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Shear rate dependence of viscosity and configurational entropy of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ metallic glass forming liquid

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Abstract

In this study the viscosity of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ (Vit 1) has been measured as a function of temperature and shear rate above the liquidus temperature, $T_{liq}=1026$ K, using a high temperature Couette Rheometer. It has been discovered that there exists a pronounced decrease in viscosity with increasing shear rate. This is contrary to the general belief that metallic systems above the liquidus temperature should show Newtonian behavior. It has also been discovered that this shear rate dependence of the viscosity decreases with increasing temperature and approaches the Newtonian behavior and viscosities of simple monatomic liquids or binary alloys at approximately 1300 K. These results are discussed in terms of configurational entropy, S_c, by using the Adam–Gibbs entropy model for viscous flow. It is suggested that a large amount of short-range order still exists above the liquidus temperature. At high shear rates this order is destroyed causing the configurational entropy to increase by a magnitude that is on the order of the entropy of fusion.

Keywords: Amorphous materials; Disordered systems; Metals; Heat capacity

1. Introduction

Fragile monatomic and binary simple metallic liquids at the melting point exhibit viscosities of about 10^{-3} Pa s and diffusivities on the order of 10^{-9} $m^2\,s^{-1}$ [1]. By containerless processing or fluxing techniques, these liquids may be supercooled below their melting points, but critical cooling rates are typically 10^7 to 10^9 $K\,s^{-1}$.

Recently, less fragile multicomponent systems have exhibited much higher viscosities at the melting point with critical cooling rates to avoid crystallization on the order of 1 $K\,s^{-1}$. Previous viscosity studies of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ (Vit 1) both above the liquidus temperature, $T_{liq}=1026$ K [11], and in the supercooled region have used a Maxwell model [3] relationship which predicts extremely small relaxation times and high atomic mobility above T_{liq}. It was therefore estimated that the atomic mobility and viscosity above the melting point would be constant with respect to shear. In this study it will be shown that there exists a shear rate dependence of viscosity above T_{liq} through Couette flow viscosity measurements. Results will be discussed in terms of configurational entropy, S_c, using the Adam–Gibbs entropy model for viscous flow.

2. Experimental method

Vit 1 samples were obtained from Liquid Metal Technologies. Viscosity measurements were performed above T_{liq} using a high vacuum rapid annealing furnace equipped with a Couette Viscometer. The rheological properties have been investigated in the viscosity range between 10^{-1} and 10^2 Pa s in a temperature range from 1070 to 1155 K. High purity graphite shear cells were heated inductively in a titanium gettered argon atmosphere. After the sample was molten, a computer controlled rotation was applied to the shear cell, which transmits torque through the testing medium and allows for viscosity measurements [4]. The temperature was measured with a type K thermocouple placed in close proximity to the liquid melt. High temperature calibrations were done using the melting point of Cu, Ag, and Al with spatial temperature variations of ±4 K [4]. Viscosity calibrations were performed using five NIST traceable Newtonian viscosity standards ranging from 9.6×10^{-3} to 102.4 Pa s at 300 K. A wide gap correction factor was applied to the collected viscosity data to take into account the geometry of the shear cell [4–6]. These results are plotted in Fig. 1 as viscosity versus shear rate.

3. Results

The results from this investigation are plotted in Fig. 1 as viscosity versus shear rate and reveal the high viscosity of Vit

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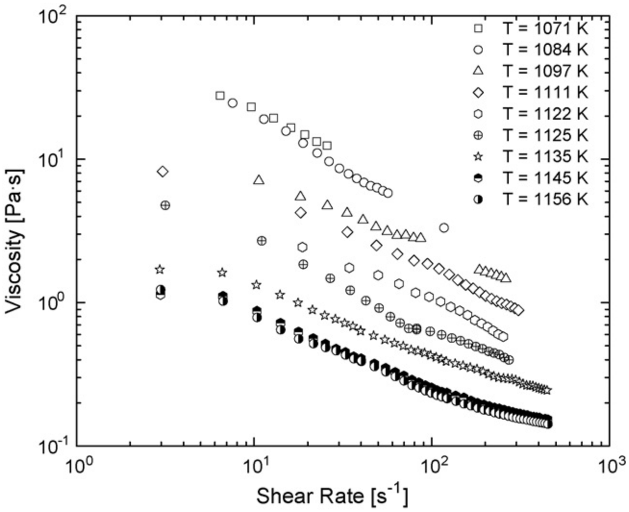

Fig. 1. Viscosity of Vit 1 as measured using a high temperature Couette viscometer with respect to temperatures and shear rates.

1 above $T_{\rm liq}$. This plot shows an order of magnitude decrease in viscosity as the temperature increased from 1071 to 1156 K. In addition, there is a strong shear rate dependence of the viscosity, which decreases by an order of magnitude as the shear rate is increased by two orders of magnitude. This slope is largest at 1071 K and decreases as the temperature is increased to 1156 K. This shear rate dependence of the viscosity must be due to substantial short or medium range order above $T_{\rm liq}$, which is destroyed by the shearing. This order will be described using the change of configurational entropy, $S_{\rm c}$, that is associated with the viscosity change calculated using the Adam–Gibbs entropy model for viscous flow.

3.1. Entropy model

Adam and Gibbs [7] developed a model to describe the viscosity in both liquid and supercooled liquids that is given by

$$\eta = \eta_0 \exp\left[\frac{C}{TS_{\rm c}}\right] \qquad (1)$$

where $\eta_0 = 4 \times 10^{-5}$ Pa s [8] is a pre-exponential factor, $S_{\rm c}$ is the configurational entropy of the system and C represents an effective free enthalpy barrier for cooperative rearrangement. The temperature dependence of $S_{\rm c}$ can be approximated by the difference between the total entropies of the liquid and crystal, ΔS, assuming that the vibrational components of the entropy are comparable for the liquid and the crystal [9]. ΔS can be directly calculated by integrating the measured specific heat capacity difference $\Delta c_p = c_{p,\rm liq} - c_{p,\rm xtl}$ between the liquid, $c_{p,\rm liq}$, and the crystalline mixture, $c_{p,\rm xtl}$. $S_{\rm c}$ is then given by

$$S_{\rm c} = S_{\rm c,liq} - \int_{T_{(S_{\rm c}=0)}}^{T_{\rm liq}} \frac{\Delta c_p}{T'}\,{\rm d}T' \qquad (2)$$

which is equal to ΔS except for an additive constant $S_{\rm c,liq}$, which represents the configurational entropy at the melting point.

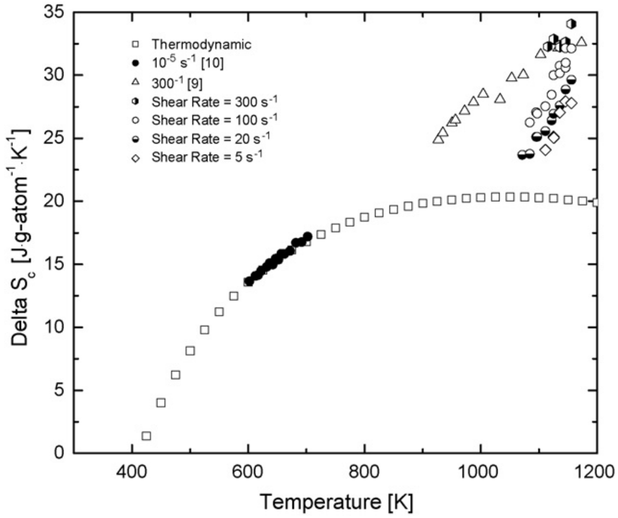

Fig. 2. Configurational entropy calculations of Vit 1 from (□) thermodynamics and by converting, (●) three-point beam bending viscosity measurements [10], (△) previous [9], and current Couette flow viscosity measurements using the Adam–Gibbs entropy model for viscous flow.

The second order polynomial relations:

$$c_{\rm p,xtl} = 3R + aT + bT^2 \qquad (3)$$

and

$$c_{p,\rm liq} = 3R + \beta T + \gamma T^{-2} \qquad (4)$$

were used to describe the heat capacities of the crystal and liquid, respectively, with parameters $R = 8.314$, $a = -9.653 \times 10^{-3}$, $b = 2.321 \times 10^{-5}$, $b = 7.560 \times 10^{-3}$, and $g = 8.167 \times 10^{6}$ in the appropriate units [2].

Fitting Eq. (1) with the functional form of $S_{\rm c}$ to a three point beam bending viscosity study with an estimated shear rate of 10^{-5} s^{-1} [10] yields constants $C = 325.191$ J g atom^{-1} and $S_{\rm c,liq} = 20.3$ J K^{-1} g atom^{-1}. Using these values and rewriting Adam–Gibbs entropy model gives,

$$S_{\rm c} = \frac{C}{T\ln(\eta/\eta_0)} \qquad (5)$$

which relates viscosity and temperature to the configurational entropy of the system with respect to an estimated shear rate of 10^{-5} s^{-1}.

Results from this analysis are shown in Fig. 2, which shows the $S_{\rm c}$ values calculated from the specific heat capacity difference between the supercooled liquid and the crystal and represent the estimated $S_{\rm c}$ at zero shear rate. This is compared to viscosity data collected from three-point beam bending [10] and Couette viscosity measurements that have been converted to $S_{\rm c}$ using Eq. (5).

4. Discussion

4.1. Non-Newtonian behavior

The shear rate dependence of viscosity for rheological fluids can be determined using the power law model [5]:

$$\eta = A\dot{\gamma}^{n-1} \qquad (6)$$

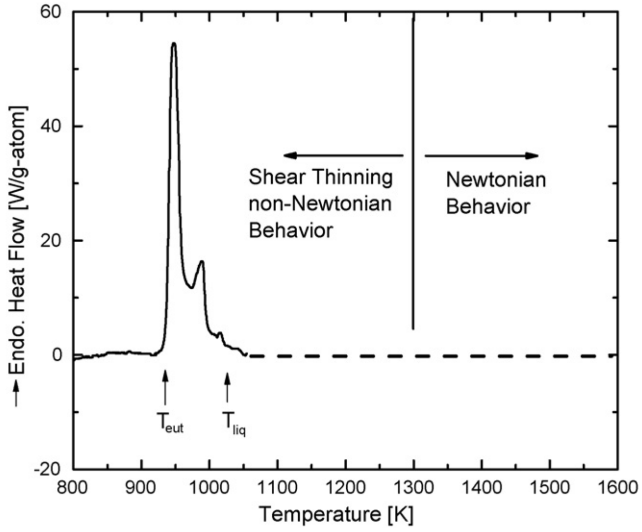

Fig. 3. Graphical depiction of the shear thinning non-Newtonian and Newtonian behavior temperature regions shown in reference to a differential scanning calorimeter analysis [2] indicating the temperature where the endothermic reaction upon melting Vit 1 occurs.

where η and $\dot{\gamma}$ represent viscosity and shear rate, respectively. The shear thinning exponent, n, can be determined by fitting Eq. (6) to the viscosity versus shear rate data plotted in Fig. 1. If this value is less than one, then the fluid's exhibits reducing viscosity with increasing shear rate or non-Newtonian shear thinning behavior. When $n = 1$, the viscosity has no shear rate dependence and exhibits Newtonian behavior. In this study the shear thinning exponent is 0.5 for 1070 K and increases to 0.7 at 1155 K indicating less non-Newtonian behavior with increasing temperature. Further testing at elevated temperatures (not shown) reveal that Vit 1 exhibits Newtonian behavior at 1300 K that is attributed to the complete thermal destruction of the short range order above this temperature. The shear thinning non-Newtonian and Newtonian behavior temperature range is graphically depicted in Fig. 3 and is shown in reference to a differential scanning calorimeter analysis [2] indicating the temperature range where the endothermic reaction upon melting Vit 1 occurs.

4.2. *Shear rate dependence of the configurational entropy*

Fig. 2 shows S_c versus temperature that is calculated from the specific heat capacity difference between the supercooled liquid and the crystal for Vit 1 and represents the zero shear rate S_c. Also shown are S_c deduced for the three point beam bending viscosity measurements [10], previous [9], and current Couette flow viscosity measurements that have been converted using Eq. (5). This shows that the three-point beam bending viscosity study is in close agreement with the thermodynamic calculated zero shear rate S_c. A previous rheological study using high shear rate viscosity measurements show a much higher S_c at elevated temperatures than is predicted by the zero shear S_c. This is thought to represent the upper limit of S_c [9] at 300 s^{-1}. The current study agrees with this elevated S_c using the same shear rate. In addition it shows that the S_c of the liquid decreases closer to values calculated from the zero shear rate S_c as the testing shear rate is decreased. This suggests that there is retained short-range order after melting that can be destroyed by shearing. At T_{liq} the amount of order that is destroyed by shearing at 300 s^{-1} is 8.2 J g atom^{-1} K^{-1}, which is on the order of the entropy of fusion [2] and further indicates that there is substantial short range order above T_{liq}.

4.3. *Configurational entropy and the entropy of fusion*

The documented value of S_{liq} for Vit 1 is 8.38 J g atom^{-1} K^{-1} [11], which is less than half the value obtained by fitting Eq. (5) to the three point beam bending viscosity study [10]. This smaller value can be attained by integrating the specific heat capacity difference between the liquid and crystal from the Kauzmann temperature, $T_K = 560$ K [2] to T_{liq}. It has been suggested that it is possible for the supercooled liquid to have a lower configurational entropy than the crystal [12] and therefore allowing the lower integrating limit for the specific heat capacity difference to be closer to T_0. T_0 is defined as the temperature at which the energy barrier for viscous flow becomes infinite [11]. If it is assume that this temperature also coincides with the point when S_c goes to zero, then the lower integration limit is calculated to be 413.3 K. This is graphically depicted in Fig. 2 as the temperature where the calculated thermodynamic $S_c = 0$. This is in close agreement with the documented Vogel–Fulcher–Tammann (VFT) fit of the same three point beam bending viscosity study [10] which gives $T_0 = 412.5$ K [13].

5. Conclusion

This study has shown that there exists a very strong shear rate dependence of viscosity and S_c for Vit 1 above T_{liq} which is attributed to the destruction of a substantial amount of retained short range order. Increasing temperature decreases this non-Newtonian behavior until viscosity and relaxation times become more like simple monatomic liquids or binary alloys at 1300 K. It is also seen through entropy calculations using the Adam–Gibbs entropy model for viscous flow that this apparent structural ordering is destroyed by shearing and comes closer to the zero shear rate configurational entropy as the shear rate is decreased.

Acknowledgments

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References

[1] T. Iida, R.I.L. Guthrei, The Physical Properties of Liquid Metals, Clarendon, Oxford, 1988.
[2] R. Busch, Y.J. Kim, W.L. Johnson, J. Appl. Phys. 77 (8) (1995) 4039.
[3] A. Masuhr, T.A. Waniuk, R. Busch, W.L. Johnson, Phys. Rev. Lett. 82 (1999) 2290.
[4] T. Shaw, C. Way, R. Busch, Mater. Res. Soc. Symp. Proc. 806 (2004) 215–220.

[5] H.A. Barnes, J.F. Hutton, K. Walters, An Introduction to Rheology, Elsevier Science B.V., 1989.
[6] I.M. Krieger, S.H. Maron, Appl. Phys. 25 (1954) 72–75.
[7] G. Adam, J.H. Gibbs, J. Chem. Phys. 43 (1965) 139.
[8] S.V. Nemilov, Glass Physics and Chemistry 21 (1995) 91–96.
[9] A. Masuhr, R. Busch, W.L. Johnson, J. Non-Cryst. Solids 250–252 (1999) 566–571.
[10] T.A. Waniuk, R. Busch, A. Masuhr, W.L. Johnson, Act. Mater. 46 (15) (1998) 5229–5236.
[11] A. Masuhr, R. Busch, W.L. Johnson, Mater. Sci. Forum 269–272 (1998) 779–784.
[12] R. Busch, W. Liu, W.L. Johnson, J. Appl. Phys. 83 (8) (1998) 4134.
[13] R. Busch, A. Masuhr, E. Bakke, W.L. Johnson, Mater. Sci. Forum. 267–272 (1998) 547–552.