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Viscous behaviour and glass formation in $Fe_{78}B_{13}Si_9$ amorphous alloy

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Using a rotational viscometer, the viscosity of molten $Fe_{78}B_{13}Si_9$ alloy was measured over the temperature range 1165–1350 °C. The temperature dependence of the viscosity of liquid alloy is adequately described by the Arrhenius equation. However, this expression cannot be directly extended to the undercooled liquid temperature region. In this paper a proper equation derived from the free volume theory is proposed to describe the viscosity–temperature behaviour of $Fe_{78}B_{13}Si_9$ alloy in the temperature range of the undercooled liquid and above its melting point. Furthermore, the isothermal time–temperature–transformation curve for crystallization is constructed based on the assumption of homogeneous nucleation and crystal growth, together with the temperature dependence of the viscosity. The critical cooling rate required to form a glass of $Fe_{78}B_{13}Si_9$ alloy was calculated to be approximately 10^5 °C s^{-1}.

1. Introduction

Amorphous alloys obtained by rapid quenching from melt are useful in many potential applications. According to the Cohen and Turnbull model [1, 2] all liquids would become glasses if they were sufficiently undercooled by quenching very rapidly. However, the critical cooling rates for glass formation range from 10^{-4} °C s^{-1} for silicate glasses to 10^{10} °C s^{-1} for pure metals [3, 4]. Considering the kinetic mechanism of homogeneous nucleation and crystal growth, the viscosity in the undercooled liquid region between the melting point and the glass transition temperature is one of the important dominant factors used to calculate the critical cooling rate. Unfortunately, such data are generally inaccessible to experimental measurement in metallic glasses, due to the intervention of crystallization. An indirect determination of the undercooled liquid viscosity from thermal measurements has been made by Chen [5]. It is assumed that the apparent activation energies for the glass transition and crystallization are seen to coincide with those for the viscous flow. However, the temperature dependence of the viscosity needs to be shifted by multiplying by a proper constant from the experimental data.

In this paper the viscosity of molten $Fe_{78}B_{13}Si_9$ alloy above the melting point was measured by using a rotational viscometer. Using these data attempts are made to extrapolate to the higher-viscosity region of the undercooled liquid according to various types of approaches, and a single expression with one set of constants can be provided to describe adequately the viscosity–temperature behaviour of $Fe_{78}B_{13}Si_9$ amorphous alloy in the region of the undercooled liquid temperature and above its melting point. The results are further used to calculate and compare the critical cooling rate for glass formation.

2. Experimental procedure

A high-temperature viscosity-measuring system was set up as shown schematically in Fig. 1. A crucible furnace with molybdenum disilicide heating elements was used. A Haake rotational viscometer was used for the viscosity measurements.

According to Newton's law of viscosity the shear stress, τ, plotted versus the shear rate, D, should yield a straight line, the viscosity, η, being defined as [6, 7]

$$\eta = \tau/D \qquad (1)$$

When a spindle rotates in a crucible filled with liquid, the shear rate at the spindle surface is proportional to the rotating speed of the spindle, and the shear stress is proportional to the mechanical torque on the spindle [7, 8], which is determined by a torque sensor and transformed into an indicatory signal on a linear scale. In other words, at a fixed rotating speed η has a linear relationship with the indicatory signal being displayed on the indicating instrument of the viscometer. The instrument was calibrated with standard fluids of known viscosity of 1.0, 4.8, 48.3 and 96.5 cP (mPa s). The shear stress reading on the instrument display was converted to a viscosity value by this calibration method.

The rotational spindle was made of graphite, coated with alumina by the plasma spraying method to prevent the graphite from dissolution. An alumina crucible filled with 700 g $Fe_{78}B_{13}Si_9$ alloy was heated to 1400 °C in a vertical furnace with an argon atmosphere to protect the alloy from oxidation. The spindle

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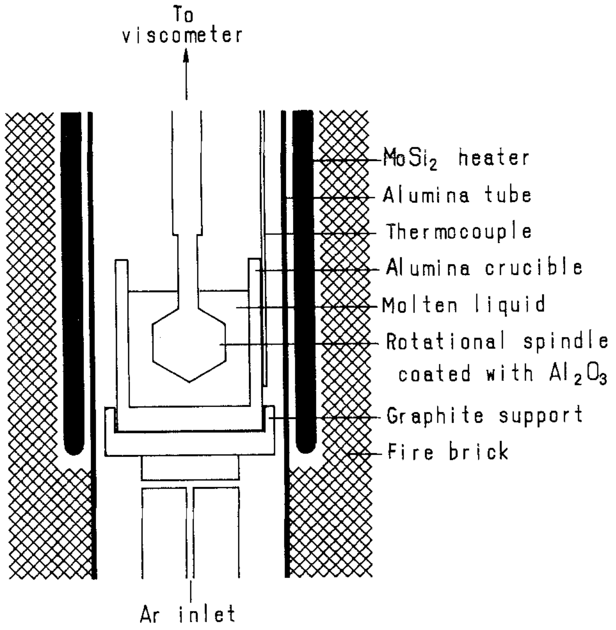

Figure 1 Schematic diagram of the high-temperature viscosity measuring apparatus.

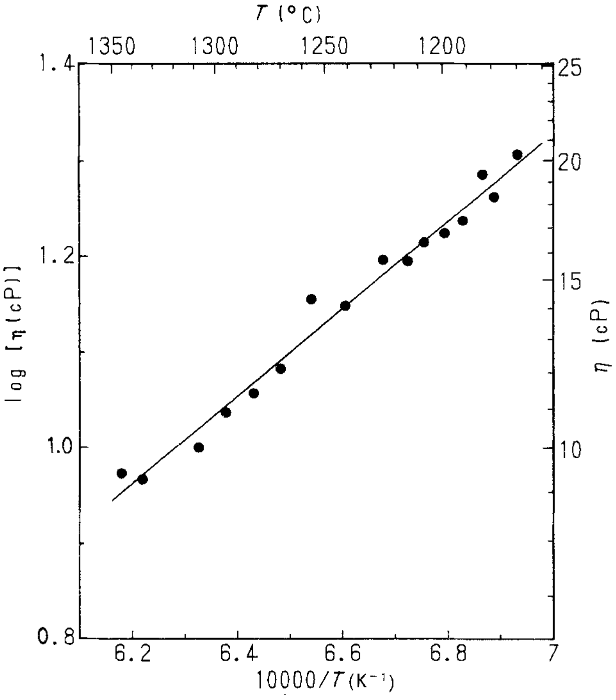

Figure 2 Plot of log(viscosity) versus reciprocal temperature for molten $Fe_{78}B_{13}Si_9$ alloy.

was slowly lowered into the melt. When the temperature of the spindle bob approached that of the melt, the bob was immersed into the melt about 5 mm below the liquid surface. The spindle was started rotating at a constant speed to obtain a thermal equilibrium. Then the melt was cooled slowly (at 5 °C min^{-1}). The data of temperature signal from the R-type thermocouple and the viscosity value from the calibration method were collected and analysed simultaneously by an IBM PS2 personal computer.

In order to calculate the critical cooling rate for glass formation, the molar heat of fusion and the melting temperature of the alloy were measured by a Setaram TGA24 thermoanalyser.

3. Results and discussion

The viscosity of liquid metals and alloys decreases with increasing temperature. The relationship between temperature and viscosity generally follows the Arrhenius equation [6]

$$\eta = \eta_0 \exp(E/RT) \qquad (2)$$

where η is the viscosity, T is the absolute temperature, R is the universal gas constant, E is the activation energy of viscosity and η_0 is a constant.

From the Haake rotational viscometer measurements, the viscosity data for molten $Fe_{78}B_{13}Si_9$ alloy in the temperature range 1165–1350 °C are plotted as log η versus 10 000/T and a straight line was obtained, as shown in Fig. 2. From this result the temperature dependence of the viscosity of $Fe_{78}B_{13}Si_9$ alloy above its melting point is given by

$$\eta = 0.0135 \exp(10\,521.5/T) \qquad (3)$$

where the viscosity is in cP. The viscosity of molten $Fe_{78}B_{13}Si_9$ alloy near its melting point is higher than that of most liquid iron-base alloys, but they are about the same order of magnitude.

When the temperature range is extended to the undercooled liquid region, direct measurement of the viscosity of this metastable phase is difficult because crystallization quickly intervenes. If the viscosity of the undercooled liquid followed the same trend as the Arrhenius equation of the form of Equation 3, the viscosity curve over the entire temperature range would be as shown in Fig. 3. It can be seen that the undercooled liquid viscosity seems to be several orders of magnitude too low because the viscosity should increase very rapidly with falling temperature below the melting point. The value 10^{13} P is traditionally taken in the vicinity of the glass transition temperature [4].

Another estimate of the temperature dependence of the undercooled liquid viscosity is obtained by fitting the Arrhenius equation to 10^{13} P at the glass transition temperature (550 °C) and the experimental data at the melting temperature. This yields

$$\eta = 1.0682 \times 10^{-17} \exp(60\,586.6/T) \qquad (4)$$

which is also plotted in Fig. 3. This curve is likely to be a good estimate of the viscosity near the glass transition temperature. However, it cannot fit the viscosity data of melt above its melting temperature.

From the above discussion it seems clear that the Arrhenius relationship with one set of constants (Equation 3 or 4) cannot provide a good description of the viscosity behaviour over the entire temperature range. Therefore, this paper attempts to introduce the free volume theory to describe the viscosity behaviour of metallic glasses.

According to the concept of free volume, Doolittle [9] described the viscosity in the high-fluidity region

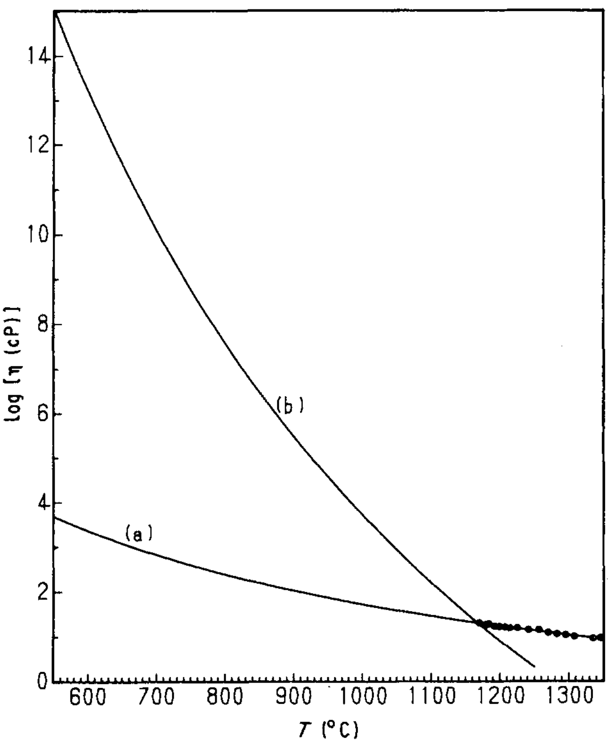

Figure 3 Temperature dependence of viscosity of $Fe_{78}B_{13}Si_9$ alloy using the Arrhenius relationship: (a) extrapolation from the observed data above the melting point (Equation 3) and (b) fitting the observed data at the melting point and assuming 10^{13} P at the glass transition temperature (Equation 4).

by an exponential expression of the form

$$\eta = a \exp(b/f_t) \qquad (5)$$

where a and b are empirical constants and f_t is the relative free volume defined by

$$f_t = (V_t - V_0)/V_0 \qquad (6)$$

where V_t is the volume of material at temperature T and V_0 is the van der Waals volume at which the atoms are closely packed and cease moving.

If the relative free volume varies linearly with temperature, and assuming that f_t is close to zero at temperature T_0, the relative free volume can then be expressed as

$$f_t = \Delta_\alpha (T - T_0) \qquad (7)$$

where Δ_α is the difference between the thermal expansion coefficients of liquid and glass. Upon substitution of Equation 7 into Equation 5, the viscosity is given by

$$\eta = A \exp[B/(T - T_0)] \qquad (8)$$

Equation 8 is equivalent to the well-known form of the empirical Vogel–Fulcher relationship [10] and also similar to the Williams–Landel–Ferry relationship [11].

On the other hand, if the temperature dependence of the relative free volume is a smooth exponential variation [12], the relative free volume can then be expressed as

$$f_t = b' \exp(-C/T) \qquad (9)$$

Upon substitution of Equation 9 into Equation 5, the viscosity is given by

$$\eta = A \exp[B \exp(C/T)] \qquad (10)$$

The temperature dependences of the relative free volume in a linear function (Equation 7) and an exponential function (Equation 9) are shown in Fig. 4. It is interesting to note that a linear temperature function for f_t goes to zero at temperature T_0, whereas an exponential function yields a smoothly decreasing value down to absolute zero. These two distinct functions are used to extrapolate to the undercooled liquid viscosity of $Fe_{78}B_{13}Si_9$ alloy.

From the experimental data for viscosity above its melting point and the assumption that the viscosity at the glass transition temperature is 10^{13} P, a smooth extrapolation is made by using the Gauss–Newton non-linear regression method [13]. According to this procedure the temperature dependence of the viscosity of $Fe_{78}B_{13}Si_9$ alloy over the temperature range 550–1350 °C can be represented by functions of the form of Equation 8 or Equation 10 as

$$\eta = 0.4635 \exp[2607.1/(T - 749.2)] \qquad (11)$$

$$\eta = 2.0156 \exp[0.06414 \exp(5159/T)] \qquad (12)$$

The smooth extrapolation curves are plotted in Fig. 5. It can be seen that the viscosity values calculated from Equations 11 and 12 are almost identical in the temperature range above its melting point. However, there is a difference between these two equations in the temperature range between the melting point and the glass transition point.

The temperature dependences of the viscosity according to the various types of extrapolation (Equations 3, 4, 11 and 12) are used to estimate the

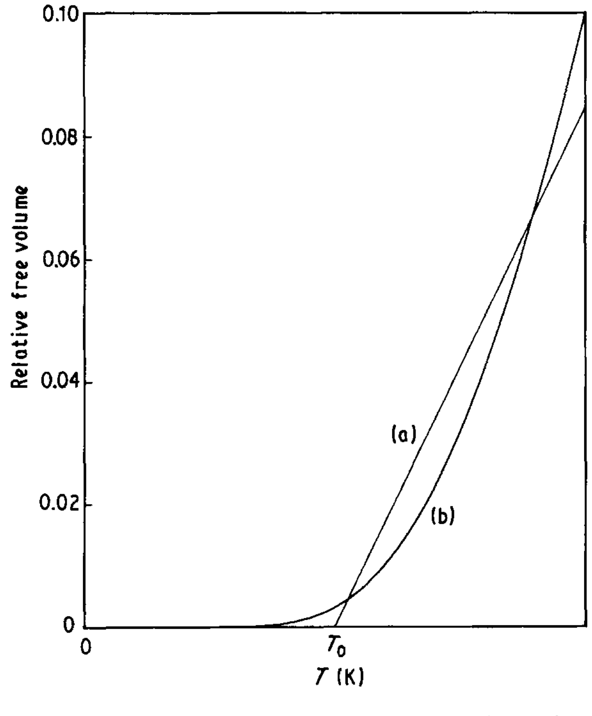

Figure 4 Temperature dependence of relative free volume (f_t): (a) linear variation and $f_t = 0$ at temperature T_0 (Equation 7) and (b) exponential variation and $f_t = 0$ at zero absolute temperature (Equation 9).

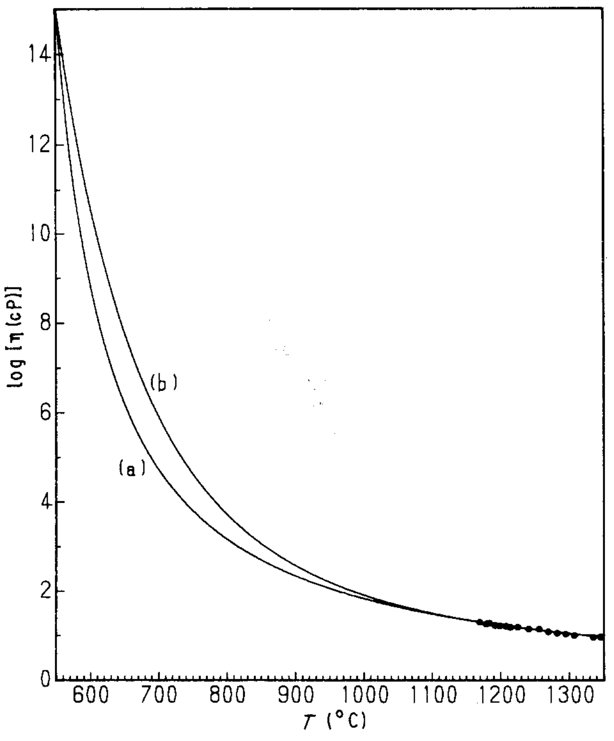

Figure 5 Temperature dependence of viscosity of $Fe_{78}B_{13}Si_9$ alloy based on the concept of the free volume theory: (a) linear variation of f_t (Equation 11) and (b) exponential variation of f_t (Equation 12).

critical cooling rates for glass formation by using the method presented by Uhlmann [3].

Considering the theories of homogeneous nucleation, crystal growth and transformation kinetics, the time t for a small volume fraction X (usually taken as 10^{-6}) crystallization at temperature T can be shown to be [3, 4]

$$t = \frac{9.32\eta}{kT}\left[\frac{a_0^4 X}{f^3 N_0}\frac{\exp(1.024/T_r^3\Delta T_r^2)}{[1-\exp(-\Delta H_f \Delta T_r/RT)]^3}\right]^{1/4} \tag{13}$$

where a_0 is the average atomic diameter, ΔH_f is the molar heat of fusion, N_0 is the number of atoms per unit volume, T_r is the reduced temperature ($= T/T_m$), ΔT_r is the reduced undercooled temperature [$=(T_m - T)/T_m$], f is the fraction of sites on the crystalline interface where atoms may be preferentially added or removed and T_m is the melting temperature.

An isothermal time–temperature–transformation (T–T–T) curve can be constructed from the above equation. The critical cooling rate for glass formation is then taken as

$$R_c = (T_m - T_n)/t_n \tag{14}$$

where T_n and t_n are the temperature and time at the nose of the T–T–T curve, respectively.

Although the kinetic approach has been shown successfully to predict the critical cooling rate, the following assumptions should be considered in Equation 13 [3, 4].

1. The nucleation of crystal from the melt takes place homogeneously.
2. The critical cooling rate is calculated from the T–T–T curve, not from the continuous cooling curve.
3. $f = 0.2\Delta T_r$ for a smooth interface.
4. The Gibbs free energy difference between the liquid and the solid phases is based on the Hoffman approximation.
5. The Gibbs free energy of forming a critical nucleus is $50kT$ at $\Delta T_r = 0.2$.

The effects of changing any one of the above assumptions on the glass formation have been studied by many investigators [14–18]. In the following the possible effect of variations in the temperature dependence of the undercooled liquid viscosity, based on various types of extrapolation, on the calculated critical cooling rate is discussed.

The melting temperature, T_m, and the molar heat of fusion, ΔH_f, of the $Fe_{78}B_{13}Si_9$ alloy were measured to be 1162 °C and 11.49 kJ mol^{-1}, respectively. The resultant T–T–T curves calculated from Equation 13 and using the viscosity values obtained according to Equations 3, 4, 11 and 12 are shown in Fig. 6. The critical cooling rates for $Fe_{78}B_{13}Si_9$ alloy were calculated to be 8.4×10^6 and 28.9 °C s^{-1} from the Arrhenius relationships in the form of Equations 3 and 4, respectively. These values of critical cooling rate are unrealistically high and low, respectively, compared with experimental evidence for iron-base amorphous alloys [19]. On the other hand, the free volume relationships of the form of Equations 11 and 12 lead to critical cooling rates of 4.27×10^5 and 1.12×10^5 °C s^{-1}, respectively. Although the two T–T–T curves differ appreciably in Fig. 6, these values are regarded as more realistic and the difference is less than half an order of magnitude. These results also suggest that the expressions for the temperature dependence of viscosity derived from the free volume

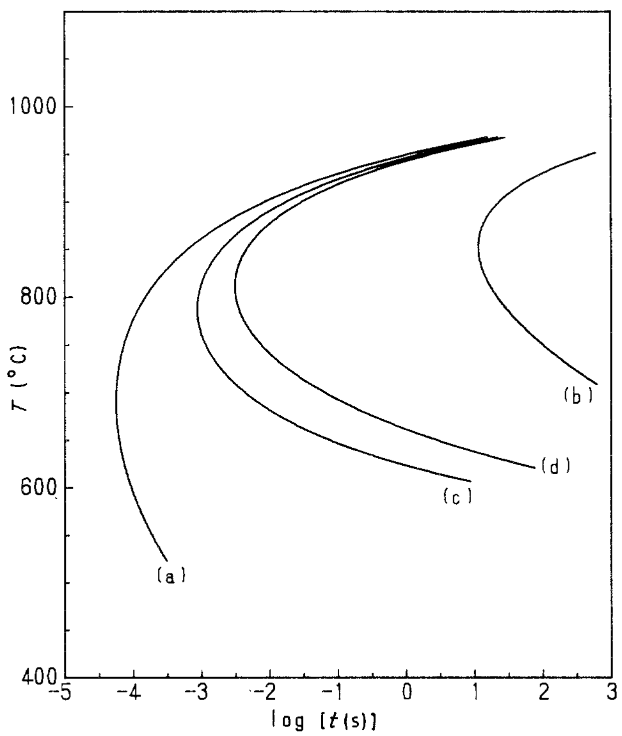

Figure 6 T–T–T curves for $Fe_{78}B_{13}Si_9$ alloy according to various extrapolated values of viscosity: (a) Equation 3, (b) Equation 4, (c) Equation 11 and (d) Equation 12.

theory (Equations 11 and 12) can adequately describe the viscous behaviour over the entire temperature range and are useful for calculations of the critical cooling rate for glass formation.

4. Conclusion

The viscosity of molten $Fe_{78}B_{13}Si_9$ alloy in the temperature range 1165–1350 °C was measured by using a rotational viscometer. The temperature dependence of the viscosity of $Fe_{78}B_{13}Si_9$ alloy over the entire temperature range from 550 to 1350 °C can be represented by the equations

$$\eta = 0.4635\exp[2607.1/(T - 749.2)]$$

or

$$\eta = 2.0156\exp[0.06414\exp(5159/T)]$$

which were extrapolated from the liquid viscosity data and based on the derivation of the free volume theory. In addition, the melting temperature and the molar heat of fusion were also measured. Using these results the critical cooling rate of $Fe_{78}B_{13}Si_9$ alloy was calculated to be approximately $10^5\,°C\,s^{-1}$ based on the mechanism of homogeneous nucleation and crystal growth.

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