Anelastic and Viscoelastic Behaviour of Amorphous Zr₆₅Cu_{17.5}Ni₁₀Al_{7.5} in the Range of the Glass Transition

W. Ulfert, H. Kronmüller

► To cite this version:

W. Ulfert, H. Kronmüller. Anelastic and Viscoelastic Behaviour of Amorphous Zr₆₅Cu_{17.5}Ni₁₀Al_{7.5} in the Range of the Glass Transition. Journal de Physique IV Proceedings, 1996, 06 (C8), pp.C8-617-C8-620. 10.1051/jp4:19968132 . jpa-00254564

HAL Id: jpa-00254564

<https://hal.science/jpa-00254564>

Submitted on 1 Jan 1996

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Anelastic and Viscoelastic Behaviour of Amorphous $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ in the Range of the Glass Transition

W. Ulfert and H. Kronmüller

Max-Planck-Institut für Metallforschung, Institut für Physik, Heisenbergstr. 1, 70569 Stuttgart, Germany

Abstract: Reversible (anelasticity) and the irreversible (viscosity) relaxations in the amorphous alloy $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ have been investigated by means of creep and mechanic after-effect measurements of the shear strain, which were performed in an inverted torsion pendulum.

For the evaluation of the measurements a new relaxation model is proposed which takes into account that in the range of the glass-transition temperature T_g the local atomic arrangement is steadily changing. By introducing a finite mean life time τ_l of local structure units we are able to trace the origin of the anelasticity and the viscosity to the same atomic relaxation processes.

The temperature dependence of the viscosity η measured between 560 K and 668 K shows a jump in the activation energy at $T_g = 606$ K from 2.1 eV below T_g to 5.6 eV above T_g .

1. Introduction

Glasses, conventional glasses as well as amorphous metallic alloys, do not show a distinct melting point according a first-order phase transition but a monotonous decrease of the viscosity η with increasing temperature. In the low-viscosity regime of the liquid state the atomic dynamic is controlled by correlated interatomic collisions. In contrast in the solid amorphous state self diffusion occurs via thermally activated atomic jumps. We are interested in the temperature range where the change of the atomic dynamic takes place. Indeed, above a certain temperature T_g , the so called glass-transition temperature, the viscosity reveals a sudden increase of its temperature dependence [1].

Well suited systems are the recently discovered Zr-based amorphous metallic alloys [2,3] showing a high thermal stability against recrystallization, which manifests itself by the large difference of up to 120 K between the glass-transition temperature T_g and the higher recrystallization temperature T_x . In this paper the atomic dynamic in $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ was studied by creep and creep-recovery measurements within a wide temperature range around T_g . We present a new relaxation model which allows a unique description of reversible and irreversible relaxation processes.

2. Experimental

After preparing a prealloy of $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ by arc melting of the pure elements an amorphous ribbon was produced by melt spinning. The dimensions of the specimens were about $20 \times 1.1 \times 0.24$ mm³. The amorphous state was controlled by transmission electron microscopy and X-ray diffraction measurements. The creep measurements were carried out in an inverted torsion pendulum in a He atmosphere of 1000 Pa. The resolution of the shear strain was 10^{-7} . In a first step the specimens were structurally relaxed by measuring the internal friction from room temperature up to 650 K and back to room temperature with a constant heating and cooling rate of 1 K/min. In addition, prior to each isothermal creep and mechanical after-effect measurement the specimens were annealed at the test temperature until the shear modulus G , monitored by a small-amplitude oscillation of the specimens, showed no further changes. The maximally acting shear stress was 2.25 MPa. The procedure of the creep and after-effect measurement is described in fig. 1.

Figure 1: Procedure of a creep and after-effect measurement:

At $t = 0$ we load the before unloaded specimen with a constant shear stress σ_0 . The specimen responds with an instantaneous elastic strain ϵ_{el} followed by a further in the course of time degressive increase of the total shear strain ϵ . At $t = t_1$ we remove the shear stress which causes an ideal elastic change of the strain of $-\epsilon_{el}$ and in the course of time an incomplete recovery of the strain ϵ . Only the reversible, elastic and anelastic parts of the shear strain, ϵ_{el} and ϵ_{an} totally recovers, whereas the irreversible, viscous part of the shear strain ϵ_v remains constant for $t > t_1$.

3. Results and Discussion

For the evaluation of the reversible and irreversible parts for the shear strain we used three models:

model ① : As usual for relaxation processes in amorphous materials we assume a quasi-continuous distribution $p(\ln \tau)$ of relaxation times τ for the anelastic relaxation. The irreversible part of the strain is described by an independent viscosity η . Then $\epsilon(t)$ may be expressed as

$$\epsilon(t) = \frac{\sigma}{2G} \left\{ 1 + \int_{-\infty}^{+\infty} p(\ln \tau) [1 - \exp(-t/\tau)] d \ln \tau \right\} + \frac{\sigma}{2\eta} t \quad (0 < t \leq t_1) \quad (1)$$

$$\epsilon(t > t_1) = \frac{\sigma}{2\eta} t_1 + \frac{\sigma}{2G} \int_{-\infty}^{+\infty} p(\ln \tau) [1 - \exp(-t_1/\tau)] \exp(-(t - t_1)/\tau) d \ln \tau \quad , \quad (2)$$

model ② : Often, relaxation processes in the range of the glass-transition temperature and above can be described by a Kohlrausch function. In contrast to model ① the Kohlrausch function takes into account in some way the structural changes during the relaxation process. But similar as in model ① there is no way to deduce a relation between reversible and irreversible parts of the strain and we have to introduce an independent viscosity term in the expression for ϵ :

$$\epsilon(t) = \frac{\sigma}{2G} \left\{ 1 + P \left[1 - \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right] \right] \right\} + \frac{\sigma}{2\eta} t \quad (0 < t \leq t_1) \quad (3)$$

$$\epsilon(t > t_1) = \frac{\sigma}{2G} P \left[1 - \exp \left[- \left(\frac{t_1}{\tau} \right)^\beta \right] \right] \exp \left[- \left(\frac{t - t_1}{\tau} \right)^\beta \right] + \frac{\sigma}{2\eta} t_1 \quad (4)$$

P is the total relaxation strength.

model ③ : In the temperature range near and above the glass transition the atomic mobility is so high that the local atomic arrangement undergoes a steady variation. This means that a local atomic arrangement has only a certain time to respond to an external stress field and to relax back after unloading. On the other hand structure units which are created within the creep time t_1 starts to relax as well. In the framework of this scenario the irreversible part of the shear strain results from relaxation centers which undergo irreversible changes within the measuring time. In order to evaluate a quantitative expression for the shear strain we assume a simple rate equation for the time dependent distribution function $p(t, \tau)$ of relaxation times:

$$\frac{dp(t, \tau)}{dt} = -\frac{p(t, \tau)}{\tau_i} + \Gamma(\tau) \quad (5)$$

τ_l is the mean life time and Γ is the generation rate of the relaxation centres. In the stationary case $dp(t, \tau)/dt = 0$ we get

$$p(\tau) = \Gamma(\tau)\tau_l \quad (6)$$

Using eq. (6) we can deduce

$$\epsilon(t) = \frac{\sigma}{2G} + \frac{\sigma}{2G} \int_0^{+\infty} p(\tau) d\tau \left\{ \frac{t}{\tau + \tau_l} + \left(\frac{\tau_l}{\tau + \tau_l} \right)^2 \left[1 - \exp \left[-t \left(\frac{1}{\tau} + \frac{1}{\tau_l} \right) \right] \right] \right\} \quad (0 < t \leq t_1). \quad (7)$$

$$\begin{aligned} \epsilon(t > t_1) = & \frac{\sigma}{2G} \int_0^{+\infty} p(\tau) d\tau \left\{ \frac{t_1}{\tau + \tau_l} + \right. \\ & \left. + \left(\frac{\tau_l}{\tau + \tau_l} \right)^2 \left[1 - \exp \left[-t_1 \left(\frac{1}{\tau} + \frac{1}{\tau_l} \right) \right] \right] \exp \left[-(t - t_1) \left(\frac{1}{\tau} + \frac{1}{\tau_l} \right) \right] \right\} \end{aligned} \quad (8)$$

Indeed, because of the finite life time τ_l eq. (7) exhibits a strain term which rises linearly with time and which represents the irreversible, viscous part of the strain. For $p(\tau)$ we assume a simple power law:

$$p(\tau) = p_0 \tau^{\lambda-1} (s)^{-\lambda} \quad (9)$$

Then the viscosity and the effective relaxation strength P_{an} can be expressed as

$$\eta = G \left[\int_0^{+\infty} \frac{p(\tau)}{\tau + \tau_l} d\tau \right]^{-1} = G \tau_l \frac{\sin(\lambda\pi)}{p_0 \tau_l^\lambda \pi} (s)^\lambda, \quad (10)$$

$$P_{an} = \int_0^{+\infty} p(\tau) \left(\frac{\tau_l}{\tau + \tau_l} \right)^2 d\tau = p_0 \tau_l^\lambda \frac{(1-\lambda)\pi}{\sin(\lambda\pi)} (s)^{-\lambda} \quad (11)$$

Fig. 2 shows a creep-after-effect measurement carried out at 620 K. In addition the best fits according to model ① to model ③ are inserted as well. The used fit parameters are listed in table 1. The fits are very good and cover the measuring points nearly perfect. The fit of model ① requires in our case 101 fit parameters (a quasi continuous distribution of relaxation times $p(\ln \tau)$ (see fig. 3) and

Figure 2: Creep and after-effect measurement at 620 K. The measurement and the fits of the three models fall nearly completely together.

Figure 3: Fitted distribution $p(\ln \tau)$ according to model 1.

Table 1: Parameters of the fits shown in fig. 2.

model ①	$P = 1.3$	continuous $p(\ln \tau)$ distribution		$\eta = 2.8 \cdot 10^{12} \text{ Pa}\cdot\text{s}$
model ②	$P = 1.7$	$\tau_k = 20 \text{ s}$	$\beta = 0.43$	$\eta = 2.7 \cdot 10^{12} \text{ Pa}\cdot\text{s}$
model ③	$P = 1.6$	$\tau_l = 204 \text{ s}$	$\lambda = 0.38$	

the viscosity η), the fit of model ② needs 4 independent parameters (the total relaxation strength P , the relaxation time τ_k , Kohlrausch exponent β and the viscosity η) and the fit of model ③ needs only 3 independent parameters (the effective relaxation strength P_{an} , the power λ and the mean life time τ_l), whereas the mean life time τ_l causes both a cutoff of the relaxation time distribution at $\tau \approx \tau_l$ and the appearance of an irreversible viscous strain contribution, respectively. We favour the new model ③ because it requires the lowest number of fit parameters and one of them, the mean life time τ_l has a reasonable physical meaning. The interpretation of the power λ needs further investigations.

Next we investigated the temperature dependence of the creep and after-effect measurements. Fig. 4 shows an Arrhenius plot of the viscosity data obtained by fits of model ① (○) and model ③ (□). Unless

Figure 4: Arrhenius plot of the viscosity data obtained by different methodes.

small deviations below 610 K both models give the same viscosity data. The two high-temperature values (*) were obtained by measuring the internal friction at which a large external restoring force was added to the restoring force of the specimen. The temperature dependence of η shows a marked change of the slope at about 606 K. We interpret this temperature as the quasi-static glass-transition temperature T_g . A. Meyer et al. [4] reported a value of 605 K for the same material. Below and above T_g the viscosity follows Arrhenius laws with activation energies of 2.1 eV and 5.6 eV respectively. A similar behaviour was found for the viscosity of $\text{Zr}_{65}\text{Cu}_{27.5}\text{Al}_{7.5}$ [1] and also for the Be diffusivity D_{Be} in $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ [5]. Geyer et al. [5] proposed that above T_g the degree of freedom of the atomic mobility increases linearly with temperature leading to an entropy term which increases linearly with temperature. This so-called "communal entropy" causes the enhanced temperature dependence of η and D_{Be} above T_g indicated by the jump of the effective activation energy at T_g .

Acknowledgments

This work has been supported by the Deutsche Forschungsgemeinschaft (SPP Unterkühlte Metallschmelzen).

References

- [1] R. Rambousky, M. Moske, K. Samwer, *Z. Phys. B* **99**, 387-391 (1996).
- [2] A. Inoue, T. Zhang and T. Masumoto, *Mat. Trans.* **31**, 177-183 (1990).
- [3] A. Peker and W.L. Johnson, *Appl. Phys. Lett.* **63**, 2342-2344 (1993).
- [4] A. Meyer, J. Wuttke, W. Petry, A. Peker, R. Bormann, G. Coddens, L. Kranich, O.G. Randl and H. Schober, *Phys. Rev. B* **53**, 12107-12111 (1996).
- [5] U. Geyer, S. Schneider, W.L. Johnson, Y. Qui, T.A. Tombrello and M.-P. Macht, *Phys. Rev. Lett.* **75**, 2364-2367 (1995).