

Solid-liquid interfacial energy on crystallization in Fe-Si-B alloy glass

YOSHITAKE NISHI, KAORU MIKAGI, FUMIO KANAZAKI

Department of Materials Science, Tokai University, Kitakaname, Hiratsuka, Japan

Isothermal crystallization on ageing is investigated in Fe-10 at% Si-15 at% B alloy glass. Based on homogeneous nucleation theory, the solid-liquid interfacial energy is estimated by use of the nucleation frequency of crystallization. The energy obtained is quite close to that estimated by extending Turnbull's assumption for alloys.

1. Introduction

Solid-liquid interfacial energy is one of the factors controlling the nucleation of a crystal in a liquid. Especially, it is very important in controlling dendrite coarsening, the decrease in melting point and the glass-forming capability. Several attempts have been made to estimate the crystal (solid)-liquid (or glass) interfacial energy [1-9]. Since the metals are not transparent and show high melting points, it is difficult to measure the interfacial energy precisely. Furthermore, no one has determined this energy in a supercooled liquid at extremely low temperatures near the glass-supercooled liquid transition temperature T_g . Thus, the purpose of the present work is to estimate the crystal-supercooled liquid interfacial energy obtained for Fe-Si-B alloy glass during isothermal ageing above T_g . This glass is the one of the most industrially useful amorphous materials [10, 11].

2. Experimental procedure

An alloy of Fe-10 at% Si-15 at% B was prepared from high-purity elemental powder: Fe 99.8 wt% metallic purity, Si 99.99 wt% purity and B 99.8 wt% purity. The powders were compacted under high pressure with a hydraulic press, and induction-melted in an argon-hydrogen atmosphere. Glass plates of this alloy of 0.100 ± 0.01 mm thickness were prepared by liquid quenching [12, 13]. The amount of sample melted in one run was about 0.2 to 0.5 g. The samples were melted at about 1600 K by three infrared furnaces. A piston-anvil type apparatus was constructed to quench the molten alloy in an argon-hydrogen atmosphere. The speed of the piston was about 0.12 m sec^{-1} .

Ageing was performed in a lead bath. The sample piece was rapidly dipped into a molten lead bath at a desired temperature above the glass transition temperature controlled within ± 1.0 K. The rapid heating and cooling rates were about 10^4 and 10^3 K sec^{-1} , respectively [14]. The microstructure change during the isothermal crystallization was monitored by metallographic observations in optical and scanning electron microscopes.

3. Experimental results

The white crystalline particles formed in glass during ageing are shown in Fig. 1. As shown in Fig. 2, the histograms of crystal size are determined by counts on the photographs. Small crystal particles cannot be observed below the minimum critical diameter of crystalline embryos as calculated by nucleation theory [15]. As shown in Fig. 2, the crystal sizes have approximately the same number density except for the large sizes. The low density is deduced to be caused by the experimental error at large sizes. The delay in reaching the ageing temperature and the temperature distribution induce this error.

Transformation kinetics are discussed in terms of the Johnson-Mehl equation [16]:

$$X = 1 - \exp [-(kt)^n] \quad (1)$$

Here X is the volume fraction transformed in time t and is estimated by use of micrographs and thermal analysis on crystallization. k is the kinetic constant and can be obtained from the dependence of X on t . n is the exponent in the transformation kinetics. If the nucleation frequency I_v and the growth rate U are assumed to be constant, the crystallization process is $n = 4$, as measured in the crystallization of



Figure 1 SEM micrograph of Fe-10 at% Si-15 at% B alloy glass aged for 30 sec at 721 K.

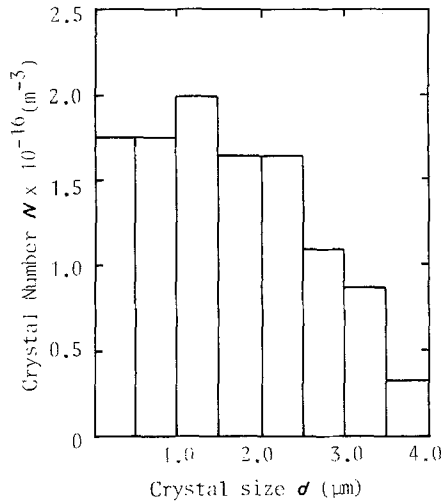


Figure 2 Histogram of crystal sizes in Fe-10 at % Si-15 at % B alloy glass aged for 30 sec at 721 K.

Pd-Cu-Si alloy glass [14]. The k values obtained are listed in Table I and Fig. 3. k is expressed by the following equation [17]:

$$k^4 = 1.047 I_v U^3 \quad (2)$$

U can be obtained using k and the nucleation frequency I_v as in Table I. The growth rate U is listed in Table I together with the experimental I_v values. The linear plots of U are shown in Fig. 3. Since k , I_v and U are usually controlled by atom diffusivity at low temperatures far below the nose temperature of the time-temperature-transformation TTT curve, these factors exhibit Arrhenius temperature dependences as shown in Fig. 3. The apparent activation energies E_a are 211 kJ mol⁻¹ for k , 234 kJ mol⁻¹ for I_v and 201 kJ mol⁻¹ for U , respectively.

4. Discussion

4.1. Homogeneous nucleation theory

For discussing nucleation in glass-forming systems, the following expression has been used for the steady-state nucleation rate [18]:

$$I_v = N_v D a^{-2} \exp\left(-\frac{16\pi\sigma^3}{(\Delta G_v)^2 RT}\right) \quad (3)$$

Here σ is the solid-liquid interfacial energy, N_v is the number of unassociated molecules per unit volume, D

TABLE I Experimental results for nucleation frequency I_v (m⁻³ sec⁻¹), growth rate U (m sec⁻¹) and kinetic constant k (sec⁻¹) during isothermal crystallization above the glass-supercooled liquid transition temperature, solid-liquid interfacial energies (mJ m⁻²) (σ_e , σ_n and σ_m are for experimental value, for non-metallic bonded case and metallic bonded case, respectively) and constants (K' and K'') of Equations 7 and 8 for Fe-10 at % Si-15 at % B alloy glass

Quantity	Temperature (K)				
	681	721	741	761	781
log I_v	15.009	15.562	16.318	16.769	17.262
log U	-7.939	-7.193	-6.446	-6.365	-5.894
log k	-2.197	-1.499	-0.750	-0.577	-0.100
Case 1					
σ_e	173.2	178.2	178.4	179.3	179.8
K'	0.400	0.413	0.414	0.417	0.419
K''	0.189	0.193	0.192	0.192	0.192
σ_n	138.4	138.0	137.8	137.5	137.3
σ_m	194.7	194.0	193.7	193.4	193.1
Case 2					
σ_e	153.7	158.4	158.6	159.6	160.0
K'	0.400	0.413	0.414	0.417	0.418
K''	0.189	0.192	0.192	0.192	0.191
σ_n	123.0	122.8	122.7	122.6	122.5
σ_m	173.0	172.7	172.5	172.4	172.2
Case 3					
σ_e	224.6	231.1	231.3	232.5	233.1
K'	0.293	0.304	0.305	0.305	0.305
K''	0.189	0.193	0.192	0.192	0.192
σ_n	204.3	203.7	203.4	203.0	202.7
σ_m	287.3	286.4	286.0	285.5	285.0
Case 4					
σ_e	199.3	205.4	205.6	206.9	207.5
K'	0.351	0.362	0.363	0.366	0.367
K''	0.189	0.192	0.192	0.192	0.191
σ_n	181.6	181.3	181.1	180.9	180.8
σ_m	255.4	254.9	254.7	254.4	254.2

is the liquid diffusivity for molecular transport across the matrix to nucleus interface, a is the molecular diameter, R is the gas constant, T is the absolute temperature of this transformation and ΔG_v is the difference between the liquid and crystal of the standard Gibbs free energy per unit volume. ΔG_v may be expressed by the following equation for large departures from equilibrium, using the model suggested by Hoffmann [19]:

$$\Delta G_v = \Delta S_f(T_m - T)T/VT_m \quad (4)$$

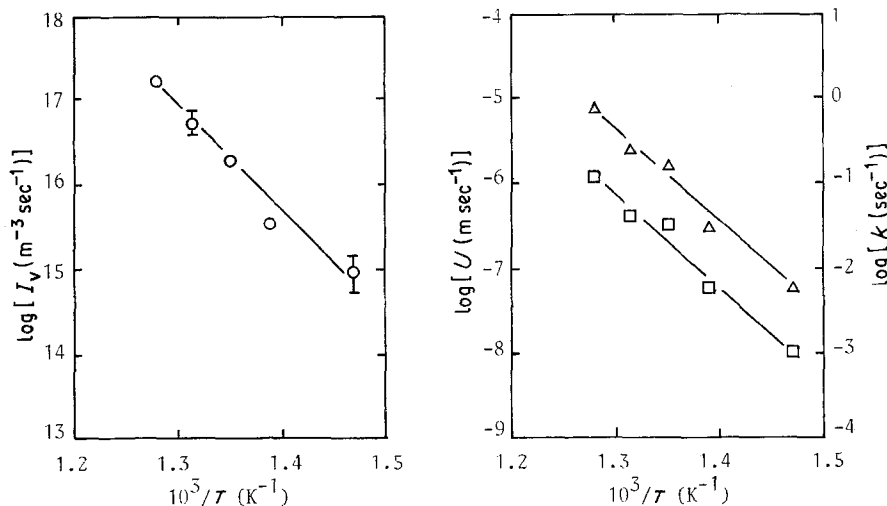


Figure 3 Change in (O) nucleation frequency I_v , (□) growth rate U and (Δ) kinetic constant k with temperature in Fe-10 at % Si-15 at % B alloy glass.

Here ΔS_f is the entropy change on solidification per mole, T_m is the melting point and V is the molar volume. Based on homogeneous nucleation theory, the solid–liquid interfacial energy is estimated by the use of the frequency of nucleation, the melting point, the entropy change on solidification and the supercooled liquid diffusivity (D). For a simple molecular liquid and even for liquid metals, D is inversely related to the viscosity (η) as suggested by Stokes and Einstein [18]. Thus it is important to know the viscosity in the supercooled liquid in which the concentration of solute is the same as that in front of the interface between the crystal and the supercooled liquid.

4.2. Supercooled liquid viscosity

The supercooled liquid viscosity η (Pa sec) is expressed by the equation of Fulcher [20]. η is calculated from the glass transition temperature T_g and the viscosities of the liquid at the melting point T_m and the nose temperature T_n in a calculated TTT curve [12, 13]. T_n is expressed by the phenomenological relation between T_n and T_m [21]

$$T_n = 0.556 T_m + 218 \quad (5)$$

Viscosities in the liquid are estimated from the relation between the critical cooling rate and the viscosities at T_m and T_n [21]. Since the critical cooling rate is $6.40 \times 10^4 \text{ K sec}^{-1}$ in Fe–10 at % Si–15 at % B alloy as measured by the piston–anvil type cooling method [22], the viscosity is about $10^{1.4} \text{ mPa sec}$ at T_m and about $10^{3.0} \text{ mPa sec}$ at T_n , respectively [12, 13].

The viscosity is 10^{13} mPa sec at T_g [23]. However, it is difficult to measure T_g in this alloy. Thus, the temperature dependence of the viscosity is calculated by the use of the growth rate U of the crystallization in Fe–Si–B alloy supercooled liquid, because the temperature dependence of the viscosity has been reported to be in good agreement with the crystal growth rate in Pd–Cu–Si alloys [14]. If the apparent activation energy of the viscosity, which probably exhibits an Arrhenius temperature dependence, the supercooled liquid viscosity η (mPa sec) is expressed by the following equation in Fe–10 at % Si–15 at % B supercooled liquid alloy:

$$\log \eta = -1.135 + 2936/(T - 342.1) \quad (6)$$

4.3. Solid–liquid interfacial energy of Fe–10 at % Si–15 at % B alloy

Since it is assumed that the nucleation rate is steady-state, I_v is estimated from the results with the optical microscope and SEM. These are for samples aged at several temperatures in the initial states of crystallization. The solid–liquid interfacial energy σ_e can be obtained using the nucleation frequency I_v in the Fe–10 at % Si–15 at % B alloy, the melting point ($T_m = 1500 \text{ K}$ [24]), the entropy change on solidification ΔS_f and the liquid molar volume V . We estimate this energy in four cases.

In the first case (Case 1) ΔS_f ($7.63 \text{ kJ mol}^{-1} \text{ K}^{-1}$) and V ($= (\text{atomic weight})M/(\text{extrapolated liquid density})\rho$) of Fe are used [25]. σ_e is $176 \pm 4 \text{ mJ m}^{-2}$ at $731 \pm 50 \text{ K}$ in Fe–10 at % Si–15 at % B alloy (Case 1

in Table I). For calculation in Case 2, use is made of the entropy change of iron and the liquid molar volume which is estimated by liquid density ρ (kg m^{-3} ; $\rho = 7.34 \times 10^{-3}$ to $5 \times 10^{-7} T$) with the temperature T (K), for Fe–2 wt % Si–3.5 wt % C alloy [26] whose properties are deduced to be similar to those of the Fe–10 at % Si–15 at % B alloy, are used. σ_e of Case 2 is then $157 \pm 3 \text{ mJ m}^{-2}$. σ_e is $229 \pm 4 \text{ mJ m}^{-2}$ in Case 3 (V is assumed to be for pure Fe and the value of ΔS_f ($10.63 \text{ J mol}^{-1} \text{ K}^{-1}$) is assumed to be an arithmetic mean of the entropy changes on solidification for pure materials in Case 3. Here ΔS_f are $24.9 \text{ J mol}^{-1} \text{ K}^{-1}$ [27] for silicon and $20.3 \text{ J mol}^{-1} \text{ K}^{-1}$ for boron [28].) In Case 4 (the value of V for the Fe–2 wt % Si–3.5 wt % C alloy and the arithmetic mean of ΔS_f for Fe–10 at % Si–15 at % B alloy are used) σ_e is $203 \pm 4 \text{ mJ m}^{-2}$. The values of σ_e obtained are between 154 and 233 mJ m^{-2} , while the temperature dependence of σ_e is small.

4.4. General expression for the interfacial energy

Several equations for σ , the solid–liquid interfacial energy, have been suggested by the use of various assumptions [6, 7–9]. However, these equations are classified into two types of expression:

$$\sigma = K' \frac{\Delta S_f T_m}{N^{1/3} V^{2/3}} \quad (7)$$

$$\sigma = K'' \left(\frac{\Delta S_f}{V} \right)^{2/3} (T_m + T)^{2/3} T_m^{1/3} \quad (8)$$

Here N is Avogadro's number. K' and K'' are constants which depend on the assumptions made. Equation 7 is applied by Turnbull [6] and Spaepen [7] while Equation 8 is applied to the assumptions of Thompson and Spaepen [8] and Uhlmann's experimental results for SiO_2 [9].

Values of K' in Equation 7 are 0.45 for metallic bonded elements (0.445 for iron, 0.444 for nickel and 0.45 for palladium) and 0.32 for non-metallic bonded elements (0.302 for antimony and 0.33 for bismuth [6]). The arithmetic mean of K' is 0.41 and is equal to the experimental values ($K' = 0.41 \pm 0.01$ of Cases 1 and 2, $K' = 0.36 \pm 0.008$ in Cases 3 and 4). Thus, the experimentally obtained interfacial energy is approximately equal to the energy calculated by the extended Turnbull's assumption for alloys, while the experimental value is far from the K' values for pure metallic ($K' = 0.445$) and non-metallic elements ($K' = 0.32$). The result is concluded that 25 at % addition of metalloid elements translates the bonding state of iron.

It is important to investigate the change in the interfacial energy with the temperature in supercooled liquids. Some notable work has been done in this field [1, 9, 29]. Equation 8 depends on temperature. The value of K'' in Equation 8 is 0.191 ± 0.002 , which is about 0.76 times smaller than that of the Thompson–Spaepen assumption ($K'' = 0.252$) [8]. If this equation is applied to this alloy, increases in σ are found and the increases are $64.2 \pm 12.0 \text{ mJ m}^{-2}$ at the melting point.

Ewing suggests the temperature dependence of the interfacial energy as following the equation [30].

$$\sigma = \sigma_h - \Delta S T \quad (9)$$

σ_h is the enthalpy term of the interfacial energy and ΔS is the entropy change from liquid to crystal. The values obtained show a change ($1.8 \pm 0.2 \text{ mJ m}^{-2}$ between 721 and 781 K, $7.4 \pm 1.1 \text{ mJ m}^{-2}$ between 681 and 781 K) with the ageing temperature. If ΔS is assumed to be 0.012 and $0.74 \text{ mJ m}^{-2} \text{ K}$ in this alloy, increases in σ are by about 13 and 53 mJ m^{-2} at the melting point.

Although these values are not close to the σ values estimated by Equation 8, the temperature dependence of the solid–liquid interfacial energy is found and the energy increases with increases in temperature.

Further experiments to explore this result and other alloy glasses are in progress.

5. Conclusion

Based on homogeneous nucleation theory and the supercooled liquid viscosity, crystal–supercooled liquid interfacial energies are estimated by the use of the nucleation frequency, the viscosity in the supercooled liquid and the melting point of an Fe–10 at % Si–15 at % B alloy. The obtained solid–liquid interfacial energy is found to be quite close to that estimated by the extended Turnbull's assumption for alloys. Considering the Turnbull's and Thompson–Spaepen's assumptions, modified expressions are suggested.

Acknowledgement

The authors would like to thank Professors T. Matsumae, E. Yajima and T. Yokabori of Tokai University for their continuous encouragement.

References

- O. HAIDA and T. EMI, *J. Iron Steel Inst. Jpn* **9** (1977) 1564.
- Y. LIMOGE and A. BARBU, in Proceeding of the 4th International Conference on Rapidly Quenched Metals, edited by T. Masumoto and K. Suzuki (Japan Institute of Metals, Sendai, 1981) p. 739.
- T. OOHASHI and W. A. FISHER, *J. Iron Steel Inst. Jpn* **61** (1975) 3077.
- J. E. HILLIARD and J. W. CHAN, *Acta Metall.* **6** (1958) 772.
- M. E. GLICKSMANN and C. L. VOLD, *ibid.* **17** (1969) 1.
- D. TURNBULL, *J. Appl. Phys.* **21** (1950) 1022.
- F. SPAEPEN, *Acta Metall.* **23** (1975) 729.
- C. V. THOMPSON and F. SPAEPEN, *ibid.* **27** (1979) 1855.
- D. R. UHLMANN, *Mater. Sci. Res.* **4** (1969) 172.
- H. FUJIMORI, H. YOSHIMOTO, T. MASUMOTO and T. MITERA, *J. Appl. Phys.* **52** (1981) 1893.
- H. FUJIMORI, H. YOSHIMOTO and H. MORITA, *IEEE Trans. Magn.* **MAG-16** (1980) 1227.
- Y. NISHI, K. SUZUKI and T. MASUMOTO, in Proceedings of the 4th International Conference on Rapidly Quenched Metals, edited by T. Masumoto and K. Suzuki (Japan Institute of Metals, Sendai, 1981) p. 217.
- Y. NISHI, T. MOROHOSHI, M. KAWAKAMI, K. SUZUKI and T. MASUMOTO, in Proceedings of the 4th International Conference on Rapidly Quenched Metals, edited by T. Masumoto and K. Suzuki (Japan Institute of Metals, Sendai, 1981) p. 111.
- Y. NISHI, Y. MIYAGAWA, K. SUZUKI and T. MASUMOTO, in Proceedings of the 4th International Conference on Rapidly Quenched Metals, edited by T. Masumoto and K. Suzuki (Japan Institute of Metals, Sendai, 1981) p. 735.
- D. R. UHLMANN, J. F. HAYS and D. TURNBULL, *Phys. Chem. Glasses* **7** (1966) 159.
- W. A. JOHNSON and R. F. MEHL, *Trans. AIME.* **35** (1939) 416.
- J. BURKE, "Introduction to kinetics of phase transformation", translated by K. Hirano and H. Hori (Maruzen, Japan, 1972) p. 190.
- D. R. UHLMANN, *J. Non-Cryst. Solids* **7** (1972) 337.
- J. D. HOFFMANN, *J. Chem. Phys.* **29** (1958) 1192.
- G. S. FULCHER, *J. Amer. Ceram. Soc.* **8** (1925) 339.
- Y. NISHI, EnD thesis, Tohoku University (1984).
- Y. NISHI, M. TACHI and T. KAI, unpublished data (1986).
- H. S. CHEN and D. TURNBULL, *J. Chem. Phys.* **17** (1969) 7.
- M. HANSEN, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958) p. 250.
- S. NAGASAKI, "Metals data book" (Japan Institute of Metals, 1974) p. 57.
- E. S. FILIPPOV and A. M. SAMARIN, "Fiziko-Khimicheskie Osnovy Proizvodstvba Stali" (Nauka, Moskva, 1968) p. 3-3.
- J. CHIPMAN, *Trans. Amer. Soc. Metals* **22** (1934) 385.
- D. Sh. TSAGAREISHVILI and G. V. TSAGAREISHVILI, *J. Less-Common Metals* **67** (1979) 541.
- A. S. SKAPSKI, *Acta Metall.* **4** (1975) 576.
- R. H. EWING, *J. Cryst. Growth.* **11** (1971) 221.

Received 25 November
and accepted 4 December 1985