Viscous flow of the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ glass forming alloy

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The viscosity of the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ glass forming alloy was determined by beam bending experiments and by a noncontact oscillating drop technique. These viscosity data can be described with the Vogel–Fulcher–Tammann relation. Using the strong/fragile classification of glasses, $Cu_{47}Ti_{34}Zr_{11}Ni_8$ is more fragile than the strong Zr–Ti–Cu–Ni–Be metallic glass formers. © *2000 American Institute of Physics.* [S0021-8979(00)07910-X]

I. INTRODUCTION

A metallic glass was first obtained from the metallic melt by Duwez *et al.* in 1961, using cooling rates on the order of $10^6\,K\,s^{-1}$. In the early 1990s, new metallic glass forming compositions were developed that form glasses with much lower cooling rates, as low as $1\,K\,s^{-1}$ for the best glass forming compositions. These alloys include La–Al–Ni,[1] Zr–Ni–Al–Cu,[2] Mg–Cu–Y,[3] Zr–Ti–Cu–Ni–Be,[4] and Cu–Ti–Zr–Ni.[5] Due to the improved stability against crystallization of these alloys, thermophysical property measurements in the amorphous solid and supercooled liquid that were previously not possible can now be performed.

In this article, we report on a study of the viscosity of the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ glass forming alloy. After measuring the viscosity with beam bending experiments and by a noncontact oscillating drop technique, the data have been described using a Vogel–Fulcher–Tammann (VFT) relation. The temperature dependent viscosity of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ is then compared to other glass formers.

II. EXPERIMENT

An alloy of nominal composition $Cu_{47}Ti_{34}Zr_{11}Ni_8$ was prepared in an arc melter with a titanium gettered, ultrahigh purity argon atmosphere, with elements of purities from 99.9% to 99.9999%. To obtain amorphous samples for the beam bending experiments, pieces of the alloy were remelted in quartz tubes with a radio frequency induction furnace and then injection cast with ultrahigh purity argon into a copper mold with dimensions 8 mm by 4 mm by 1 mm. Beams for the beam bending experiments were made by cutting the 1 mm thick amorphous strip on a diamond saw. The beams had cross sectional areas ranging from 0.25 to 0.8 mm^2.

Viscosity for the amorphous solid and the supercooled liquid was measured by three point beam bending experiments using a thermomechanical analyzer (Perkin–Elmer TMA-7). In these experiments, a constant load was applied to the center of a beam of uniform cross section which was supported on its ends. Heating the sample up (at a heating rate of $100\,K\,s^{-1}$ to 623 K and then at a heating rate of 50 $K\,s^{-1}$ to the desired temperature) and holding it isothermally resulted in a deflection of the center of the beam. Viscosity (in Pa s) at a given temperature is given by the equation[6–8]

$$\eta=\frac{gL^3}{144I_c\nu}\left(M+\frac{5\rho AL}{8}\right), \tag{1}$$

where g is the gravitational constant ($m\,s^{-2}$), L is the support span length (5.08×10^{-3} m for our experiments), I_c is the cross sectional moment of inertia (m^4), ν is the midpoint deflection rate ($m\,s^{-1}$), M is the applied load (kg), ρ is the density of the sample ($kg\,m^{-3}$), and A is the cross sectional area (m^2). Loads ranging from 100 to 900 mN were used in these experiments. This method can be used to measure viscosities ranging from 10^7 to 10^{14} Pa s.

Viscosity measurements in the equilibrium liquid were made for this alloy using a noncontact oscillating drop technique.[9] A noncontact technique offers the advantages of possibly being able to access the undercooled liquid regime and of avoiding contamination of the sample. These measurements were made under microgravity conditions using TEMPUS (Tiegelfreies Elektromagnetisches Prozessieren Unter Schwerelosigkeit, see Ref. 10), an electromagnetic processing facility that flew on board the National Aeronautics and Space Administration's (NASA) space shuttle. By measuring the damping of oscillations of the spherical sample, the viscosity can be determined for the fundamental surface oscillation mode $n=2$ by

$$\eta=\frac{3}{20\pi}\frac{M\Gamma}{R_0}, \tag{2}$$

where M is the sample mass, Γ is the damping constant, and R_0 is the unperturbed sample radius.

III. RESULTS

For the thermomechanical analyzer (TMA) experiments, the samples were annealed until equilibrium was reached. The data can be fit to a stretched exponential relaxation function

$$\eta(t)=\eta_a+\eta_{eq}(1-e^{-(t/\tau)^\beta}), \tag{3}$$

where η_a is the viscosity of the amorphous alloy before relaxation, η_{eq} is the equilibrium viscosity, t is time, τ is the average shear flow relaxation time, and β is a stretching

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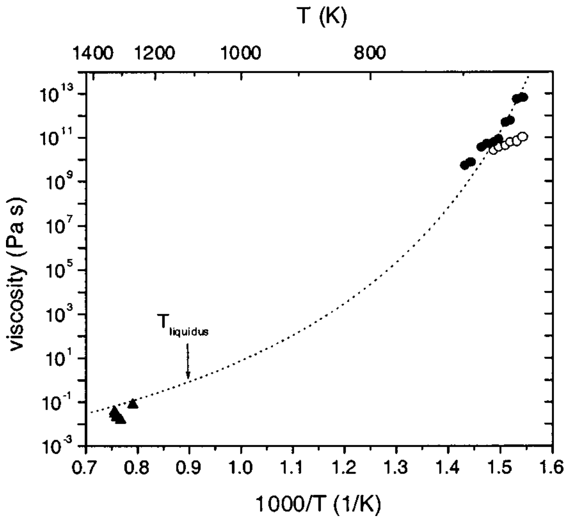

FIG. 1. Arrhenius plot of the viscosity of $Cu_{47}Ti_{34}Zr_{11}Ni_8$. Lower temperature viscosity of the amorphous solid and the supercooled liquid both before reaching equilibrium (○) and after reaching equilibrium (●) were measured with three point beam bending experiments. Higher temperature viscosity was measured with the noncontact oscillating drop technique (▲). The equilibrium data are fit with the VFT relation (dotted line).

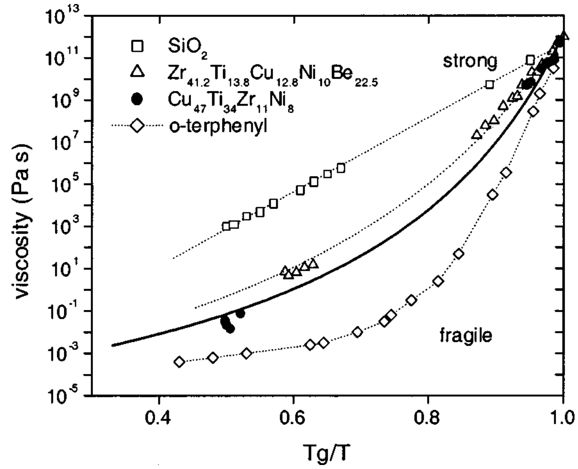

FIG. 2. Arrhenius plot of viscosity data, normalized by the glass transition temperature T_g. T_g is taken to be the temperature at which the viscosity is 10^{12} Pa s, commonly regarded as the viscosity at which a liquid becomes a solid. SiO_2 shows strong liquid behavior while o-terphenyl shows fragile liquid behavior. $Cu_{47}Ti_{34}Zr_{11}Ni_8$ is more fragile than one of the best metallic glass formers, $Zr_{41.2}Ti_{13.8}Cu_{12.8}Ni_{10}Be_{22.5}$. Data for the glass formers in this plot were taken from Ref. 18.

exponent. The equilibrium viscosity, when measured on a long time scale, is equivalent to the viscosity of the supercooled liquid.[11]

The viscosity data for $Cu_{47}Ti_{34}Zr_{11}Ni_8$ are plotted in an Arrhenius plot in Fig. 1. Viscosity could not be measured at higher temperatures with the three point beam bending experiments due to crystallization of the sample. These data can be fit with a Vogel–Fulcher–Tammann (VFT) relation,[12–14] an empirical equation that has been shown to fit the temperature dependence of viscosity for glass forming liquids.[15] The VFT relation, in a modified form,[16] is

$$\eta = \eta_0 \cdot \exp\left(\frac{D^* T_0}{T - T_0}\right), \tag{4}$$

where D^* is the fragility parameter and T_0 is the VFT temperature. η_0 is the high temperature limit of viscosity, determined according to the relationship[17]

$$\eta_0 = h/V_a. \tag{5}$$

In this relation, h is Planck's constant, and V_a is the atomic volume of the liquid. $V_a = M/(N_a \rho)$, where M is the molar mass (60.87 g g atom^{-1}), N_A is Avogadro's number, and ρ is the density of the liquid ($\sim$6 g cm^{-3}). This gives a value for η_0 of 4×10^{-5} Pa s.

A fit of the data with the VFT equation yields $D^* = 12.0$ and $T_0 = 500$ K.

IV. DISCUSSION

As a liquid is cooled below its melting point, if nucleation and growth of crystalline phases is avoided, the viscosity of the liquid increases until the liquid is frozen in a solid form, i.e., a glass. For some liquids, such as silicate glasses, the viscosity of the liquid follows an Arrhenius behavior; these liquids are called ''strong'' liquids. Other liquids, such as organic and ionic glasses, show a non-Arrhenius behavior of viscosity; these liquids are called ''fragile liquids.'' Angell[16] popularized this classification of strong and fragile liquids. When the viscosity data are fit with the VFT relation, strong liquids have fragility parameters of 100, while fragile liquids have fragility parameters as low as 2. The fragility parameter of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ is 12.0. A comparison of strong and fragile glass formers is in Fig. 2, an Arrhenius plot normalized to the glass transition temperature T_g. T_g is taken as the temperature at which the viscosity reaches a value 10^{12} Pa s.

The fragility parameter is also a good indicator of the glass forming ability of the system. Glass forming ability is the ability to avoid nucleation when cooling the liquid from the melt. The larger the fragility parameter, the better the glass forming ability of the liquid. Glasses with large fragility parameters have sluggish kinetics in the supercooled liquid regime, inhibiting crystallization of the liquid. A comparison of the critical cooling rates for glass formation and the fragility parameters of a number of glass formers is given in Table I.

TABLE I. Critical cooling rates and fragility parameters for a number of glass formers. The data were taken from Refs. 18 and 19.

	Critical cooling rate (K s^{-1})	Fragility parameter
SiO_2	7×10^{-4}	100
$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$	<10	22.7
$Zr_{41.2}Ti_{13.8}Cu_{12.8}Ni_{10}Be_{22.5}$	1	18.5
$Pd_{48}Ni_{32}P_{20}$	<10	16.6
$Cu_{47}Ti_{34}Zr_{11}Ni_8$	250	12.0
$Pd_{77.5}Cu_6Si_{16.5}$	500	11.1
$Au_{77.8}Ge_{13.8}Si_{8.4}$	$\sim10^5$	8.4

V. CONCLUSIONS

The viscosity of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ was measured in the amorphous solid, the supercooled liquid, and the equilibrium liquid states. The data are described well using the VFT relation. The fragility parameter, a term in the VFT relation, is a good indicator of the glass forming ability of glass forming liquids.

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[1] A. Inoue, T. Zhang, and T. Masumoto, Mater. Trans., JIM **31**, 425 (1990).
[2] T. Zhang, A. Inoue, and T. Masumoto, Mater. Trans., JIM **32**, 1005 (1991).
[3] A. Inoue, A. Kato, T. Zhang, S. G. Kim, and T. Masumoto, Mater. Trans., JIM **32**, 609 (1991).
[4] A. Peker and W. L. Johnson, Appl. Phys. Lett. **63**, 2342 (1993).
[5] X. H. Lin and W. L. Johnson, J. Appl. Phys. **78**, 6514 (1995).
[6] F. T. Trouon, Proc. R. Soc. London **77**, 426 (1906).
[7] M. Reiner, in *Rheology*, edited by F. R. Eirich (Academic, New York, 1956), Vol. 1, p. 9.
[8] H. E. Hagy, J. Am. Ceram. Soc. **46**, 93 (1963).
[9] I. Egry, J. Non-Cryst. Solids **250**, 63 (1999).
[10] J. Szekely, E. Schwartz, and R. Hyers, JOM **47**, 50 (1995).
[11] R. Busch and W. L. Johnson, Appl. Phys. Lett. **72**, 2695 (1998).
[12] H. Vogel, Phys. Z. **22**, 645 (1921).
[13] G. S. Fulcher, J. Am. Ceram. Soc. **8**, 339 (1925).
[14] G. Tamman and G. Hesse, Z. Anorg. Allg. Chem. **156**, 245 (1926).
[15] L. Battezzati and A. L. Greer, Acta Metall. Mater. **37**, 1791 (1989).
[16] C. A. Angell, Science **267**, 1924 (1995).
[17] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941).
[18] T. A. Waniuk, R. Busch, A. Masuhr, and W. L. Johnson, Acta Mater. **46**, 5229 (1998).
[19] R. Busch, E. Bakke, and W. L. Johnson, Acta Metall. Mater. **46**, 4725 (1998).