from the supercooled liquid region

In order to provide further information on the relaxation origin, we performed IF measurements on annealed samples quenched from the supercooled liquid state. For this purpose, as-cast samples were put into either a sealed thin-walled quartz tube (with inner and outer diameters equal to 1 and 3 mm, respectively) or copper container (the specimen was placed just in between two Cu plates), heated at 5 K min^{-1} up to $T_q = 608 \text{ K}$ and water quenched immediately after this. The initial quenching rate directly determined by 50 kHz digitizing of the thermocouple signal was found to be 9 and 180 K s^{-1} for quenching in the quartz tube and copper container, respectively. X-ray study of samples after this treatment confirmed their glassy state. Quenched samples were next carefully glued into the testing instrument and IF scans were performed in the way described above.

The results of this experiment for the ribbons are shown in figure 2. It is seen that quenching from the supercooled liquid state at 9 K s^{-1} leads to significant IF recovery (an increase of the IF and occurrence of related relaxation-induced hysteresis) upon thermal cycling in the whole temperature range (figure 2(a)). An increase of the quenching rate up to 180 K s^{-1} slightly enhances this effect, as illustrated by figure 2(b). However, the IF level and hysteresis remain on the whole significantly smaller as compared with as-cast melt spun ribbons (figure 1(a)).

As in the case of as-cast specimens, the IF hysteresis in samples quenched after annealing seem to originate from the recovery of the viscoelasticity as well as plastic deformation of samples during their handling, and these components are hard to separate. We believe, as mentioned above, that thermal cycling at $T_{\max} \leq 500 \text{ K}$ fully removes deformation-induced IF. However, at higher T_{\max} some IF hysteresis is still observed. It is also to be noted that several samples were quenched at a rate of 1 K s^{-1} and this did not lead to any IF recovery; $Q^{-1}(T)$ -dependences in this case were identical to those after slow cooling (5 K min^{-1}) from $T_{\max} = 570 \text{ K}$.

Quenching experiments on annealed bulk samples led to unexpected results shown in figure 3. The main feature in this case is that the IF level in the whole temperature range as well as the hysteresis behaviour drastically increase after quenching as compared with the initial state (figure 1(b)). For instance, at a temperature $T = 550 \text{ K}$ the internal friction in initial bulk samples $Q^{-1} \approx 0.09$, whereas heating up to 608 K and subsequent quenching at either 9 or 180 K s^{-1} lead to an increase of Q^{-1} up to ≈ 0.14 at the same temperature. Although no traces of deformation-induced IF component were observed after heating up to 570 K (or 608 K) and subsequent slow cooling (5 K min^{-1}), the IF scans of quenched samples after gluing into the IF instrument reveal a huge IF hysteresis during first two heating cycles up to $T_{\max} = 370\text{--}400 \text{ K}$ (figure 4). We believe that this is again a manifestation of small room-temperature deformation occurring upon handling of samples, which is expected to disappear after heating up to $450\text{--}500 \text{ K}$, as discussed above. However, at higher temperatures the IF in quenched samples is nevertheless bigger than in the initial state and tends to increase with the quenching

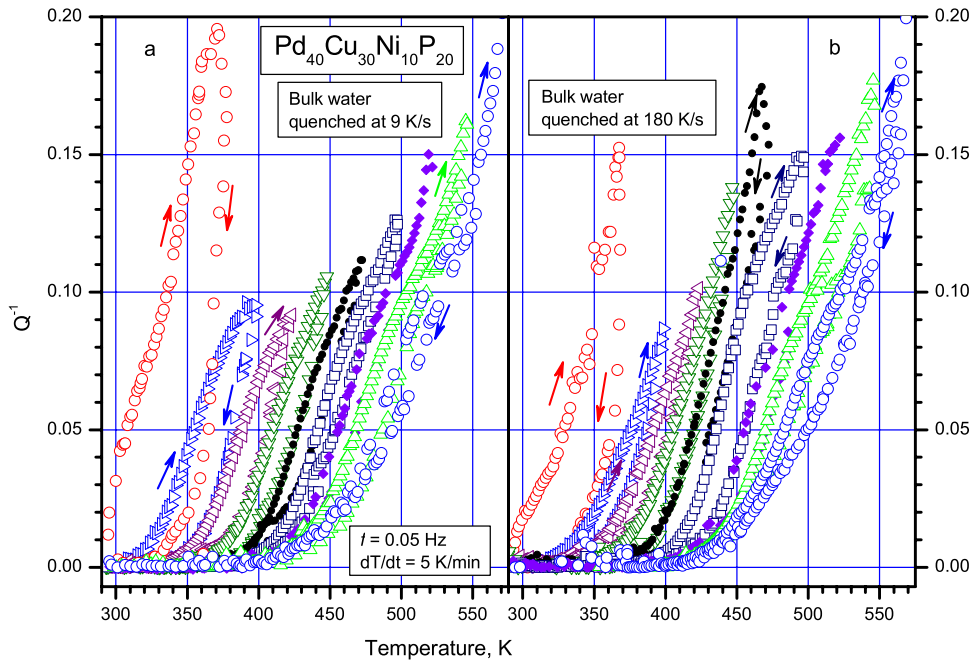


Figure 3. Changes of the internal friction during cyclic heating of annealed bulk glassy $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ after water quenching from the supercooled liquid state at 9 (a) and 180 (b) K s^{-1} .

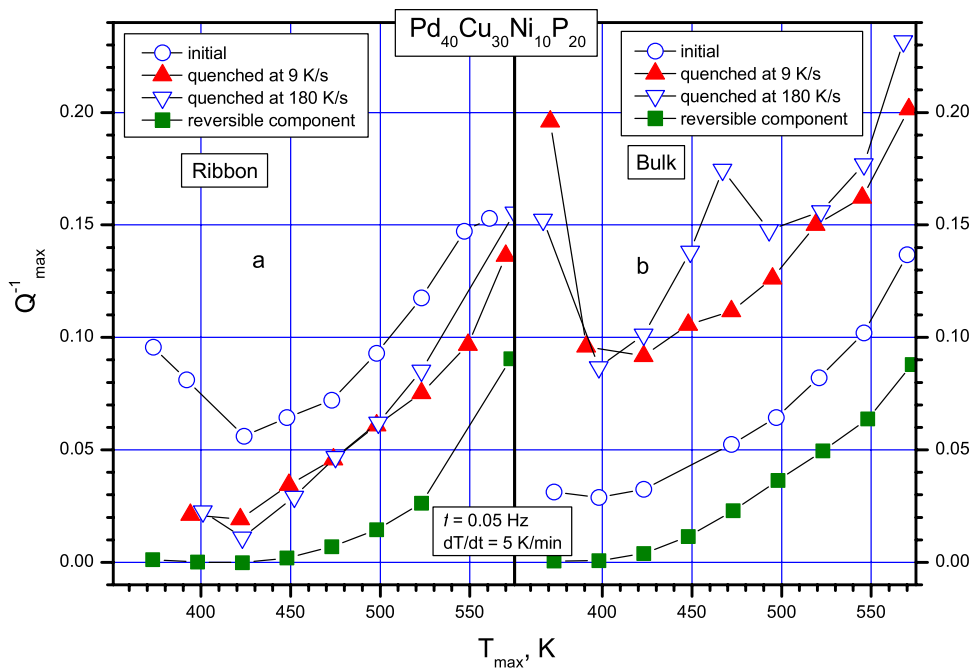


Figure 4. The maximal internal friction achieved in a heating cycle as a function of the maximal temperature reached in this cycle for initial, annealed and quenched ribbon (a) and bulk (b) glassy $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$. Straight lines connecting the points are drawn as guides for the eye.

rate (figure 3). It is to be emphasized that the quenching rate of 180 K s^{-1} applied in this experiment is fairly close to the production quenching rate ($\approx 200 \text{ K s}^{-1}$) of bulk samples. As in the case of the ribbons, quenching at 1 K s^{-1} does not lead to any increase of the IF as compared with samples heated up to 570 K and next slowly cooled down.

4. Discussion

4.1. The effect of quenching on the internal friction behaviour

The results of all performed IF tests can be rationalized in terms of the maximal IF value Q_{max}^{-1} reached in a given heating cycle as a function of the maximal temperature T_{max} achieved in this

cycle, as shown in figure 4. The following features are to be noted.

- (i) The maximal IF in the initial state is always bigger for the ribbons, indicating their higher relaxation ability. Structural relaxation decreases Q_{\max}^{-1} several-fold to nearly the same level in both ribbon and bulk samples as illustrated by the ‘reversible component’ in figure 4, which gives reversible changes of $Q_{\max}^{-1}(T_{\max})$ observed after heating up to 570 K and subsequent slow cooling.
- (ii) Quenching of annealed samples from the supercooled liquid region at 9 or 180 K s⁻¹ always increases the IF level and Q_{\max}^{-1} tends to increase with the quenching rate. Quenching at 1 K s⁻¹ or slow cooling do not lead to any IF changes as compared with the reversible component.
- (iii) Quenching of annealed ribbons leads to ~50% IF recovery while Q_{\max}^{-1} in quenched bulk samples is two to three times *bigger* than that in the initial state. This is the most surprising finding of the present investigation. It is to be noted in this connection that very similar behaviour was recently observed in [19] by means of electric resistance monitoring of structural relaxation: for the same bulk/ribbon samples and the same quenching rates, the resistance relaxation in the ribbons after quenching was smaller than that in the initial state, while bulk samples displayed relaxation which was several times bigger as compared with the initial state.

A major issue to be understood is a distinction in the relaxation behaviour of bulk and ribbon samples, which are approximately twofold different in the amount of the starting free volume, as was mentioned above. An increase of the relaxation ability of bulk samples after quenching much over that in the initial state clearly indicates that the above distinction cannot be attributed solely to the free volume amount. Indeed, quenching of bulk samples was performed from $T_q = 608 \text{ K} > T_g$ at a rate pretty close to that applied during their production. Therefore, from the viewpoint of the standard understanding of the glass transition as a kinetic relaxation phenomenon with related behaviour of the specific volume [31], one has to expect that the amount of the free volume in the initial state and after quenching should be about the same. Ascribing the capability of structural relaxation solely to the amount of the free volume, one has to expect that the relaxation behaviour of initial and quenched bulk samples should be similar, which is clearly not the case.

In a general sense, different relaxation behaviour of as-cast and quenched bulk samples could be connected with complex rheological behaviour of the melt, depending on different kinds of prehistory. It is to be mentioned in this connection that Way *et al* [32] found that the shear viscosity of both supercooled and equilibrium (i.e. above the liquidus temperature) melt is strongly dependent on the melt thermal prehistory and even on the preceding *solid* state, i.e. whether this state was amorphous or crystalline. This effect was attributed to modifications of melt medium- and short-range order upon thermal cycling. Another important fact was reported by Manov *et al* [33], who noticed that significant hysteresis of melt properties is also seen in the variations of several properties of metallic glasses

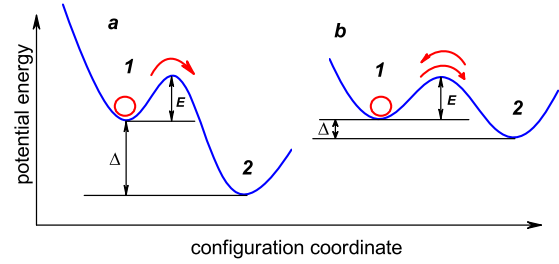


Figure 5. Schematic drawing of relaxation centres capable of ‘irreversible’ (a) and reversible (b) transformations.

quenched from the melts with different thermal prehistories. In our case, the temperatures T_q for initial production ($T_q = 903 \text{ K}$) and quenching of annealed bulk samples ($T_q = 608 \text{ K}$) are fairly different, that might constitute a reason for different relaxation behaviour even if the quenching rate is about the same.

4.2. Comments on the origin of the internal friction

A simple phenomenological approach for the understanding of basic features of structural relaxation of glasses and related property changes dating back to the 1980s is widely used in the literature [3, 34–36]. Microscopic events of structural relaxation are believed to occur in local structurally unstable regions called relaxation centres (or shear transformation zones). These centres can be viewed as asymmetrical two-well systems undergoing structural transitions between their high energy (metastable) and low energy (stable) states 1 and 2, as schematically shown in figure 5. The main parameters of a relaxation centre are the activation energy E and the energy difference Δ between the metastable and stable states. Depending on these parameters, either ‘irreversible’ or reversible relaxation can be observed. In the as-cast state, the relaxation centres (RCs) predominantly occupy metastable states and structural relaxation is viewed as RCs’ transitions into their stable states (figure 5(a)). Since the potential asymmetry is big in this case ($\Delta \gg kT$, where k is the Boltzmann’s constant), the probability of the reverse transition $2 \rightarrow 1$ is small and the relaxation event can be considered as ‘irreversible’. At low frequencies $f < 0.1 \text{ Hz}$, as in the present investigation, the ‘irreversible’ transitions to the stable configurational state 2 upon linear heating result in the viscoelastic internal friction [25],

$$Q_{ve}^{-1}(T) = GN_0(E_0(T))\Omega C A \dot{T} / \omega, \quad (1)$$

where G is the shear modulus, N_0 the volume density of RCs per unit activation energy interval, E_0 the characteristic activation energy, which is temperature dependent as $E_0 = AT$ ($A = \text{const} \approx 3.1 \times 10^{-3} \text{ eV K}^{-1}$), Ω the volume embracing a relaxation event, C the parameter characterizing the orienting impact of the external stress on elementary relaxation events, \dot{T} the heating rate and ω the circular frequency. The IF given by equation (1) implies that structural transitions $1 \rightarrow 2$ occur only *once*, giving rise

to the viscoelastic damping. Such a picture was confirmed for infralow-frequency IF behaviour of conventional ribbon MGs [25, 26]. Equation (1) exactly corresponds to the well known Maxwell viscoelastic internal friction $Q_{ve}^{-1} = G/\eta\omega$ [37], with $\eta(T) = [N_0(E_0(T))\Omega CA\dot{T}]^{-1}$ being the shear viscosity. The latter relationship was verified [25] to describe the viscosity behaviour of MGs below T_g [22, 24]. We, therefore, ascribe a part of the observed hysteresis IF behaviour (figure 1) to ‘irreversible’ structural transitions in RCs. The other part seems to originate from inhomogeneous deformation of samples, as discussed above.

Continued structural relaxation according to the above mechanism leads to transformation of nearly all RCs accessible for thermal activation into their stable states 2 and, consequently, disappearance of the viscoelastic IF given by equation (1). However, there still remains an IF component, which reversibly changes with temperature (the ‘reversible component’, figure 4). We attribute this component to distributed reversible structural transitions in RCs with low asymmetry $\Delta \sim kT$ (figure 5(b)). Calculation of the corresponding anelastic IF gives a rather complicated expression, which was shown to accord with the experiment [38].

Returning back to highly asymmetric RCs (figure 5(a)), one has to notice that the probability x to find such a system in the metastable state 1 after prolonged annealing should attain the equilibrium value given by the Boltzmann distribution, $x_{eq} = \exp(-\Delta/kT)$. Then, if temperature is increased after this, the equilibrium probability x_{eq} will *increase* as well. In other words, increasing temperature should lead to the repopulation of RCs in their metastable states 1. This can be greatly facilitated above T_g due to a decrease of the shear modulus, which is currently considered to be the main physical quantity controlling the potential barrier height [17, 39, 40]. This is why, after annealed glass is heated into the supercooled liquid region and next quenched to room temperature, one should expect that some amount of RCs is returned into the initial metastable state 1. Therefore, upon subsequent heating one can observe viscoelastic IF according to the mechanism outlined above. As was mentioned earlier, a similar procedure applied to ribbon $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ leads to the complete recovery of the creep viscoelastic strain, which was strongly decreased in the course of preceding creep runs [12]. It was also determined that the recovery of the creep strain is accompanied by heat absorption [12], as one would expect for the repopulation of RCs in the metastable state 1. The procedure of the recovery was repeatedly performed on the same sample, indicating that the defect structure can be reversibly cycled between different states.

The following important issue has to be noted. The IF recovery in the present investigation was observed only if the quenching rate was high enough, $dT/dt \geq 9 \text{ K s}^{-1}$. To recover the relaxation of the electrical resistance in the same samples, just the same quenching rate has to be applied [19]. On the other hand, the quenching rate of only 18 K min^{-1} is sufficient to recover the viscoelastic creep strain in the aforementioned experiments [12]. The origin of this huge difference in the quenching rates is basically unclear. A possible reason

could arise from the peculiarities of the intrinsic potential energy landscape (PEL) of the glass [31]. In this case, the quenching rate defines sampling of different PEL ‘sub-basins’ confined within the inherent landscape ‘megabasin’: slow quenching provides more time for PEL sampling to find a configuration corresponding to a deep and narrow ‘sub-basin’. Fast quenching allows shorter time to sample the energy landscape, forcing the glass to ‘land’ in a shallow and wide ‘sub-basin’. If this is true, one has to further suppose that different relaxation centres (i.e. with different energies in the stable state 2, figure 5) are responsible for infralow-frequency IF and creep behaviour, although all these centres constitute two-well systems and provide the viscoelastic response upon loading.

5. Conclusions

We performed an infralow-frequency internal friction (IF) investigation of structural relaxation and recovery in bulk and ribbon glassy $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ samples differing $\sim 10^4$ -fold in the production quenching rates and, consequently, ≈ 2 -fold in the amount of the starting free volume. The obtained results can be summarized as follows:

- (1) Thermal cycling of bulk and ribbon samples (production quenching rates $\approx 200 \text{ K s}^{-1}$ and $\sim 10^6 \text{ K s}^{-1}$, respectively) results in a decrease of the IF and occurrence of related large IF hysteresis, which reflect (i) structural relaxation and (ii) room-temperature plastic deformation of specimens during their preparation and handling. The IF level and hysteresis is bigger in the ribbons but this cannot be ascribed solely to their higher free volume. High-temperature annealing fully removes the IF hysteresis, leaving only reversible (with temperature) IF component, which is several times smaller than the IF in the as-cast state.
- (2) Quenching of annealed samples from the supercooled liquid region at either $dT/dt = 9$ or 180 K s^{-1} results in an increase of the IF and recovery of the IF hysteresis. In the case of the ribbons, the IF level after quenching is two to three times smaller than in the as-cast state (while being larger by approximately the same amount than the reversible IF component). However, the IF level in quenched bulk samples is two to three times *bigger* as compared with the as-cast state. This is the most striking finding of the present investigation. It is argued that such a behaviour cannot be attributed solely to the free volume amount. The phenomenon of the IF recovery is discussed in terms of the repopulation of two-well relaxation centres in their metastable states upon heating into the supercooled liquid region.

Quenching at 1 K s^{-1} and slow cooling (5 K min^{-1}) from the supercooled liquid region do not lead to any IF recovery. This poses the interesting question of why only ultrafast quenching from the supercooled liquid state provides the recovery of the viscoelastic IF while the viscoelastic creep strain can be recovered just by relatively slow cooling. A possible reason for such a behaviour is discussed.

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