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Different metastable equilibrium states in metallic glasses occurring far below and near the glass transition

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ABSTRACT

Precise measurements of the high-frequency shear modulus of two bulk Zr- and Pd-based glasses in the initial and strongly preannealed states in a wide temperature range are performed. Isothermal structural relaxation of preannealed samples leads to either decrease or increase of the shear modulus. At temperatures below particular temperature T_{pc} , one observes cross-over relaxation (decrease→increase) of the shear modulus. The minimal shear modulus attained upon relaxation corresponds to the quasi-metastable equilibrium, which depends both on temperature and thermal prehistory. At higher temperatures $T > T_{pc}$, the relaxation always leads to shear modulus decrease towards the “true” metastable equilibrium, which depends only on temperature. The temperature T_{pc} for both glasses is by ≈ 25 K smaller than the calorimetric glass transition temperature. It is shown that this temperature constitutes the low temperature limit of the linear extrapolation of the shear modulus from the supercooled liquid state. By definition, the temperature T_{pc} corresponds to the pseudocritical temperature introduced by Kauzmann in 1948 (W. Kauzmann, Chem. Rev. 43 (1948) 219).

A detailed discussion of the microscopic relaxation mechanism below and above T_{pc} based on the Interstitial theory is presented.

1. Introduction

It was suggested long ago [1–3] and now is commonly accepted that glasses are thermodynamically unstable with respect to a metastable equilibrium state. The existence of this state implies that small isothermal alterations of thermodynamic parameters result in an increase of the Gibbs free energy while their large changes can lead to a state with lower energy [3]. Glass is formed when a supercooled liquid fails to follow the metastable equilibrium upon cooling during the time scale of the experiment.

All this fully applies to metallic glasses (MGs) [4–7]. Upon annealing close to the glass transition temperature T_g , many physical properties of MGs change as the structure relaxes towards the metastable equilibrium, which depends only on temperature. Consequently, on isothermal annealing, the properties reach time-independent saturation values [5, 8, 9]. Thermal cycling reproduces the values of the properties in the metastable equilibrium after certain relaxation transient. These values coincide with those obtained by extrapolation from the supercooled liquid state [7, 8]. Upon testing well below T_g , the metastable equilibrium state becomes kinetically unachievable on the experimental time scale and the properties often demonstrate well known logarithmic

time kinetics [7, 10]. The microstructural origin of the relaxation towards the metastable equilibrium is frequently attributed to relaxation of the free volume [11–13].

After certain heat treatment, MGs display a change of the relaxation sign (property increase→decrease or vice versa) upon isothermal testing. This phenomenon was found long ago in both non-metallic [14] and metallic [15, 16] glasses and referred to as the cross-over relaxation effect.

Fundamental issues related to the metastable equilibrium were raised by Kauzmann in 1948 in his aforementioned famous work [3]. He noticed that the extrapolation of the entropy of supercooled liquids far below T_g leads to a paradoxical result – the extrapolated entropy of a supercooled liquid far below T_g becomes smaller than that of the reference (maternal) crystal. Similar behavior was documented by Kauzmann for a few other properties. This result was later named the Kauzmann paradox. The temperature corresponding to the equality of a property extrapolated from the supercooled liquid state to its value for the maternal crystal was called the “Kauzmann temperature”. Big literature exists on how to resolve the Kauzmann paradox (e.g. Refs [17, 18] and papers cited therein) and whether it really exists or not (e.g. Refs [19, 20]).

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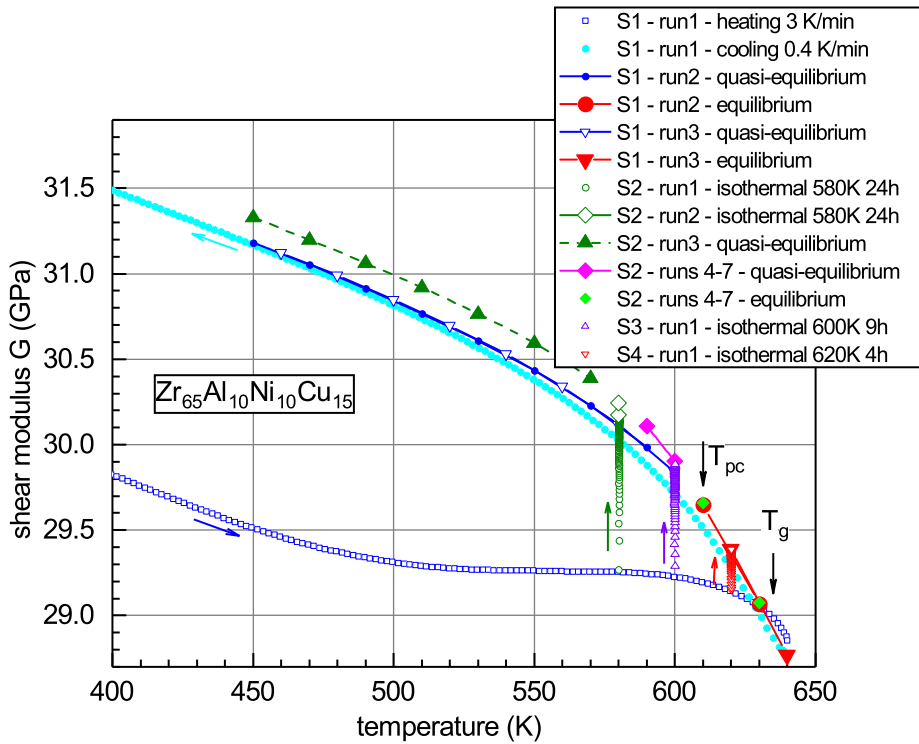


Fig. 1. Temperature dependence of the shear modulus of bulk glassy $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ in the initial state and after different relaxation procedures. Both linear heating and isothermal data are shown as explained in the text. Calorimetric glass transition temperature T_g obtained at a heating rate of 3 K/min is shown by the arrow. “Quasi-equilibrium” data points correspond to the minimal shear modulus in the cross-over relaxations (similar to that shown in the inset of Fig. 3). “Equilibrium” data points correspond to the relaxation kinetics with saturation.

It is much less known that a resolution of this paradox was suggested by Kauzmann himself in the same work [3]. He argued that the above extrapolation far below T_g is not permissible because the metastable equilibrium state of a supercooled liquid cannot exist below certain temperature, which he called the *pseudocritical temperature*. This statement actually constitutes one of the key ideas of his work [3]. Thus, according to Kauzmann, the paradox named later after him does not exist.

A search for the Kauzmann pseudocritical temperature T_{pc} constitutes a complicated task. Most of relaxation studies showing isothermal property kinetics with saturation (which can be used for the identification of the supercooled liquid state) were carried out relatively close to the glass transition region because of experimental limitations (e.g. Ref. [12]). Nonetheless, recent high-precision measurements of the shear modulus in glassy $Pd_{40}Cu_{30}Ni_{10}P_{20}$ allowed determination of the shear modulus G_{eq} in the metastable equilibrium state in a very wide temperature range $(T_g - 185 \text{ K}) \leq T \leq T_g + 13 \text{ K}$, where calorimetric $T_g \approx 560 \text{ K}$ [21]. It was found that the slope $|dG_{eq}/dT|$ of shear modulus temperature dependence decreases by several times (as compared with this slope above T_g) at a temperature, which is by about 40 K below T_g . This temperature T_{pc} separates the regions of the supercooled liquid and glass. Since the metastable equilibrium was reached isothermally, the temperature T_{pc} was attributed to the Kauzmann pseudocritical temperature. We are unaware of any other results showing deviations from the behavior expected by extrapolating thermodynamic properties from above T_g in MGs. For polymer glasses, such deviations are reported [22].

The kinetics of the attainment of the metastable equilibrium below the glass transition is also unclear. The relaxation kinetics is often fitted by phenomenological stretched exponential relaxation (KWW) function [8, 23], which is, however, criticised for producing artifacts and flawed conclusions [24]. Any other approaches for the understanding of the kinetics leading to the metastable equilibrium in MGs seem to be absent. In the case of glass-forming polymers, a study of the enthalpy recovery well below T_g for aging times up to 1 year revealed double-step recovery kinetics at low temperatures [25].

The aforementioned facts determined the motivation for the present

work. We performed high precision measurements of the high-frequency shear modulus well below the glass transition on two typical Zr- and Pd-based glasses. In both cases, we found deviations from the extrapolated supercooled liquid behavior and clear two-step relaxation kinetics below certain temperature, which is considered to be the Kauzmann pseudocritical temperature. Possible reasons for these findings are discussed.

2. Experimental

Typical bulk Zr-based ($Zr_{65}Al_{10}Ni_{10}Cu_{15}$) and Pd-based ($Pd_{40}Cu_{30}Ni_{10}P_{20}$) glasses (at.%) were chosen for the investigation. The samples were prepared by melt suction and melt jet quenching, respectively. The glass transition temperature T_g was determined by differential scanning calorimetry (DSC) using a Hitachi DSC 7020 instrument in flowing N_2 (99.999% pure).

Shear modulus was measured by the electromagnetic acoustic transformation (EMAT) method (see e.g. Ref. [26]) on $5 \times 5 \times 2 \text{ mm}^3$ samples vibrating at transverse resonant frequencies $f = 500 - 600 \text{ kHz}$ (depending on sample's chemical composition and heat treatment). Time/temperature dependence of the shear modulus was calculated as $G(T, t) = G_{RT} \frac{f^2(T, t)}{f_0^2}$, where f_0 and G_{RT} are the initial room-temperature vibration frequency and shear modulus, respectively. The relative error of frequency measurements was about 5 ppm well below T_g and ≈ 100 ppm in the supercooled liquid state. Room-temperature shear moduli G_{RT} were taken to be 30.3 GPa [27] and 33.6 GPa [21] with an error of less than 0.5% for Zr- and Pd-based glasses, respectively. Calculation of G using the above formula ignores possible changes of the density during relaxation, which can be accepted to be about 1% at most. Thus, the absolute error of shear modulus measurements should be estimated as $\leq 1.5\%$.

3. Results

3.1. Zr-based glass

Experiments were performed on four samples designated as S1 to S4

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