Kohlrausch exponent of amorphous $Zr_{65}Al_{7.5}Cu_{27.5}$ determined by anelastic relaxation measurements

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Anelastic relaxations of amorphous $Zr_{65}Al_{7.5}Cu_{27.5}$ have been studied in the range of the glass transition and in the supercooled liquid. Applying a force step function, an anelastic aftereffect of the form $\exp(t/\tau)^{\beta}$ (Kohlrausch–Williams–Watts function) is expected with an exponent $\beta < 1$. From the measurement a value of $\beta = 0.67 \pm 0.03$ is determined at T_g which confirms the empirical correlation between the fragility index m (36.4 for $Zr_{65}Al_{7.5}Cu_{27.5}$) and β, established by Böhmer *et al.* This result is another indication for the metallic glass $Zr_{65}Al_{7.5}Cu_{27.5}$ being a rather strong glass former. Furthermore, a strong increase in β just above T_g is found and is interpreted in the framework of a cluster model. © *1996 American Institute of Physics.* [S0003-6951(96)00647-X]

For the classification of metallic glasses as strong or fragile glass forming systems, the fragility index m introduced by Böhmer and Angell[1] is commonly used. Because of the pronounced stability against crystallization[2], it is possible to measure the equilibrium viscosity of this alloy in the supercooled liquid, as described by Rambousky *et al.*[3] From these measurements the fragility index was calculated to be $m = 36.4$. Here T_g was determined from the kink in the $\ln[\eta(T)]$ plot. Böhmer *et al.*[4] found an empirical correlation between the fragility index m and the Kohlrausch–Williams–Watts (KWW) exponent β. The aim of this letter is to determine the KWW exponent β from the time dependent anelastic strain following a jump in external stress[5] and to verify whether the relation between m and β also holds for metallic systems. Because the fragility index was obtained from an isothermal viscosity measurement, it is conclusive to measure β in a similar way.

$Zr_{65}Al_{7.5}Cu_{27.5}$ splats were prepared from the pure elements by arc melting in a Ti gettered Ar atmosphere and subsequent ultrarapid quenching. The measurements were carried out in tension (Perkin Elmer DMA 7) in a He–N gas flow to minimize oxidation of the samples ($10 \times 1.05 \times 0.04$ mm³ in size). With applied load, the samples were heated to a temperature T with a rate of 50 K/min followed by isothermal creep experiment to remove excess free volume quenched in during preparation. After approaching a nearly constant creep velocity, the load was reduced to half of its initial value causing elastic and anelastic reponse of the sample (Fig. 1). The viscosity η

$$\eta = \frac{\sigma}{3\dot{\varepsilon}} \tag{1}$$

is calculated from the measured strain ε and the applied stress σ to make the anelastic effect more visible (Fig. 2). Before and far beyond the change in creep force the response of the sample is merely viscous flow, without anelastic effects (regions I and III in Fig. 2). Therefore these data were fitted to the function[6]

$$\eta(t) = \underbrace{\frac{\eta_0 + \eta_{eq} \cdot \left(\frac{\eta_{eq} - \eta_0}{\eta_{eq}^2} \cdot k_2\right) \cdot t}{1 + \left(\frac{\eta_{eq} - \eta_0}{\eta_{eq}^2} \cdot k_2\right) \cdot t}}_{\text{bimolecular model}} \cdot \underbrace{(1 + \Theta(t - t_{SRO}) \cdot 2.5 \cdot \{1 - \exp[-a \cdot (t - t_{SRO})^3]\})}_{\text{viscosity change due to short range ordering}} \tag{2}$$

with the fitting parameters η_{eq}, k_2, a, t_{SRO}. The first part of Eq. (2) describes the viscosity increase due to annihilation of excess free volume with bimolecular kinetics[6]. Here, η_0 and η_{eq} are the initial viscosity (determined from the measurement) and the equilibrium viscosity respectively, k_2 is the rate constant for the approach of equilibrium. The second part models the viscosity increase arising from small rigid particles dispersed in a viscous medium[6,7], where a is a time constant for short range ordering, and t_{SRO} is the corresponding incubation time. Although it is not known so far, whether this is the correct microscopic picture, the functional dependency describes the viscosity in the limited time range of the experiment very well. Indeed, EXAFS measurements indicate the occurrence of short range order during annealing[8] which may be the reason for the observed increase in viscosity on long times scales.

From the viscosity under constant load (Eq. 2), the strain due to viscous flow can be calculated by re-integration:
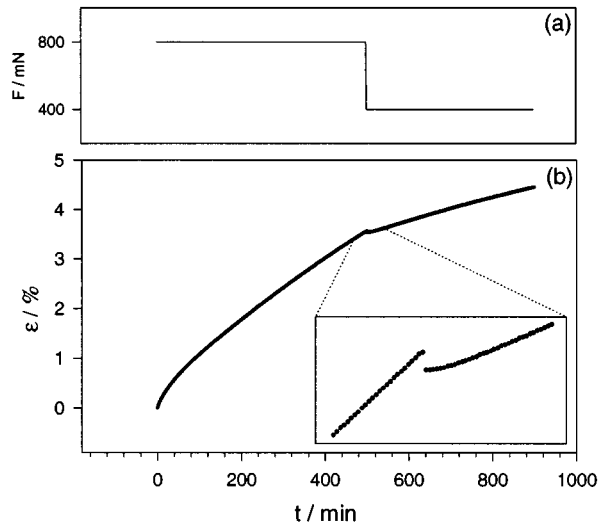
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FIG. 1. (a) Applied force F, (b) measured strain ε as response of the sample to the applied force. The inset shows a magnified region where the force is reduced to half of its initial value, including the anelastic aftereffect of the sample.

$$\varepsilon(t) = -\int_{t_1}^{t} \frac{\sigma}{3\,\eta(t')}\,dt'. \tag{3}$$

The pure anelastic effect is then given by subtracting the viscous strain contribution from the measured strain. Its time dependence, as shown in Fig. 3 for 623 K, is not simply exponential, but can be adapted by a KWW function of the following form:

$$\varepsilon(t) = \varepsilon_0 \cdot \exp\left[-\left(\frac{t}{\tau}\right)^{\beta} \right] + d. \tag{4}$$

Because of finite measurement time, the zero point of anelastic strain cannot be determined directly. Therefore, we use the parameter d to account for finite anelastic strain at the end of the measurement. However, d is smaller than 1% of ε_0 in all cases.

The KWW-exponent β and the relaxation time τ have been determined for temperatures in the vicinity of T_g as well as in the supercooled liquid. The results are shown in
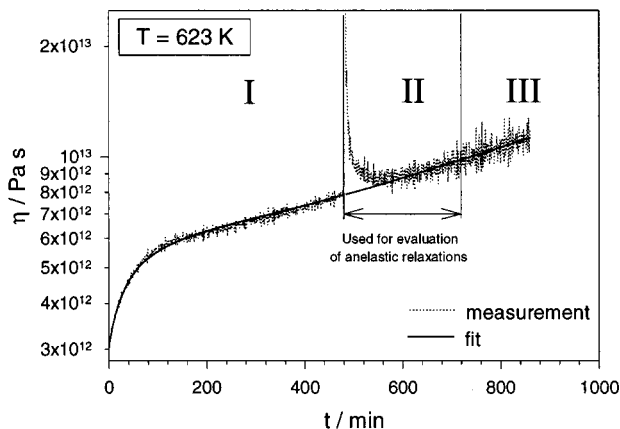

FIG. 2. Viscosity of ZrAlCu as a function of time at 623 K, calculated from the measured strain. Regions I and III have been used for adapation of Eq. (2) (solid line).
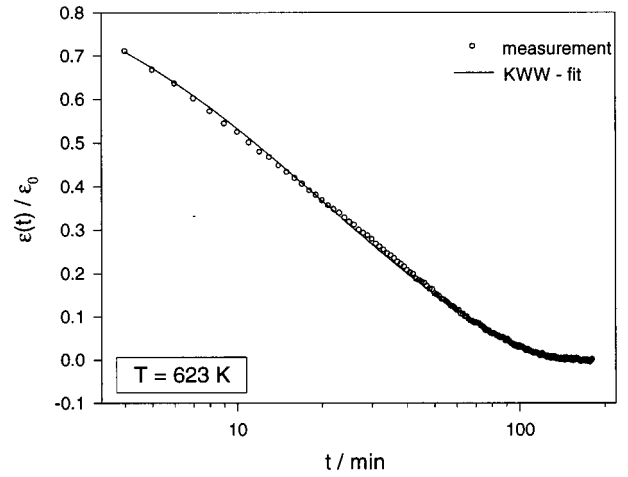

FIG. 3. Example for the separated anelastic strain of ZrAlCu as a function of time at 623 K. The solid line is the fit with a KWW-function [Eq. (4)].

Figs. 4 and 5. The glass transition temperature T_g is marked by the kink in temperature dependence of both, β and τ. Its value of 623 K is in accordance with former measurements of the equilibrium viscosity[3]. At T_g a value of $\beta = 0.67 \pm 0.03$ is obtained. Thus the correlation between the KWW-exponent β and the fragility index m[4]

$$m = 250 - (320 \pm 30) \cdot \beta, \tag{5}$$

suggesting a value $0.57 < \beta < 0.76$ for $m = 36.4$ is confirmed for $Zr_{65}Al_{7.5}Cu_{27.5}$. To the knowledge of the authors, this is the first time the KWW-exponent β has been determined for an amorphous metallic system. Regarding the relaxation time τ, it has to be mentioned that Böhmer $et\ al.$ compiled the data on the definition of T_g as the temperature where τ reaches a value of 100 s. The discrepancy in magnitude of the relaxation times in the definition of Böhmer $et\ al.$ and our measured value at T_g (1295 ± 100 s) can be understood in terms of a Kelvin chain[9]. In the case, when stress relaxation is used as a probe of non-exponential relaxation behavior, all elements, especially the viscous part is involved in the relaxation. In contrast, in a creep-recovery experiment only the anelastic part of the Kelvin chain contributes to the relax-
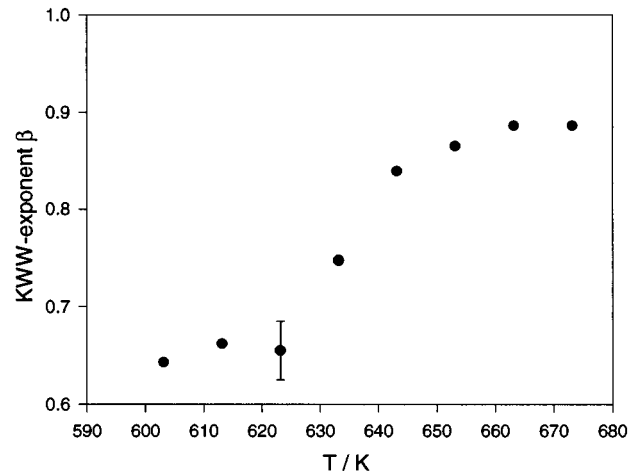

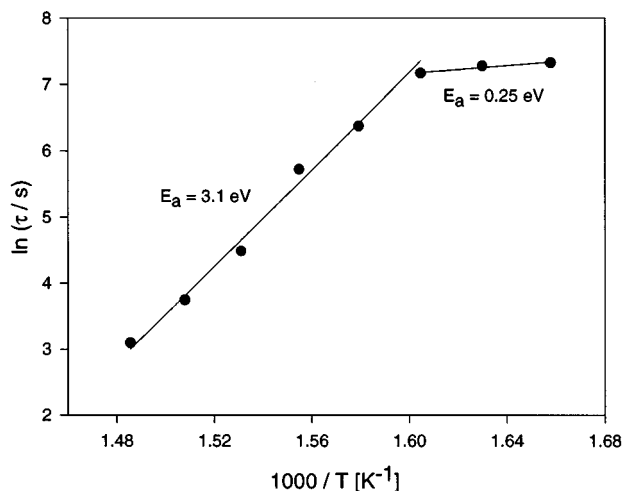FIG. 4. KWW-exponent β of ZrAlCu in the vicinity of T_g and in the supercooled liquid.

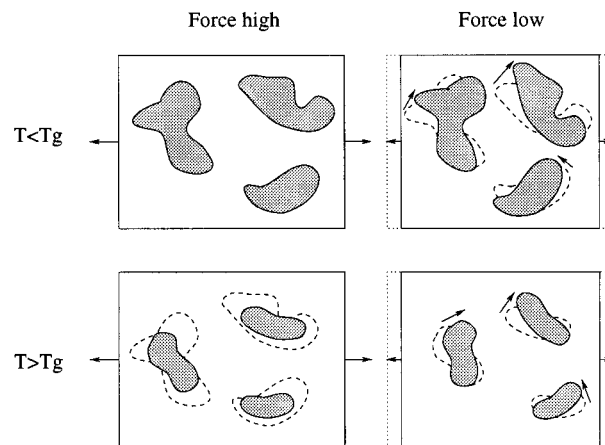FIG. 5. Anelastic relaxation time τ of ZrAlCu in the vicinity of T_g and in the supercooled liquid.

FIG. 6. Schematic view of an amorphous material with regions (clusters) consisting of immobile atoms surrounded with atoms of high mobility. From left to right: change in external force causing reorientation of clusters. From top to bottom: change in cluster size and shape with increasing temperature.

ation whereas the viscous response is separated. Therefore a larger value of τ is expected in the latter case.

The rapid change of β above T_g (Fig. 4) can be explained in the framework of a cluster model[10,11] where regions of almost immobile atoms (''solid-like'' clusters) are surrounded with atoms of high mobility (''liquid-like''). The change in external force then might cause a time dependent reorientation of the clusters leading to the anelastic effect, as shown in a schematic in Fig. 6. The variation in size and shape of the individual clusters leads to a distribution of relaxation times and thus to $\beta < 1$. Above T_g the clusters become rapidly smaller causing a narrower distribution of relaxation times and a larger value of β. An additional effect which enhances the increase of β may be a change in shape due to cooperative rearrangements of the atoms within the clusters above T_g. Therefore the individual cluster relaxation time is less dependent of cluster size and shape leading to a narrower relaxation time distribution. Furthermore, the cooperative rearrangements would result in a faster approach of equilibrium with respect to the external force and thus in a smaller relaxation time, as observed in the experiment. Fur-

ther analysis of the proposed model for anelastic effects in metallic glasses and supercooled liquids is the subject of future work.

[1] R. Böhmer and C. A. Angell, Phys. Rev. B **45**, 10091 (1992).
[2] A. Inoue, T. Zhang, and T. Masumoto, J. Non-Cryst. Solids **150**, 396 (1992).
[3] R. Rambousky, M. Moske, and K. Samwer, Z. Phys. B **99**, 387 (1996).
[4] R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, J. Chem. Phys. **99**, 4201 (1993).
[5] R. Böhmer and C. A. Angell, in *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer, Berlin, 1994).
[6] S. S. Tsao and F. Spaepen, Acta Metall. **33**, 881 (1985).
[7] A. Einstein, Ann. Phys. **19**, 289 (1906).
[8] H. Mysz, Diploma thesis, University of Cambridge, Augsburg, 1996.
[9] J. Zarzyki, *Glasses and the Vitreous State* (Cambridge University Press, 1982).
[10] M. Li, Ph.D thesis, Caltech, Pasadena, 1994.
[11] J. Jäckle, Phys. B l. **52**, 351 (1996).