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Influence of stress and temperature on damping behavior of amorphous $Pd_{77.5}Cu_{6.0}Si_{16.5}$ below T_g

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Abstract. In this work we analyzed the mechanical damping behavior of amorphous $Pd_{77.5}Cu_{6.0}Si_{16.5}$ below the glass transition temperature (T_g) with creep/recovery measurements. Here a correlation between temperature stimulation and external stress is found in an exponential, multiplicative way. This demonstrates that not only is the yield stress of the material influenced by temperature variation (mechanical melting) but also the secondary relaxation is modified under stress and temperature.

1 Introduction

The nature of the glass transition of amorphous alloys has been the subject of a long-standing debate. As commonly known, the primary relaxation mode (α-relaxation), which is connected to the viscosity of the material, changes its maximum in the frequency domain with temperature. Also the secondary relaxation or JG mode varies its position with temperature. Both relaxation modes merge at higher temperatures ($T \gg T_g$) but follow a very different temperature dependence towards lower temperatures. Under applied stress recent simulations suggest a quadratic dependence of applied stress and temperature suggesting that the material can go viscous (plastic) either by temperature (T_g) or mechanical stress (σ_{yield}) [1]. This elastic-plastic transition has been studied systematically by Harmon *et al.* [2] to obtain the stored mechanical energy (work) in the "elastic" amorphous metal, which can be described as an Eshelby field in a coarse-grained picture of the microscopic objects [3]. Once the material becomes viscous (via temperature) or plastic (via stress) no more enthalpy can be stored and irreversible processes are dominant. Mechanical or thermal "melting" of the glassy structure might even lead to a random first-order transition as discussed theoretically by Stevenson and Wolynes *et al.* [4] Some experimental evidence is given recently by Li *et al.* [5]. In this paper the damping behavior (secondary relaxation) of amorphous $Pd_{77.5}Cu_{6.0}Si_{16.5}$ below T_g is described in connection with external stress. Thereby, the results are analyzed in terms of a potential energy landscape (PEL) from Stillinger and Weber for a description of α- and β-processes [6–8]. On the one hand, the system is changing via viscous flowing into a new configuration with irreversible changed potential energy (α-relaxation) and on the other hand, the stress reduction takes place by local reversible configuration changes (β-relaxation) [2,6,9,10]. The β-transitions are described as statistical *hopping events* in the fine structure of the PEL (transition of a subbasin to the next one) called *intrabasin hopping* [6,8]. If there are sufficient events activated, it is possible to cross into a new metabasin (*e.g.* via an increasing temperature). This is described as an *interbasin hopping* (α-relaxation) [8]. By stress-strain curves and creep/recovery measurements of metallic glasses the transition was analyzed from the linear, the so-called elastic part, in which the β-relaxation is the dominating process, up to the plastic flow [6,9–12]. Within one metabasin the local structural excitations (strings or chains) seem to be mainly reversible as ultrasonic measurements of the shear moduli showed recently [13]. This is known for creep experiments at low temperatures for a long time [14], which by the way demonstrates the shape memory aspects of amorphous metals. Here we systematically analyze the damping behavior of the metallic glass PdCuSi below T_g as a function of stress and temperature and give a first temperature-stress relationship for the secondary relaxation mode.

2 Sample preparation and measuring setup

Samples of $Pd_{77.5}Cu_{6.0}Si_{16.5}$ are produced as thin ribbons by melt spinning [15] and used for mechanical analysis as cast. The amorphous state was validated by X-ray measurements (data not shown). For experiments ribbons with a length of about 11–13 mm, a width of approx. 1.8 mm and a thickness of 0.025–0.033 mm were used. Measurements were done in a creep/recovery mode using a DMA

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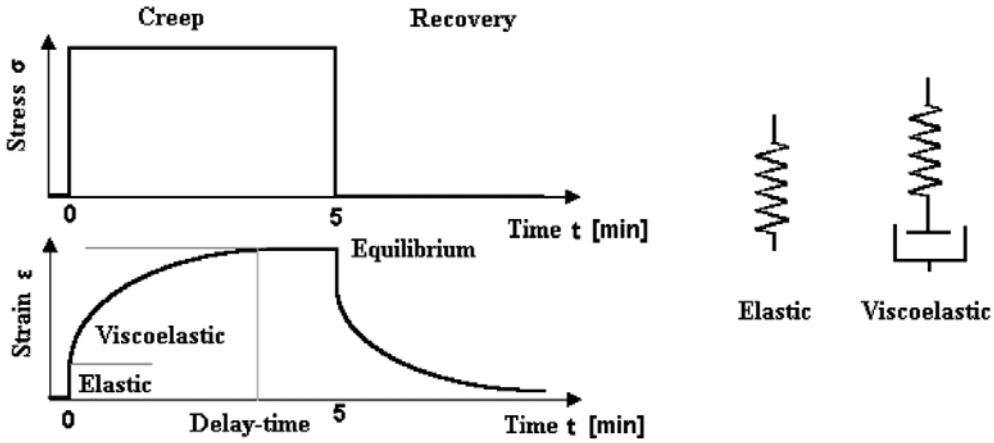

Fig. 1. Schematic picture of a creep/recovery measurement.

7 from PerkinElmer [16] at constant temperature in the region of room temperature up to 630 K. Thereby only the area after a force jump up to the new equilibrium and this specific time, which is named *delay-time*, is utilized. The delay-time can be used as measure for the damping of the system (see fig. 1), which means that a long delay-time is equivalent to a high damping of the system to get into a new "equilibrium" under a given stress. A linear part of the ε *versus* t curve for long times at high temperatures and stresses is deducted for both types of samples.

Figure 1 shows schematically a creep/recovery measuring. The measurement splits into the sections *creep* (force jumps up) and *recovery* (force jumps back to the lower level) as shown schematically in the upper part of fig. 1. The strain change of the material follows the stress (here loading is tensile) and is represented in the lower picture part. First a fast linear, elastic response can be seen. This is proportional to the stress, so that the Young's modulus E can be calculated [16]

$$E = \frac{\Delta\sigma}{\Delta\varepsilon}\,. \tag{1}$$

Then, a viscoelastic creep (in some metallic glass literature this is called anelastic) caused by damping processes like the β-relaxation is observed. The time to reach a new "equilibrium" (*delay-time*) is proportional to the damping. For a highly damped system it takes longer to reach the new "equilibrium". This is valid both for the creep and for the recovery part of the measurement. The delay-time is measured in steps of 25 K from room temperature up to a maximum of 630 K and with a force of 50 mN up to a maximum 950 mN for PdCuSi. At every temperature the force jumps were repeated six times and the force is held between the jumps for 5 minutes. From the repetitions the mean average value was formed and the error was determined from the standard deviation. The force jumps ΔF between the creep and recovery part were always 200 mN to the relative mean. So for every measurement there was a difference of the two forces of 400 mN. Only in two tests (see results, figs. 3 and 4) different conditions were used which are explained later. For every new temperature or force-test a new sample is used. To have a reference point and exclude all creep of the DMA 7 apparatus, all measurements were standardized to the delay-time of crystalline PdCuSi samples, because they showed only pure elastic response (see results, fig. 2) on this scale.

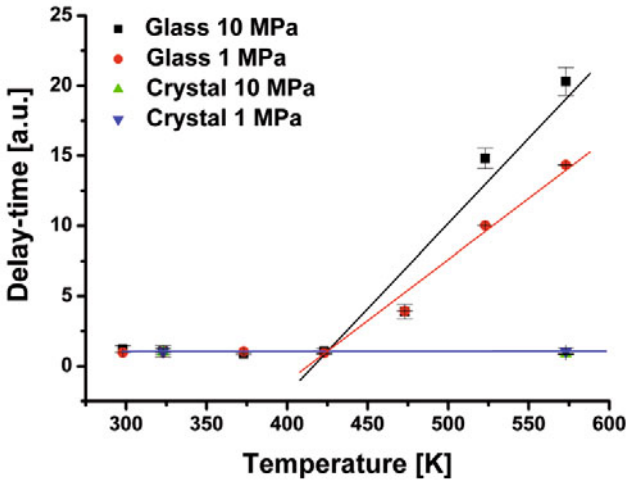

Fig. 2. Delay-time of PdCuSi glass in comparison with a crystalline PdCuSi sample for two different stresses.

3 Results

To analyze the rheological parameters of amorphous PdCuSi, the creep behavior was measured in comparison with a crystallized sample.

A first set of measured delay-times are represented in fig. 2. Two different stresses —a lower force of 50 mN (corresponding to a stress of 1 MPa) and an upper one adjusted to 450 mN (corresponding to 10 MPa)— were used. The measured delay-times are shown for the lower stress as red points and for the upper in black squares in arbitrary units. The data for the crystalline sample are shown at 325 K and 570 K (blue triangles for lower stress and green

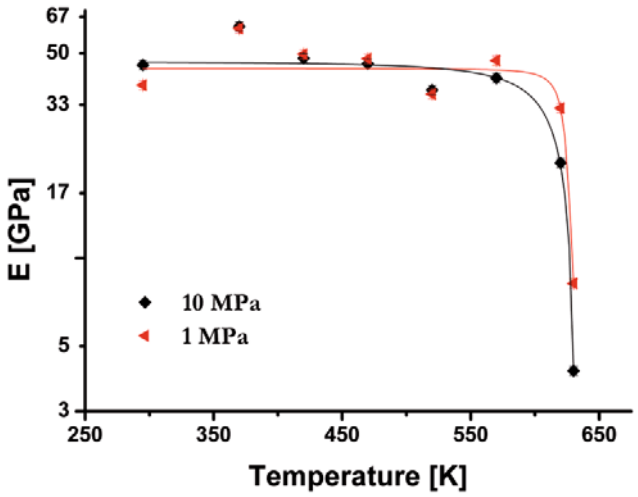

Fig. 3. Comparison of the Young's modulus of amorphous PdCuSi using two different stresses.

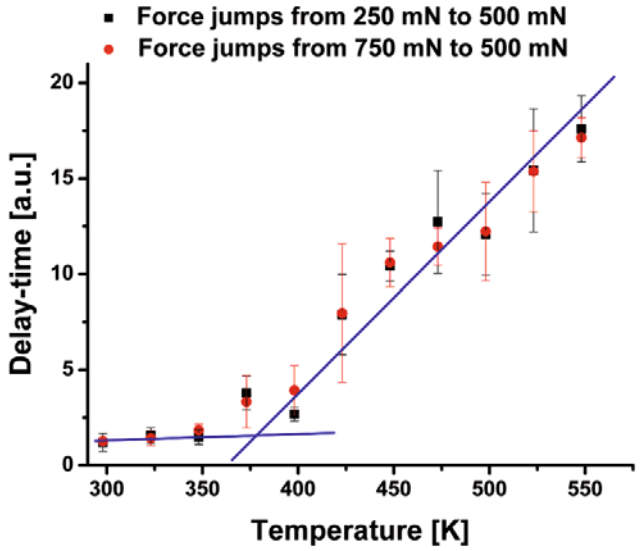

Fig. 4. Delay-time *versus* temperature for PdCuSi with a variation in force jump direction.

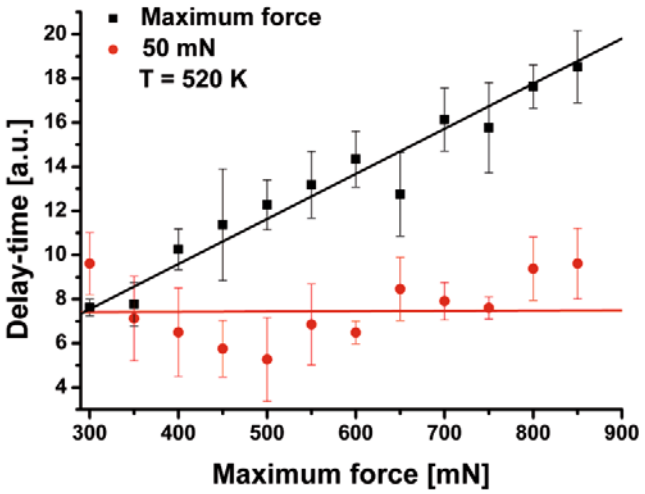

Fig. 5. Delay-time *versus* maximum force for PdCuSi with a variation in ΔF at constant temperature. For every measurement a new sample is used.

triangles for upper stress). First, it is seen that the delay-time for the crystalline samples show no temperature- or stress-dependent changes in this temperature and stress range. The constant behavior is represented in fig. 2 as a straight blue line. The amorphous samples show also no difference compared to the crystalline one up to 425 K. Only at higher temperatures a deviation is recognized. For both stress values the delay-time is now rising and a stress-dependent behavior can be observed. At temperatures above 475 K the delay-time for the upper stress is always higher then for the lower one. These are shown as linear relationships here.

In fig. 3 a comparison of Young's modulus for the amorphous samples is shown by using eq. (1), for the higher stress plotted in black and for the lower one in red. A constant and stress-independent behavior is recognized up to 610 K with a modulus of approximate 45 GPa. The modulus decreases as the glass transition temperature is approached on heating.

To make sure that the jump directions do not influence the measurement, the delay-time of amorphous PdCuSi is determined with different stresses. Thereby the force jumps are such that always a jump to 500 mN as a mean force is chosen and the damping behavior of jumps from 750 mN to 500 mN (red points) is compared to jumps from 250 mN to 500 mN (black squares) at different temperatures (see fig. 4).

As one can see, the direction of the jump does not influence the measured delay-time and its temperature dependence. At all temperatures the material damping shows the same behavior. From 300 K up to 375 K the delay-time is approximately constant. At higher temperatures an increase up to 17.5 at 550 K is observed. These two behaviors are shown here as straight lines.

Second, the influence of the height of the force jumps is tested (see fig. 5). The lower force is always 50 mN (red points), and the higher force in absolute numbers differs from 300 mN to 850 mN (black squares) at a constant temperature of 520 K. For the lower force the normalized delay-time (from the down jump) is constant at approximately 7 for every measurement as already seen in fig. 2. Here it is seen that the damping is not influenced by the height of the back jump ΔF (red line) but rather the absolute value F. For the higher force the damping increases approximately linearly (black line) up to 18.5 at 850 mN.

For further analysis of the damping behavior, the temperature- and stress-dependent delay-time is observed in 25 K steps from room temperature up to 575 K, with the force varied between 100 mN and 950 mN in 50 mN steps at every temperature. The results can be seen in fig. 6, where the delay-time is also normalized to the crystalline sample and plotted *versus* the stress (y-axis) and the temperature (x-axis) in a 3D plot (damping landscape).

The measured points are shown in black and temperature-stress contour lines are given in 2D for constant

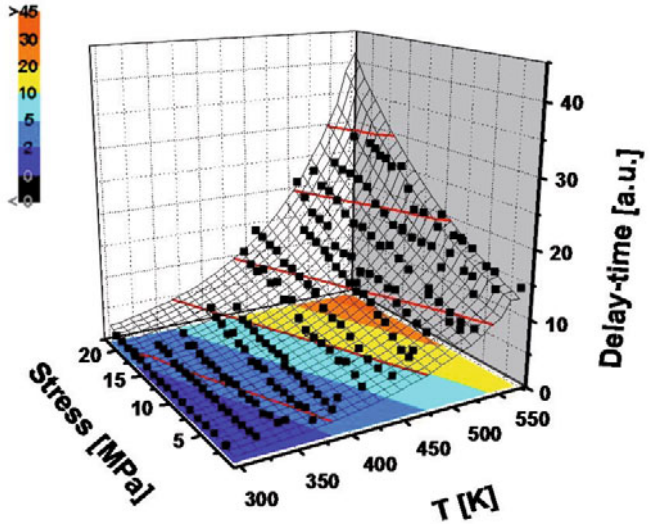

Fig. 6. 3D plot of delay-time of an amorphous PdCuSi sample below T_g. The measured delay-time is plotted *versus* stress and temperature in arbitrary units.

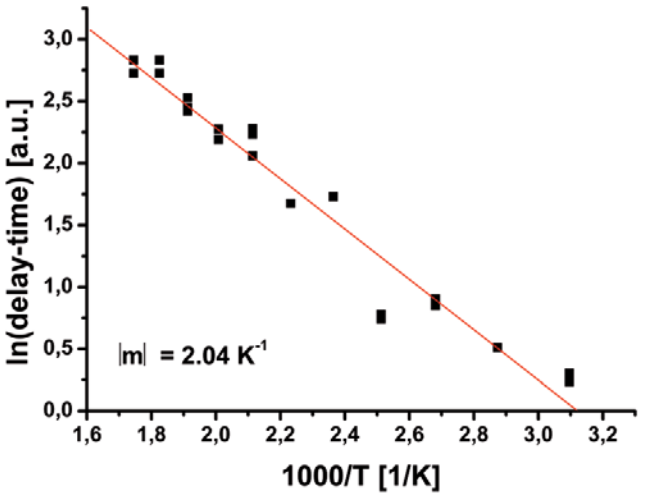

Fig. 7. Temperature dependence of the delay-time at constant stress (approximately 5 MPa).

Table 1. Parameters used in eq. (2) to fit the data shown in fig. 5.

c_T	0.792
c_σ	0.792
λ_T	$0.01\,\mathrm{K}^{-1}$
λ_σ	$0.0562\,\mathrm{MPa}^{-1}$
T_0	423.5 K
σ_0	10.28 MPa

damping levels, which is projected as colored x-y level. The color axis can be seen on the left in fig. 6. In addition, the boundaries between the individual color steps were marked in the data net as red lines. It can be recognized that the delay-time rises with temperature and with stress. Near room temperature a constant behavior up to a normalized delay-time of 2 (deep blue in the color coding) is observed, which shows a nearly pure elastic behavior at lower temperatures. At higher temperatures the damping rises with increasing stress. The highest values for the delay-time (over 27) were found for the highest temperatures and stresses. This means that the damping level increases by a factor of more than 10 from low temperature and stress to the top temperature and stress. Note that this behavior of amorphous PdCuSi is measured below the glass transition temperature. Thereby, the material shows a similar response behavior on the temperature and the stress. To fit the data a double-exponential function, described by the equation

$$\text{Delay-time (normalized)} = e^{c_T+\lambda_T(T-T_0)} \cdot e^{c_\sigma+\lambda_\sigma(\sigma-\sigma_0)} \tag{2}$$

is used as the best empirical description. The parameters used for the fit in fig. 5 are listed in table 1. Here, it is important to mention that the delay-time is connected with temperature and stress in a multiplicative way and can be described with the same set of parameters. This indicates that there must be very similar processes which are activated via temperature and stress.

The used parameter λ_T shows the change of damping with temperature and λ_σ with stress. A recognizable change of the damping was observed at room temperature only for more than 10.28 MPa or above 423.5 K (at an external stress of 1 MPa). The constants c_T and c_σ were needed for standardization at low temperatures and/or stresses.

The dependence of the delay-time due to temperature at constant stress of approximately 5 MPa is shown in fig. 7. An Arrhenius correlation is found between the delay-time and the temperature, so that an activation energy E_a for the dominant process can be calculated, as Hachenberg *et al.* showed [17]. It is found that the activation energy is in the same range with $E_a = 0.41 \pm 0,01\,\mathrm{eV}$, as Hachenberg *et al.* showed for the β-process ($0.67 \pm 0.11\,\mathrm{eV}$) for the same system [17].

4 Discussion

The relaxation behavior of amorphous materials below the glass transition temperature is discussed as cooperative, string-like fluctuations (slow β-relaxation) [18], which is the dominant process up to T_g [13]. Within the picture of the potential energy landscape these relaxations are translated to reversible excitations of different energetic subbasins within the fine structure of the PEL. The discussion of Johnson and Samwer of an influence of the barrier height between two metabasins under external stress [6] leads to the conclusion that it is possible to stimulate also reversible subbasin processes by tilting the PEL.

The comparison of the damping behavior below T_g of an amorphous PdCuSi sample to a crystalline one shows a different connection to the external stress (see fig. 2).

Unlike the crystalline sample, one can recognize an influence of the damping of the amorphous alloy by increasing stress. In the "creep" experiment of the crystalline sample, only an elastic behavior is observed on this scale, even with rising temperature. The glassy sample shows a viscoelastic behavior, and the damping rises. A connection to temperature and external stress is observed, whereby the stress dependence is clearly recognized above 425 K. These dependencies suggest that the position within the PEL is changing under external stress. Thereby, figs. 4 and 5 demonstrate that the direction and height of force jumps is not essential, only the mean absolute stress influences the damping behavior. If the PEL is tilted by an external stress the system can reach higher states within the PEL with higher damping due to more activated β-processes. Also a superposition of the processes with increasing stress or temperature is suggested.

For a coupling of damping behavior in the β-relaxation regime below T_g due to stress and temperature a double-exponential adaptation is used as the best empirical fit (see the damping landscape in fig. 5). Thereby, temperature and stress are connected in a multiplicative way (see eq. (2)), which shows that the contribution to the barrier height within the PEL is not simply added linearly. This indicates a similar process due to temperature and/or stress which is found by the simple mathematical relationship in eq. (2). MD simulations show that string-like motions are excited by thermal energy. There seems to be no reason to assume different mechanisms for mechanical excitations in these systems. Thereby, the calculated activation energy in fig. 6 showed that the reviewed process needs the same energy as the dominant β-process below T_g. This leads to the assumption that the stress and temperature dependence has a direct influence on the β-process.

5 Summary

With the help of creep/recovery measurements we could show that temperature and external stress influence the damping behavior of amorphous PdCuSi below the glass transition temperature. A combination of these processes is suggested, because a very similar behavior is found for damping changes. Thereby temperature and stress are connected in an exponential, multiplicative way, which shows that the contribution to the barrier height within the PEL is not simply linear but connected. This suggests a similar process due to increasing temperature or applied stress, which shows that tilting the barrier height due to external stress has the same effect to the system as increasing the temperature.

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