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Anelastic relaxation behavior and thermal stability of undercooled metallic melts in the amorphous $\mathrm{Zr}_{65}\mathrm{Al}_x\mathrm{Cu}_{35-x}$ system

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The anelastic relaxation behavior of amorphous $\mathrm{Zr}_{65}\mathrm{Al}_x\mathrm{Cu}_{35-x}$ in the vicinity of the glass transition is found to be very sensitive on the aluminum content. The description is given in terms of a Kohlrausch-Williams-Watts function which is characterized by the stretching exponent β and the relaxation time τ. The dependence of these parameters on temperature as well as on Al content can be consistently described with the existence of a correlation length or dynamical heterogeneity which seems to reach a critical size at the crystallization temperature, independent of alloy composition. In this sense the thermal stability appears to be closely connected to the anelastic relaxation behavior.
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I. INTRODUCTION

Amorphous and glassy materials, from silica glasses to polymers and metals are of considerable fundamental and technological interest. The transition from liquid to solid behavior upon cooling is an old[1] but unresolved problem in physics.[2–4] Metallic glass formers have been expected to be an ideal system for the description of the glass transition since they should be comparable to a hard-sphere system.

For a characterization of different glass formers the classification scheme of Angell[5] is widely used. This classification can be quantified with the so-called fragility index m (Ref. 6),

$$m=\left.\frac{d\log\eta}{dT_g/T}\right|_{T=T_g}, \tag{1}$$

which is determined by the temperature dependence of the viscosity $\eta(T)$ at the glass transition temperature T_g.

Glass formers which have a temperature-independent activation energy of viscous flow (Arrhenius-like behavior) exhibit only small changes of the local atomic configuration and are therefore called *strong glass formers*. These materials are characterized by small values of m down to $m\approx16$. In contrast, a temperature-dependent local configuration of fragile glass formers is responsible for a temperature-dependent activation energy. Corresponding values for the fragility index up to $m=191$ are found.[7]

Another common way for the description of glass formers is the characterization of the relaxational behavior of a quantity Φ (dielectric polarization, mechanical stress, anelastic strain[7]) in terms of a Kohlrausch-Williams-Watts (KWW) function[1,8,9]

$$\Phi(t)\propto\exp(-(t/\tau)^{\beta}) \tag{2}$$

with a characteristic relaxation time τ and a stretching exponent β which is a measure for the nonexponentiality.

A compilation of experimental results shows a correlation of the fragility and the nonexponentiality of the relaxational behavior at T_g for various amorphous materials,[10] i.e.,

$$m\approx250-320\beta. \tag{3}$$

Hard-sphere systems should be fragile in this classification. However, new metallic glass formers which are (meta-)stable in the supercooled liquid state[11–16] show relatively small values of m and large values of β, e.g., $m=36.4$ (Ref. 17) and $\beta\approx0.67$ at T_g for $\mathrm{Zr}_{65}\mathrm{Al}_{7.5}\mathrm{Cu}_{27.5}$ (concentrations in at. %)[18] in accordance with Eq. (3). These results, which are confirmed by other viscosity measurements[19] and neutron scattering,[20] mean that these alloys belong to the group of strong glass formers, in contrast to the expectations for a hard-sphere system.

We refer to this problem in terms of the anelastic relaxation behavior which can be described with a KWW function [Eq. (2)].[18] Two different scenarios for the origin of the stretching of relaxation are discussed in literature. First, β may be attributed to a nonexponential relaxation behavior of a homogeneous system.[21–23] The second possible interpretation for the experimental results is a heterogeneous distribution of relaxing units which seems to apply in many cases and is briefly reviewed in the following section.

II. DYNAMIC HETEROGENEITIES

These heterogeneities have a finite ''lifetime''[24] and are therefore often said to be dynamic. Such a dynamic heterogeneity has been suggested from lattice-gas models.[25,26] But even more realistic molecular-dynamics simulations in two dimensions[27–29] showed regions of different atomic mobility. Recent simulations of Kob, Donati, Plimpton, Poole, and Glotzer show regions of different density and mobility even in three dimensions.[30] Smaller mobility of the atoms forces enhanced cooperativity, i.e., the total number of atoms involved in molecular motions is larger in a region of enhanced density. This corresponds to a larger correlation length of atomic movements.

The idea of cooperativity has led to huge efforts to find these regions experimentally. The most direct approach was given by Arndt, Stannarius, Groothues, Hempel, and Kremer who confined the glass former salol into nanopores of diffent sizes (2.5–7.5 nm).[31] Due to the confinement the maximum correlation length is limited, and the relaxation-time spectrum is shifted towards shorter times which was interpreted in terms of a correlation length exceeding 7 nm. Multidimensional nuclear magnetic resonance (NMR) investigations[24,32] confirm the heterogeneous nature of this so-called α relaxation.[33] By means of dielectric hole burning, Schiener, Böhmer, Loidl, and Chamberlin demonstrated that the dielectric data can be analyzed in terms of Al relaxation-time distribution of spacially distributed relaxators.[34] Concerning anelastic response of amorphous metallic alloys, a crossover experiment in $Fe_{40}Ni_{40}B_{20}$ showed that the anelastic relaxation process for these amorphous alloys is not hierarchical as proposed from dielectric response experiments,[35] but is better described with a distribution of relaxation times.[36] However, a distribution of relaxation times is widely used for the interpretation of mechanical relaxation data.[37–39] The anelastic relaxation times in $Pd_{40}Ni_{40}P_{20}$ are much longer compared to characteristic times for short-range order.[39] We therefore conclude that the anelastic behavior in metallic glasses at least in the vicinity of T_g is affected by more atoms than nearest neighbors.

The correlation length found in light-scattering experiments[40,41] is usually larger than in computer simulations. This may be due to local orientational ordering as Weber, Paul, Kob, and Binder suggested.[42] Another problem may arise from the small simulation cell, and it has been argued that for long relaxation times simulation mechanisms other than molecular dynamics are favorable.[43]

The existence of a correlation length is unexpected in theories that treat the glass transition as a purely kinetic phenomenon, such as mode coupling theory.[44] However, there are several theoretical approaches to describe cooperative behavior.[45–48]

Since glass forming liquids seem to be heterogeneous in nature, the question may arise whether the strong liquid behavior of metallic glass formers may be attributed to a certain heterogeneity. In fact, it has been speculated that the observed increase in β with temperature arises from regions of different atomic mobility that change size with increasing temperature.[18] Another question is whether the good thermal stability of supercooled liquid $Zr_{65}Al_{7.5}Cu_{27.5}$ is connected to the relaxational behavior.

To answer these questions, we performed concentration dependent anelastic relaxation experiments in the $Zr_{65}Al_xCu_{35-x}$ system which is well suited for the investigation of these questions since the thermal stability of $Zr_{65}Al_xCu_{35-x}$ samples changes with Al content x.[49] The fact that this system consists of only three components makes the interpretation of concentration dependence more simple. Furthermore, $Zr_{65}Al_xCu_{35-x}$ provides the most stable supercooled liquid ($x=7.5$) of all known ternary alloys, which is an advantage in time consuming equilibrium experiments like anelastic relaxation measurements.

III. EXPERIMENTAL

The alloys have been prepared from the elements of high purity (Zr: 99.935%, Al, Cu: 99.999%) by arc melting in 99.999% Ar atmosphere. Subsequent splat quenching provides a foil of 40 μm thickness, which is fully amorphous for all Al contents as checked by x-ray diffraction. The composition of the alloys has been checked with energy dispersive x-ray analysis (EDX) and a deviation smaller than 1% from the nominal concentration was found.

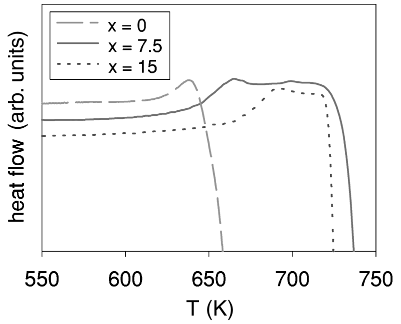

FIG. 1. Heat flow of three different $Zr_{65}Al_xCu_{35-x}$ samples measured with 0.83 K/s in a DSC experiment. The sample containing 7.5% Al exhibits the largest temperature interval $\Delta T_x = T_x - T_g$ between glass transition T_g and crystallization temperature T_x ($\Delta T_x = 90$ K).

The stability of the supercooled liquid was determined by differential scanning calorimetry (Perkin Elmer DSC 7) with a heating rate of 0.83 K/s. Figure 1 shows the temperature-dependent heat flow of the sample in reference to the corresponding crystallized sample. The glass transition at T_g is marked by an endothermic step and is shifted to higher temperatures for higher Al content. In contrast, the crystallization temperature T_x is maximum for 7.5% Al. As a result, a supercooled liquid region $\Delta T_x = T_x - T_g$ of about 90 K is obtained for $Zr_{65}Al_{7.5}Cu_{27.5}$, which indicates the good quality of the samples.

The anelastic relaxation experiments have been carried out in tension in a Dynamic-Mechanical Analyzer (Perkin Elmer DMA 7), where force and temperature are programmed and the resulting strain is measured. The whole device was operated under controlled Ar atmosphere ($O_2 < 1$ ppm) to prevent sample oxidation. Figure 2 shows the applied force (a) and the corresponding strain (b) of a $Zr_{65}Al_{7.5}Cu_{27.5}$ sample at 623 K as a function of time.

The sample strain is dominated by viscous flow over the whole experiment. At the beginning, the viscosity of the

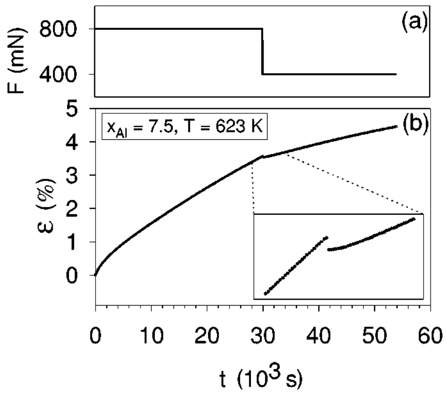

FIG. 2. (a) Applied force F and (b) measured strain ε as the response of the sample to the applied force. The inset shows a magnified region where the force is reduced to half of its initial value, including the anelastic aftereffect of the sample [curvature in $\varepsilon(t)$ after load change].

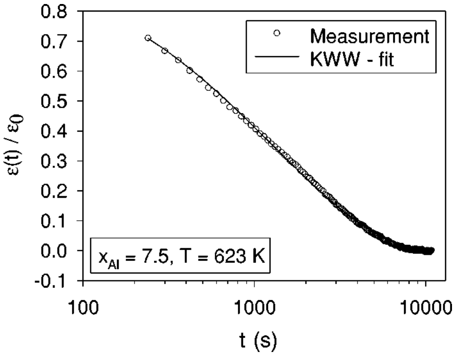

FIG. 3. Example for the separated anelastic strain of $Zr_{65}Al_{7.5}Cu_{27.5}$ as a function of time at 623 K. The solid line is the fit with a KWW function according to Eq. (2).

sample rises due to annealing of excess free volume quenched in during the preparation process. This is commonly referred to as irreversible structural relaxation.[50–53] After 25 ks the sample is close to metastable equillibrium as indicated by an almost constant creep velocity. The force is then reduced to half of its inital value, causing an instantaneous elastic contraction and a time dependent anelastic aftereffect. The separation of the anelastic strain from viscous flow was performed using the derivative of the experimental data to improve the accuracy. This is described in detail in an earlier paper.[18] Figure 3 shows the separated anelastic strain, which is calculated from the data in Fig. 2, and the fit with a KWW relaxation function according to Eq. (2). As main results, the exponent β and the characteristic relaxation time τ are obtained from the fit and are the basis for further investigations.

IV. RESULTS

First, the reversibility of the observed increase of β in the supercooled liquid region[18] is checked for a $Zr_{65}Al_{7.5}Cu_{27.5}$ sample because most glass forming materials show only weak temperature dependence or lower values of β in the vicinity of T_g.[6,54–56]

For this purpose, β is measured first at 633 K. Then the sample was cooled down to 623 K. To remain in metastable equillibrium, the cooling was performed with a rate of 0.017 K/s, followed by an isothermal anneal for 4200 s, before the anelastic experiment was performed. The determination of β, now at 623 K, shows consistent values compared to measurements on individual samples without this heat pretreatment and proves its reversibility in the supercooled liquid.

The temperature dependence of the KWW exponent β for different Al contents are compared in Fig. 4. For each value an individual sample was used to avoid problems with beginning crystallization, especially for $x=0$ and $x=15$. However, for $x=0$ no values above T_g could be determined because of the rapid crystallization of the sample at elevated temperatures.

In the glassy state, β is constant within the experimental error of about 3% for all three compositions, but the absolute value is concentration dependent and a maximum is reached for $x=7.5\%$. In the supercooled liquid the increase in β is less pronounced for $x=15\%$ compared to $x=7.5\%$. A similar behavior, weak temperature dependence of β below T_g and its increase above T_g, can be observed in some polymers[55] as well as in semiconductors.[54]

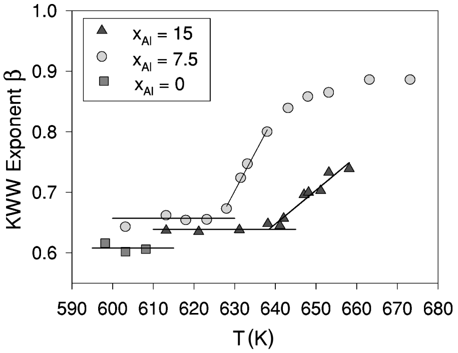

FIG. 4. KWW exponent β of $Zr_{65}Al_xCu_{35-x}$ determined from anelastic relaxation measurements in the vicinity of T_g and in the supercooled liquid for three different Al concentrations x.

Figure 5 shows the characteristic relaxation times τ corresponding to the β values in Fig. 4 in an Arrhenius plot. The most striking feature is the very short relaxation time for $Zr_{65}Cu_{35}$, even below T_g (T_g estimated from DSC measurement), whereas $Zr_{65}Al_{7.5}Cu_{27.5}$ shows the largest values for all temperatures. The temperature dependence of τ in the glassy state is largest for $x=0$ and is only weak for $x=7.5$. Close to the glass transition, a change in temperature dependence is observed for both $Zr_{65}Al_{7.5}Cu_{27.5}$ and $Zr_{65}Al_{15}Cu_{20}$. The experiments are performed up to temperatures just before the onset of crystallization in the timescale of the measurement. At temperatures close to T_x the anelastic relaxation time is almost equal for all three investigated alloys.

V. DISCUSSION

As stated above, anelastic response experiments are well described by a distribution of relaxation times which may arise from density fluctuations. For larger regions of dense packing undergoing a cooperative rearrangement, larger anelastic relaxation times are expected.[18,45] Therefore, a broader distribution in the size of these regions should reduce the KWW exponent.

Additionally, it might be expected that the addition of Al leads to a broader distribution of relaxation times due to a different binding strength between Zr-Cu and Zr-Al, which is

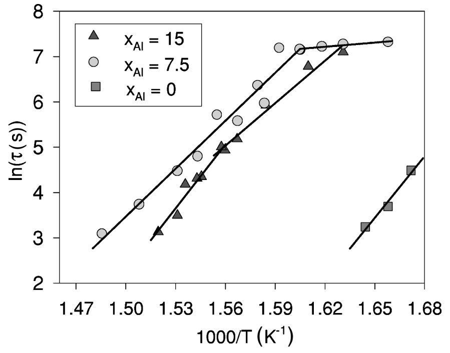

FIG. 5. Anelastic relaxation time τ of $Zr_{65}Al_xCu_{35-x}$ in the vicinity of T_g and in the supercooled liquid for three different Al concentrations x.

represented by the more negative heat of mixing of Zr-Al (-45 kJ/mole) compared to Zr-Cu (-24 kJ/mole).[57] However, this is not the case. Although the addition of Al leads to a shift of T_g to higher temperatures which can be attributed to the higher binding strength of Zr-Al,[58,59] the increasing KWW exponent indicates a clear reduction of the width of the relaxation time spectrum upon addition of Al.

The narrower distribution of relaxation times of the alloys containing Al may be of statistical origin. Desré showed that the concentration fluctuations are reduced by a factor of 10 when the number of components of an alloy is increased by 1.[60] This in turn should lead to an enhanced thermal stability of the supercooled liquid, a tendency which is indeed observed for multicomponent glass forming alloys.[61]

Since the stability decreases for Al contents larger than 7.5%, another mechanism must come into play. Inoue *et al.*[49] argued that the reduced thermal stability of $Zr_{65}Al_{15}Cu_{20}$ has its origin in the existence of a second crystalline phase in this alloy, Zr_2Al, because this enables a crystallization without long-range distribution of Al atoms. Besides this, it is possible that an Al content of 7.5% enables a maximum of packing density which is known to be very important for stable supercooled liquids[13] and can often be achieved by addition of elements with small atomic radii such as beryllium or carbon.[15,62] In fact, the smaller anelastic relaxation times of $Zr_{65}Al_{15}Cu_{20}$ compared to $Zr_{65}Al_{7.5}Cu_{27.5}$ indicate that the density of packing is reduced in this alloy. This would also explain the broader distribution of relaxation times (smaller value of β) in $Zr_{65}Al_{15}Cu_{20}$.

This picture is supported by the the almost equal relaxation times close to T_x for all three alloys. Obviously the supercooled liquid crystallizes when the mobility of the atoms ($\propto \tau^{-1}$) reaches a certain critical value which seems to be identical for all three alloys. Since these alloys differ in various aspects from each other, a critical size of the correlation length may be a measure valid for all three compositions.

VI. CONCLUSION

Anelastic relaxation experiments for three glass forming alloys of the $Zr_{65}Al_xCu_{35-x}$ system in the glassy state as well as in the supercooled liquid have been presented. The relaxation was characterized with the stretching exponent β and the relaxtion time τ according to a KWW function. The results can be consistently described with the existence of a correlation length of decreasing size with increasing temperature and increasing deviation from an Al content of 7.5%. The experiment suggests the existence of a critical size of such a correlation length close to the onset of crystallization. This critical size appears to be identical for all compositions.

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