

The viscosity of the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ bulk metallic glass forming alloy in the supercooled liquid

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The viscosity of the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ bulk metallic glass forming alloy in the supercooled liquid was measured using parallel plate rheometry. The measurements were carried out with different heating rates between 0.0167 and 1.167 K/s as well as isothermally. Because of the high thermal stability above the glass transition of this bulk metallic glass former with respect to crystallization, it was possible to measure viscosities in the range from 10^{10} to 10^6 poise. This region of viscosities has not been previously measured for supercooled metallic melts. Our measurements suggest that the viscosity of the supercooled liquid of this bulk glass former exhibits a small Vogel–Fulcher temperature relative to the glass transition temperature, similar to silicate glasses. © 1995 American Institute of Physics.

Viscosities of metallic supercooled liquids close to the glass transition region have been previously measured, for example by Chen and Turnbull,¹ Tsao and Spaepen,² and Volkert and Spaepen.³ They found a strong temperature dependence of the viscosity which could be fitted well with a Vogel–Fulcher equation.^{1,2} The viscosities were measured not far above the glass transition temperature and the onset of crystallization halted further measurement of the supercooled liquid. The lowest viscosities thus attained were of order 10^{10} poise or larger.

In recent years, metallic glasses were found with a high thermal stability that have a large supercooled region when heated above the glass transition temperature.^{4,5} Their stability enables thermophysical properties, such as specific heat capacity⁶ and diffusion,⁷ to be measured far into the supercooled region. One such bulk glass forming alloy is $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$. We have measured the viscosity in a region from 10^{10} to 10^6 poise that corresponds to 120 K in the supercooled liquid region. We will show that for this bulk metallic glass former, the viscosity above the glass transition does not show a strong viscosity dependence on temperature.

As a metallic glass is heated up through the glass transition region, the viscosity changes dramatically as the alloy relaxes into the metastable equilibrium state of the supercooled liquid.³ To perform equilibrium viscosity measurements in the region of 10^{10} poise or larger in the supercooled liquid region, prior investigators (see, for example, Refs. 1, 2, and 3) reached equilibrium after annealing at a given temperature for a time period that reflects the relaxation time of the liquid. Without annealing for a long enough period of time, the viscosity measurements are made during relaxation in the glass transition region, where the viscosity varies with the characteristic time scale of the experiment. This will be evident in the heating rate dependence of the measured viscosity, or changes in viscosity with time during isothermal measurements.

The high thermal stability of the alloy $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$, in contrast, allows the tempera-

ture to be further increased in the supercooled liquid, here the viscosity decreases with increasing temperature until the onset of crystallization. In this region, after the glass transition and before crystallization, the viscosity drops below 10^{10} poise. For these low viscosities, the relaxation time becomes much smaller than 1 s and allows measurements of the equilibrium viscosity to be done at relatively high heating rates. This enables us to measure viscosities far into the supercooled liquid above the glass transition.

Amorphous $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ alloys were prepared from a mixture of the elements of purity ranging from 99.5% to 99.9% by induction melting and subsequent water quenching in a 6.35-mm-d silica tube. Parallel plate rheometry as described by Stefan⁸ and Diennes and Klemm⁹ was used to study the viscosity of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ as a function of temperature in the supercooled liquid. The experimental apparatus used was a Perkin–Elmer thermal mechanical analyzer (TMA 7) with 3.7-mm-diam quartz penetration probes as parallel plates. Measurements were performed with different heating rates and isothermally. In these experiments, the sample completely filled the area between the plates in a helium flushed atmosphere. By measuring the height of the sample versus time, the viscosity at any temperature is given by the Stefan equation^{8,9}

$$\eta = - \frac{2Fh^3}{3\pi a^4(dh/dt)}, \quad (1)$$

where F is the applied load, a is the radius of the plates (1.85 mm), and h is the height of the sample.

A typical viscosity measurement is shown in Fig. 1. This particular measurement was done with a heating rate of 0.833 K/s, a force of 2.6 N, and an initial height of 0.3 mm. The measured viscosity decreases with increasing temperature from 2.0×10^8 poise at 685 K to 6.0×10^6 poise at 743 K. At this temperature, the supercooled liquid finally begins to crystallize, resulting in a sudden stiffening of the sample. For temperatures smaller than 695 K, the measured viscosities are higher than the equilibrium viscosities. Here, the alloy is still in its glass transition region for the respective

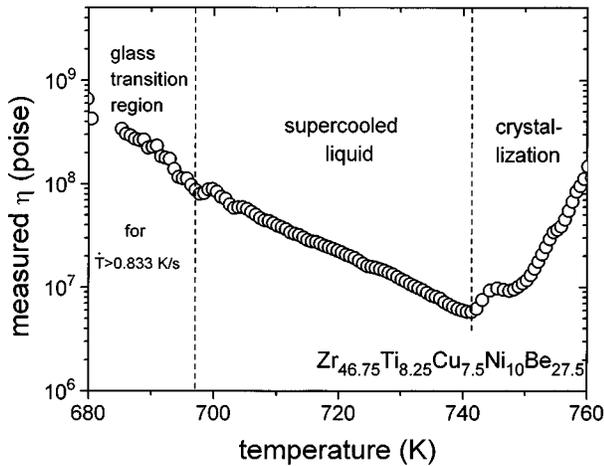


FIG. 1. Measured viscosity in the supercooled liquid for a heating rate of 0.833 K/s.

heating rate, as DSC investigations (not shown) reveal. In this region, smaller heating rates or isothermal measurements must be used to obtain the equilibrium viscosity of the supercooled liquid. By using small heating rates, as low as 0.0167 K/s, which account for larger relaxation times (about 1 s at 10^{10} poise), equilibrium viscosities in the range below 683 K can be measured. On the other hand, large heating rates shift the crystallization to higher temperatures (e.g., up to 763 K at a rate of 1.167 K/s). Thus, the low viscosity range down to 10^6 poise can be measured as well using large heating rates.

Since Eq. (1) was derived by neglecting the velocity normal to the plates, the measured value of the viscosity [i.e., the value calculated according to Eq. (1)] depends on the aspect ratio between the sample height, h , and the radius of the probes, a . Applying results obtained by Gent,¹⁰ the measured viscosity fits a parabolic function:

$$\eta = b + cx^2, \quad (2)$$

where x is the aspect ratio (h/a), and b and c are fitting parameters. This relationship was verified experimentally with isothermal measurements performed using silicone at ambient temperature.¹¹

Viscosity measurements of the glass forming $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ alloy were made with different aspect ratios between 0.15 and 1. Figure 2 shows the measured viscosity as a function of the aspect ratio for the alloy at a temperature of 703 K with different heating rates as well as isothermally. This plot reveals that the measured viscosity does not change with heating rate. For this temperature, the relaxation time to obtain an equilibrium viscosity is smaller than the experimental times for these heating rates. However, there is a considerable dependence of the measured viscosity with aspect ratio. The reason for this dependence is that the velocity component of the liquid normal to the plates can only be neglected for small aspect ratios. The measured viscosity data at each temperature were fitted with the parabolic function (2). The value of viscosity obtained by extrapolating the aspect ratio to zero was taken as the real equilibrium

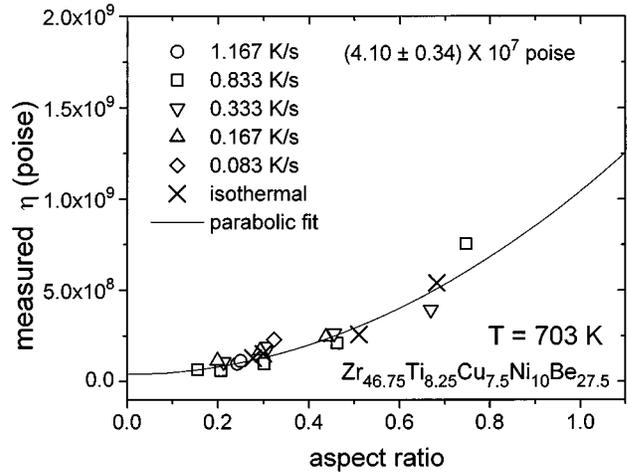


FIG. 2. Measured viscosity as a function of aspect ratio at 703 K for different heating rates and isothermal measurements. The parabolic fit to the data is included.

viscosity value. The measured values of viscosity obtained for aspect ratios smaller than 0.25 correspond to these equilibrium viscosity values within the experimental error.

The viscosity was measured isothermally from 663 to 713 K at 10 K intervals for sample thicknesses in the same range as above. A typical isothermal measurement is shown in Fig. 3 for a temperature of 703 K. Note that, during the first 10 s, the measured viscosity decreases with time. This is not a relaxation effect in the sample. Since the height is decreasing as the measurement proceeds, the aspect ratio approaches the smaller values, and the viscosity follows the functional form of Eq. (2). After taking into account the aspect ratios, the isothermally measured viscosities in the supercooled liquid are in agreement with the values measured using different heating rates (see Fig. 2).

The viscosity of the metastable supercooled liquid as a function of temperature as extracted from the measurements with different heating rates and isothermally is shown in Fig. 4 as an Arrhenius plot. The viscosity data cover about 30% of the whole supercooled liquid region of this alloy between

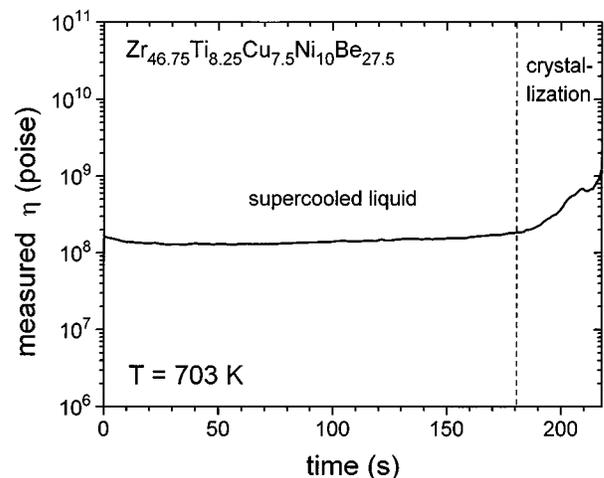


FIG. 3. Measured isothermal viscosity at 703 K.

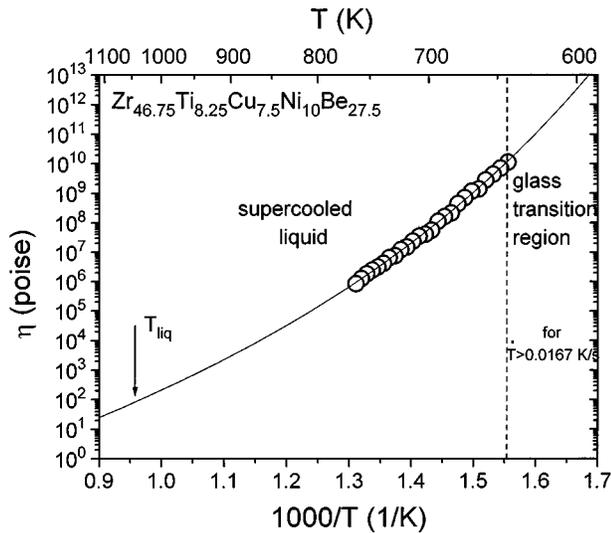


FIG. 4. Equilibrium viscosity as a function of temperature for the undercooled liquid. The precision of the measurement is better than the size of the symbols. Also shown is the Vogel–Fulcher fit to the data.

the glass transition region (for a heating rate smaller than 0.0167 K/s) and the liquidus temperature, $T_{\text{liq}} = 1050$ K. The data were fitted by a Vogel–Fulcher relation:

$$\ln \eta = A + B/T - T_0, \quad (3)$$

where A , B , and T_0 are fitting parameters. The best fit to the viscosity data was found for $T_0 = 352$ K. We find that $A = (-9.0 \pm 2.0)$ and $B = (9.44 \pm 1.64) \times 10^3$ K. With this small Vogel–Fulcher temperature, T_0 , relative to the glass transition temperature, a Vogel–Fulcher relationship yields a viscosity of about 70 poise at the liquidus temperature.

So called “strong” glasses like silicates exhibit Arrhenius behavior, whereas a Vogel–Fulcher relationship best describes the viscosity dependence with temperature for “fragile” glasses like some polymers.¹² In this same region, our alloy shows an intermediate viscosity temperature dependence with a Vogel–Fulcher temperature of about $\frac{1}{2}$ of the glass transition temperature. The “strong” glass behavior of silicates exhibits a large viscosity at the melting point of order one thousand poise. As mentioned above, extrapolating the Vogel–Fulcher fit for the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ alloy to the liquidus temperature, T_{liq} , a viscosity of about 70 poise is found. This value is smaller than for the silicate

glasses because the slope of the viscosity curve and the Vogel–Fulcher temperature, T_0 , are larger for this bulk metallic glass former compared to silicates. The extrapolated melting point viscosity is of the same order as the measured melting point viscosities of some multicomponent metallic melts, such as 69.3 and 61.5 poise for $\text{Pd}_{77.5}\text{Si}_{16.5}\text{Cu}_6$ (Ref. 13) and $\text{Pd}_{82}\text{Si}_{18}$,¹⁴ respectively. However, this is a relatively large value compared to other multicomponent metallic melts, such as $\text{Au}_{77.8}\text{Ge}_{13.8}\text{Si}_{8.4}$ (Ref. 15) and $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$,¹⁴ where viscosities of 0.115 and 0.169 poise, respectively, are found at the melting point. The measurement of the equilibrium melt viscosity and the viscosity in the glass transition region of the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ alloy will be subject to further investigations.

In conclusion, for the first time parallel plate rheometry has been used to measure the viscosity in the supercooled liquid of a metallic glass in the range between 10^6 and 10^{10} poise. The high thermal stability of glass forming $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ allowed measurements far into the metastable supercooled liquid. The viscosity has been measured as a function of temperature over 120 K, which corresponds to about one-third of the entire supercooled liquid region of this alloy. In this range, the viscosity above the glass transition region exhibits a Vogel–Fulcher behavior with a very small T_0 relative to the glass transition temperature. This type of viscosity variation with temperature is intermediate between “strong” and “fragile” glass behavior.

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