

The kinetic glass transition of the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ bulk metallic glass former-supercooled liquids on a long time scale

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Viscosity and enthalpy relaxation from the amorphous state into the supercooled liquid state was investigated in the bulk metallic glass forming $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ alloy below the calorimetric glass transition. At different temperatures, the viscosities relax into states that obey the same Vogel–Fulcher–Tammann relation as the data obtained at higher temperatures in the supercooled liquid. Enthalpy recovery experiments after relaxation in the same temperature range show that the enthalpy of the material reaches values that also corresponds to the supercooled liquid state. The glass relaxes into a metastable supercooled liquid state, if it is observed on a long time scale. Equilibration is possible far below the calorimetric glass transition and very likely even below the isentropic temperature. © 1998 American Institute of Physics. [S0003-6951(98)03221-5]

Undercooling (supercooling) of a liquid below the melting point is associated with a large increase of the viscosity that represents the slowdown of the kinetics in the liquid. When the viscosity reaches a value of the order of 10^{12} Pa s, structural arrest occurs on the time scale of the cooling process. This kinetic glass transition involves sudden changes of the specific heat capacity and the expansion coefficient. Free volume, enthalpy, and entropy are frozen in. A lot of research has been devoted to understand the glass transition^{1,2} in terms of thermodynamics and kinetics.

Up to recently, in metallic systems cooling rates of the order of 10^4 – 10^6 K/s were necessary to form a glass by rapidly quenching the melt.^{3,4} The resulting thin ribbons showed a low thermal stability with respect to crystallization when heated into the glass transition region where the structural relaxation time reaches a value of about 10^2 s. In many of these materials the glass transition cannot even be observed since crystallization sets in at lower temperatures.

Novel multicomponent bulk metallic glass formers^{5–7} exhibit a high resistance with respect to crystallization in their supercooled liquid region and at the glass transition.⁸ In the present study the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ alloy serves as a model system to investigate the relaxation from the amorphous state into the supercooled liquid state. This alloy has one major advantage compared to other bulk metallic glass formers, like the $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$ alloy. It does not show phase separation in the supercooled liquid that leads to a destabilization of the noncrystalline state with respect to primary crystallization of nanocrystals.^{9,10} We will show in this letter that the amorphous alloy relaxes isothermally into a metastable state, in which it behaves thermodynamically and kinetically like a supercooled liquid when observed on a long time scale.

Bulk metallic glasses with a composition of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ were prepared by cooling the melt with a rate of approximately 10 K/s. The viscosity was measured by three-point beam bending with constant heating

rate as well as isothermally.¹¹ Calorimetric measurements were performed in a Perkin Elmer DSC7 and a Setaram DSC 2000 K. In order to calculate the thermodynamic functions in the supercooled liquid, heats of fusion, heats of crystallization, and specific heat capacities, c_p , were determined experimentally, as shown in Ref. 12 for the $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$ alloy. The enthalpy recovery after isothermal annealing below the calorimetrically observed glass transition was measured in experiments with constant heating rate in the DSC.

In Fig. 1 viscosity data on the alloy in a range between 10^6 and 10^{13} Pa s are depicted. This region corresponds to an interval of structural relaxation times between about 10^{-2} and 10^5 s. Beam bending data measured with a constant heating rate of 0.833 K/s (\diamond) and viscosity values after

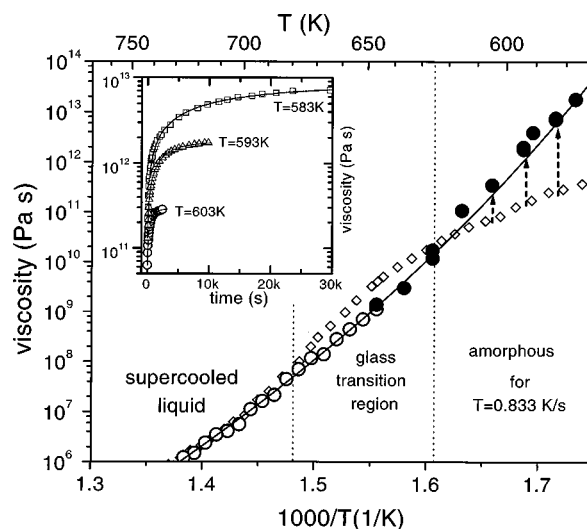


FIG. 1. Viscosity in the glass transition region, measured by beam bending with a constant heating rate (\diamond) and viscosity values after equilibrating the material isothermally (\bullet). The equilibrium data measured by parallel plate rheometry are also shown (\circ).¹³ The solid line corresponds to a Vogel–Fulcher–Tammann fit. The insert shows isothermal relaxation measurements of the viscosity. The data are fitted with a stretched exponential function.

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equilibrating the material in isothermal experiments (●) are plotted. Furthermore, equilibrium viscosity data obtained by parallel plate rheometry (○)¹³ are included. If a sample is heated with a constant rate of 0.833 K/s, the viscosity relaxes into the equilibrium value between 623 and 673 K. This is the same temperature range where the calorimetric glass transition is observed at the same heating rate. Above 673 K the measured viscosity reaches the equilibrium value as measured by parallel plate rheometry (○). For lower temperatures isothermal experiments are used to reach equilibrium. Three examples of the viscosity relaxing into the equilibrium state are shown in the insert in Fig. 1. The pathways of the relaxation are indicated in Fig. 1 by arrows. The solid symbols in Fig. 1 represent the equilibrium viscosities obtained from fitting the relaxation curves with a stretched exponential relaxation function.^{14–16} The viscosities reach values that are an extension of the viscosity data of the supercooled liquid measured at higher temperatures. All equilibrium data can be fitted well with one Vogel–Fulcher–Tammann (VFT) relation

$$\eta = \eta_0 \exp[DT_0/(T - T_0)], \quad (1)$$

with a fragility parameter $D = 22.7$ and a VFT temperature $T_0 = 372$ K. The pre-exponential factor, η_0 , was set as 4×10^{-5} Pa s (see Refs. 14 and 15). The good agreement of all equilibrium viscosity data indicates that the amorphous alloys relax isothermally into the supercooled liquid state with relaxation times that become increasingly longer at lower temperatures. In this sense the measurements shown in the insert in Fig. 1 represent the isothermal glass transition for three different temperatures. The average relaxation time is proportional to the equilibrium viscosity with a proportional constant of 6.8×10^8 Pa.

To investigate the thermodynamics of the alloy on a long time scale, the specimens were first equilibrated above the calorimetric glass transition and cooled with 0.083 K/s in order to assure the same thermal history for all samples. The alloys were then heat treated isothermally at different temperatures. The annealing times were chosen to be ten times the relaxation time that was determined during viscosity relaxation (e.g., 1.2×10^5 s at 583 K). This guarantees that the samples reach states that are very close to metastable equilibrium. After the heat treatment the specimens were first cooled to room temperature with a rate of 3.33 K/s. Subsequently a DSC experiment with a constant heating rate of 0.083 K/s was performed.

Figure 2 shows the results of these enthalpy recovery experiments after annealing at four different temperatures as well as for an unrelaxed sample that was heated above the glass transition and cooled at the same rate (0.083 K/s) prior to the experiment. The annealed samples show a large endothermic heat recovery in the calorimetric glass transition region, whereas the unrelaxed reference sample does not exhibit this effect.

Van den Beukel and co-workers¹⁷ observed enthalpy recovery in metallic glasses previously in the Ni–Pd–P system. They developed a model that describes the functional form of the DSC curves based on free-volume theory. In the present study we use the enthalpy recovery to determine the

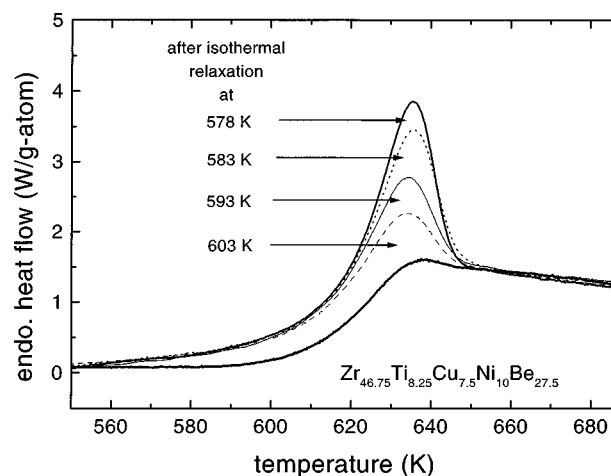


FIG. 2. Enthalpy recovery measurements in the glass transition region after isothermal relaxation from the amorphous into the supercooled liquid state at different temperatures. In addition the measurement for an unrelaxed sample is shown.

change of the enthalpic state of the sample that occurred during the preceding relaxation.

Enthalpy recovery increases with decreasing annealing temperature. The amount of enthalpy that was released during the isothermal heat treatment and that was recovered during reheating the sample, is the area between the curve of the relaxed sample and the unrelaxed material. In Fig. 3 the measured recovered heats are plotted into an enthalpy diagram. The enthalpy, ΔH , of the supercooled liquid in reference to the crystalline state (solid line) was determined independently by DSC measurements.¹²

The enthalpy differences measured during enthalpy recovery are plotted, starting from the enthalpy of the supercooled liquid state in positive ΔH direction. The result is the enthalpy curve (solid circles) of the frozen-in amorphous alloy that was initially formed by cooling all samples with 0.083 K/s. We observe that the enthalpy of the amorphous alloy only increases slightly with temperature. This is due to the small specific heat capacity difference between the crystal and the amorphous alloy (see Fig. 4).

The measured enthalpy change with temperature can be attributed to a finite specific heat capacity difference between

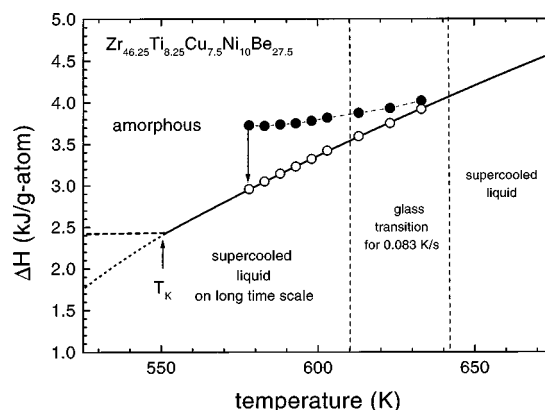


FIG. 3. Enthalpy difference, ΔH , with respect to the crystalline mixture for the supercooled liquid. The enthalpy changes from the frozen-in amorphous state (●) into the supercooled liquid state (○) as recovered with a rate of 0.083 K/s, are added in the diagram. The isentropic temperature, T_K , is marked by an arrow.

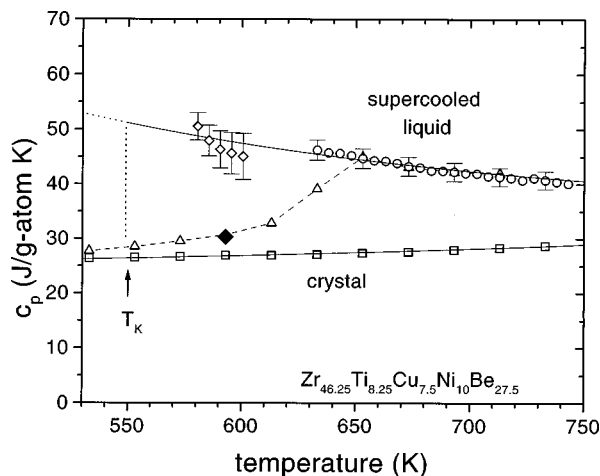


FIG. 4. Specific heat capacity of the supercooled liquid (\circ) measured with constant heating rate. The specific heats of the crystal (\square) the amorphous state (\triangle) where measured in steps in reference to sapphire. The specific heat capacity of the supercooled liquid on a long time scale was obtained from the enthalpy recovery experiments (\diamond). On a short time scale (\blacklozenge) the measured value for the relaxed sample corresponds to that of the amorphous alloy.

the amorphous alloy and the supercooled liquid. This specific heat capacity difference between supercooled liquid (sl) and amorphous (am) state at a temperature $T_1 + (T_2 - T_1)/2$ is calculated as

$$\Delta c_p^{\text{sl-am}} = [\Delta H^{\text{sl-am}}(T_1) - \Delta H^{\text{sl-am}}(T_2)] / (T_2 - T_1), \quad (2)$$

where $\Delta H^{\text{sl-am}}(T_i)$ are the recovered enthalpies after annealing at the temperatures T_1 and T_2 , respectively. The absolute specific heat capacity $c_p^{\text{sl}} = c_p^{\text{am}} + \Delta c_p^{\text{sl-am}}$ of the supercooled liquid on a long time scale (\diamond) is shown in Fig. 4 in comparison with other c_p data of the crystal (\square), the amorphous state (\triangle), and the supercooled liquid at higher temperatures (\circ). The data for the supercooled liquid on a long time scale are in good agreement with the extrapolation of the specific heat capacity data of the supercooled liquid obtained at higher temperatures.

It is important to note that the high c_p in the supercooled liquid at low temperatures cannot be measured in the laboratory directly. A c_p measurement always involves a temperature change. The time to perform this temperature change (seconds) is always much shorter than the enthalpy relaxation time (days) in the studied temperature range. Therefore, the enthalpic state of the alloy will only change by a fraction of what is expected after full relaxation. Thus, the measured c_p only accounts for the amount of enthalpy that relaxed during this time period. In fact, when measured on laboratory time scale, the supercooled liquid exhibits an apparent c_p equal to that of the amorphous alloy (see Fig. 4). If c_p experiments could be performed on a much longer time scale (e.g., geological time scale) the c_p of the supercooled liquid could be measured at lower temperatures directly. In this sense, the observed location of the calorimetric glass transition on the temperature axis is merely a result of our very subjective feeling for time.

It is an interesting question whether one would observe a thermodynamic glass transition at the isentropic (Kauzmann) temperature, T_K , after proper equilibration or whether the amorphous alloy would keep on relaxing into the super-

cooled liquid below the isentropic temperature. The latter case implies that the entropy of the supercooled liquid can become smaller than that of the crystal. This was observed during "inverse melting" in Ti-Cr and related alloys.¹⁸ It was also proposed for the $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ bulk glass former. For this alloy it was shown that thermodynamics and kinetics of the supercooled liquid are only in good agreement if it is assumed that the configurational entropy of the liquid vanishes close to T_0 but not at T_K .¹⁶ It is most likely that this condition also applies to the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ alloy. It is, in principle, possible to investigate if there is a physical meaning to the isentropic temperature, because the relaxation at that temperature would take about 10^8 s (three years), whereas crystallization would take ten times as long according to estimations from the heating rate dependence of the primary crystallization.

In this letter, the relaxation from the amorphous state into the supercooled liquid state was studied below the temperatures where the calorimetric glass transition is observed in a DSC experiment (laboratory time scale). The relaxation of the viscosity and the enthalpy was measured in isothermal experiments and compared with data obtained at higher temperatures where the existence of a metastable supercooled liquid state is out of the question. The comparison suggests that at low temperatures there exists a metastable supercooled liquid on a long time scale. It is most likely that the configurational entropy of the supercooled liquid does not vanish at the isentropic temperature but at a far lower temperature close to the VFT temperature. This means that a metastable equilibrium supercooled liquid can exist even below the isentropic temperature.

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