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Solid–liquid interfacial energy of non-metallic bonded elements

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Based on homogeneous nucleation theory, the temperature dependence of the nucleation frequency for crystallization is calculated for a supercooled liquid. Here the solid–liquid interfacial energy of an alloy is estimated by means of an extension of Turnbull's assumption. Equations are suggested which correlate the energy with the ionization energy and the entropy of fusion for non-metallic bonded elements.

1. Introduction

If a liquid is supercooled sufficiently, it should be solidified in the glassy state [1]. From the engineering point of view, it is very important to know the glass-forming capability of various metals and alloys. Several attempts have been made to obtain the critical cooling rate for glass formation [2–6]. Considering the kinetic treatment of the nucleation and growth of crystallization, we have pointed out that the glass-forming capability is determined by the viscosity, melting point and entropy change of solidification. The solid–liquid interfacial energy has been known to be one of the most sensitive factors controlling the nucleation of a crystal in a liquid [7]. Since it is difficult to measure this energy, the effects of the energy on glass-forming capability cannot be easily discussed. Several attempts have been made to estimate the crystal (solid)–liquid (or glass) interfacial energy [8, 9]. However, no one has determined this energy at extremely low temperatures near the glass–supercooled liquid transition temperature. Based on nucleation theory, we have recently calculated these energies for several glassy alloys [10, 11]. With these results, we have started the present study to estimate the solid–liquid interfacial energies of non-metallic bonded elements and the solid–liquid interfacial energy for alloys.

2. Extension of Turnbull's assumption

Turnbull [12] suggested the following equation for the interfacial energy Q:

$$Q = K\Delta H_f / N^{1/3} V^{2/3} \tag{1}$$

Here ΔH_f is the enthalpy change per mole on solidification, N is Avogadro's number of K is a constant. K is 0.45 for metallic bonded elements and 0.32 for non-metallic elements [12]. The solid–liquid interfacial energy can be obtained by means of an extension of the Turnbull's assumption. For alloys the values (K_e) of K obtained by experiment is between the values for metallic and non-metallic elements [12]. K may be affected by structures and atomic interactions in the crystal on liquid. If these effects are negligible, the value of K is expressed by a summation over the elemental components of the alloys:

$$K_e = \sum_{i=1} N_i K_i \tag{2}$$

Here K_i and N_i are the K value and the mole fractions of pure elements, respectively. K_e is summarized in Table I. The weaker the metallic bonding, the lower K_e becomes [12].

3. Solid–liquid interfacial energy of non-metallic bonded elements

3.1. Ionization energy

Besides the atom site and the phonon energy, an electron state varies on crystallization. The density of free electrons in molecular liquids is higher than that in the solid for most of the non-metallic bonded elements [13]. Since melting converts a few bonded electrons to free electrons in the non-metallic elements, the ionization energy E_i is suggested to be a useful tool: the larger E_i, the lower K_e may become for non-metallic bonded elements. Fig. 1 shows the linear change in K_e [12] with E_i [14]. Thus, we suggest a phenomenological equation correlated with the ionization energy (where E_i is in kJ mol^{-1}):

$$\log K_0 = \frac{10^{-3}}{2} E_i - 0.08 \tag{3}$$

The K value for phosphorus is estimated by means of our results [11] and is approximately plotted on the line in Fig. 1 expressed by Equation 3. The value for boron lies on the plot for Equation 3, though boron is not an element with a tetrahedral structure. Thus, since the boron is a semi-conducting element, Equation 3 seems to be strongly dominated by the electron state.

3.2. Entropy change of fusion

On the other hand, the entropy change ΔS_f for fusion is a possible scaling parameter. Figs 2 and 3 show plotted against ΔS_f [14] and $\Delta S_f^{2/3}$, respectively. The solid line is for covalent bonded elements of Groups IV and V, while the dotted line is for Group III elements. K_e for Group III elements is expressed by the

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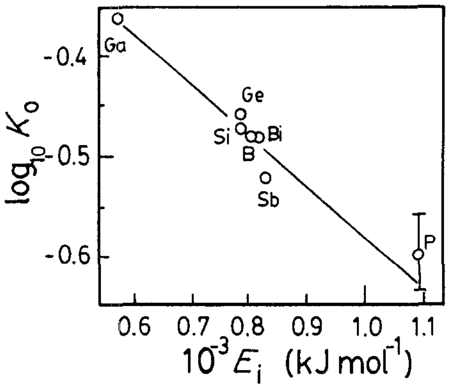

Figure 1 Change in logarithmic constant K_0 with ionization energy E_i of non-metallic bonded elements. Solid line is $\log K_0 = -(10^3/2)E_i - 0.08$.

following equations:

$$K' = 11.7\Delta S_f + 0.222 \qquad (4)$$

$$K'' = 4.17\Delta S_f^{2/3} + 0.146 \qquad (5)$$

The correlation coefficients (f) of these changes are 0.992 and 0.996. For covalent bonded elements in Groups IV and V, K_e is expressed by the equations

$$K' = 3.08\Delta S_f + 0.251 \qquad (6)$$

$$K'' = 1.03\Delta S_f^{2/3} + 0.240 \qquad (7)$$

The f values are 0.884 and 0.891. The entropy change of fusion is mainly dominated by the change in the phonons. The larger the change in the phonons, the larger Q and K_e become. Since the heavy elements show large entropy changes and high K_e values, a large change of atom vibration is deduced for the heavy elements. K_e for Group III elements strongly depends on ΔS_f, while K_e for Groups IV and V slightly changes with ΔS_f. The electrical resistivity increases for Group III and decreases for Groups IV and V on melting [13]. Thus, K_e is mainly dominated by a change in the atom vibration for Group III elements, while K_e for the covalent bonded elements in Groups IV and V is dominated by the change in the density of free electrons at the melting point. Since the influence of atom vibration on K_e is probably small for boron (see Fig. 2), the value of K is approximately equal to those of the covalent elements in Groups IV and V.

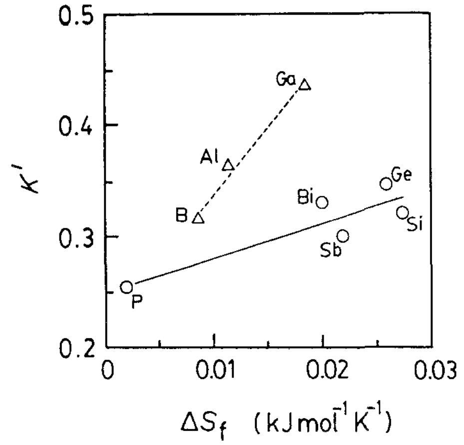

Figure 2 Change in logarithmic constant K' with entropy change of fusion ΔS_f. Solid line is for Group IV and V elements. Dotted line is for Group III elements.

3.3. Calculation method

Although it is difficult to obtain K_e for the non-metallic bonded elements, it is easy to estimate K_0, K' and K'' by the use of Equations 3 to 7. They are summarized in Table I. K can be obtained for various alloys from Equation 2. Table II and Fig. 4 show that these estimated values are quite close to the experimentally obtained K values for $Fe_{75}Si_{10}B_{15}$ [10], $Fe_{40}Ni_{40}P_{14}B_6$ [15], $Ni_{40}Pd_{40}P_{20}$ [11], $Pd_{84}Si_{16}$ [15] and $Pd_{78}Cu_6Si_{16}$ [15] alloys.

4. I_v calculation for alloys

For discussing nucleation in glass-forming systems, the following expression has been used for the

TABLE I Constant K_0 estimated by Equation 3 and ionization energy E_i [14] of non-metallic bonded elements, constants K' and K'' estimated by Equations 6 and 7 for Groups IV and V, and experimentally obtained constants K_e [12]

Element	E_i(kJ mol^{-1})	K_0	K'	K''	K_e
Non-metals					
As	1012	0.259	0.330	0.329	
B	798	0.332	0.323*	0.321*	
Bi	815	0.325	0.313	0.316	0.33
C	1087	0.238*†	–	–	
Ga	577	0.428	0.438*	0.438*	0.436
Ge	782	0.338	0.331	0.330	0.348
P	1058	0.246	0.257	0.256	0.255 ± 0.023‡
Si	786	0.337	0.336	0.334	
Sb	832	0.319	0.319	0.321	0.302
Te	869	0.306	0.327	0.327	
Metals					
Au					0.436
Co					0.490
Cu					0.439
Fe					0.445
Ni					0.444
Pd					0.450

*Estimated by Equations 4 and 5 for Group III.
†Apparent value.
‡Estimated from author's results [10, 11].

TABLE II Constants K_0, K' and K'' estimated by Equations 2 and 3, Equations 2 and 4 or 6, and Equations 2 and 5 or 7, and experimentally obtained constants K_e [10, 11] for alloys

Alloy	K_0	K'	K''	K_e
$Ni_{40}Pd_{40}P$	0.407	0.409	0.409	0.409 ± 0.005
$Ni_{80}P_{20}$	0.404	0.407	0.406	
$Pd_{78}Cu_6Si_{16}$	0.431	0.431	0.431	0.421 ± 0.003
$Pd_{80}Au_4Si_{16}$	0.431	0.431	0.431	
$Pd_{84}Si_{16}$	0.432	0.432	0.431	0.445 ± 0.011
$Fe_{75}Si_{10}B_{15}$	0.417	0.415	0.415	0.413 ± 0.01
$Fe_{80}P_{13}C_7$	0.405	0.448	0.430	
$Fe_{83}B_{17}$	0.426	0.424	0.424	
$Fe_{82.7}C_{17.3}$	0.409	0.512	0.468	
$Fe_{80}P_{20}$	0.405	0.407	0.407	
$Fe_{40}Ni_{40}P_{14}B_6$	0.410	0.411	0.411	0.407
$Co_{70.5}Fe_{4.5}Si_{10}B_{15}$	0.449	0.447	0.447	
$Te_{85}Ge_{15}$	0.311	0.328	0.328	
$Ga_{50}As_{50}$	0.344	0.384	0.384	

steady-state nucleation rate [16–18]:

$$I_v = N_v D a^{-2} \exp(-16.2 Q^3 / \Delta G_v^2 R T) \qquad (8)$$

Here N_v is the number of unassociated molecules per unit volume, D is the liquid diffusivity for molecular transport across the matrix–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 following equations for large departures from equilibrium. Equation 9 below is applied in supercooled conditions and is assumed by Hoffmann [19]:

$$\Delta G_v = \Delta H_f (T_m - T) T / V T_m^2 \qquad (9)$$

Here 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 simple molecular liquids and even for liquid metals, D is inversely related to the viscosity ($\bar{v}$) suggested by Stokes–Einstein theory [17]. Thus, it is very important to know the viscosity in the supercooled liquid, where the solute concentration of the liquid is assumed to be equal to that in front of the interface between the crystal and the supercooled liquid.

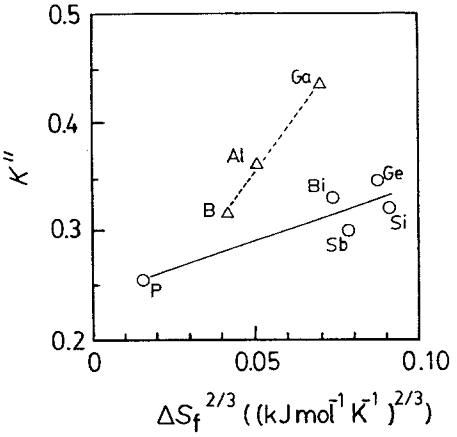

Figure 3 Change in logarithmic constant K'' with $\Delta S_f^{2/3}$. Solid line is for Group IV and V elements. Dotted line is for Group III elements.

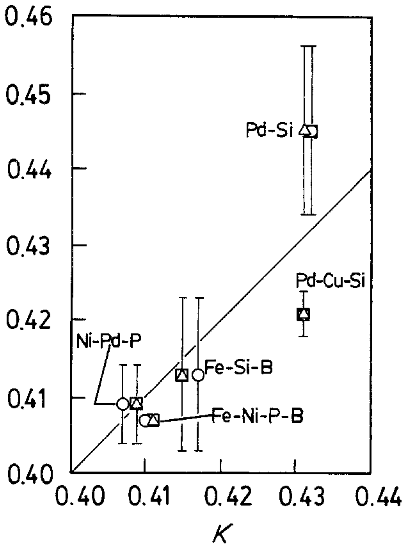

Figure 4 Relation between K_e and calculated values K_0, K' and K'', for $Fe_{75}Si_{10}B_{15}$, $Fe_{40}Ni_{40}P_{14}B_6$, $Ni_{40}Pd_{10}P_{20}$, $Pd_{84}Si_{16}$ and $Pd_{78}Cu_6Si_{16}$ alloys. Values estimated from (○) ionization energy E_i, (□) entropy change of fusion ΔS_f, (△) $\Delta S_f^{2/3}$.

The temperature dependence of viscosity has been derived by a Fulcher-type equation [10, 11]. The viscosity $\bar{v}$ is expressed by the equation

$$\log \bar{v} = A + \frac{B}{T - T_0} \qquad (10)$$

Here A, B and T_0 are constants. B is correlated with the glass transition temperature T_g and is expressed [20] by the equation

$$B = 13(T_g - T_0) \qquad (11)$$

Thus the viscosity $\bar{v}$ (Pa sec) is calculated from the viscosities of the liquid above the melting point T_m or the activation energy of the growth rate [10, 11].

The nucleation frequency (I_v) curve for $K = 0.413$ is calculated by means of Equations 1 to 3 and 8 to 10. Fig. 5 shows the I_v change with temperature together with a plot of the $Fe_{75}Si_{10}B_{15}$ alloy results [10]. If the value of K is 0.445 for the metal (iron), the I_v values for $K = 0.445$ (Fe) are about × 10^4 smaller than those for $K = 0.413$ and the experimentally obtained plots in

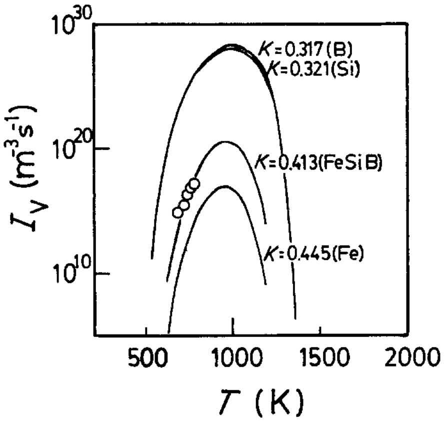

Figure 5 Temperature dependence of nucleation frequency I_v of $Fe_{75}Si_{10}B_{15}$ alloy. Upper curves are for $K = 0.321$ and $K = 0.317$ of non-metallic elements (silicon and boron). Lower curve is for $K = 0.445$ of pure metal (iron).

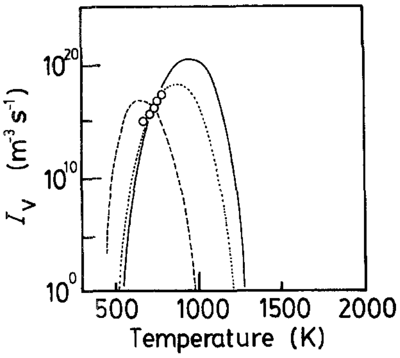

Figure 6 Temperature dependence of nucleation frequency I_v of $Fe_{75}Si_{10}B_{15}$ alloy. Estimated by (——) Equation 1 as suggested by Turnbull, (····) Equation 12, (– – –) Equation 13; (○) experimental values.

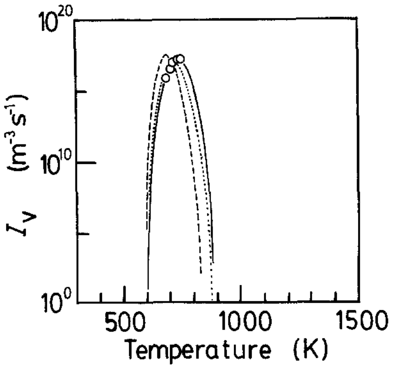

Figure 7 Temperature dependence of nucleation frequency I_v of $Pd_{78}Cu_6Si_{16}$ alloy. Estimated by (——) Equation 1 as suggested by Turnbull, (····) Equation 12, (– – –) Equation 13; (○) experimental values.

Fig. 5. On the other hand, the I_v values for silicon and boron are about $\times 10^7$ larger than for $K = 0.413$, if the K values are assumed to be 0.321 and 0.317 for the non-metallic bonded elements silicon and boron. Therefore, the solid–liquid interfacial energy is found to be one of the dominant factors for crystal nucleation. Thus, it is concluded that the estimation of K by Equations 2 and 3 is a useful tool to estimate I_v.

The temperature dependence of I_v has been estimated by Equations 1, 8 and 9 and the following equations [21–23]:

$$Q = K_0' \left(\frac{\Delta S_f}{V}\right)^{2/3} (T_m + T)^{2/3} T_m^{1/3} \qquad (12)$$

$$Q = K_0'' \frac{\Delta S_f T}{N^{1/3} V^{2/3}} \qquad (13)$$

Here K_0' and K_0'' are constants. Based on the equations and the midpoints of the experimentally obtained I_v values [10, 11], Figs 6 and 7 show the temperature dependence of the I_v values for Fe–Si–B and Pd–Cu–Si alloys. Although the starting point of the analysis, Equation 1, is 30 years out of date, the temperature dependence of experimentally obtained I_v values agrees with the Turnbull's equation for both alloys.

Besides our results for alloys, a result for H_2O [24] and results for metals and non-metallic pure elements [25] agree with a fundamental nucleation (gas–liquid) theory [26]. On the other hand, a modified expression for a liquid–crystal homogeneous nucleation was suggested by Pond [27]. The effect of the modified terms has been discussed [28–32]. However, the predictions are not yet confirmed.

Considering the liquid structure in front of a growing crystal, Ewing [33, 34] suggested a calculation method by the use of a radial distribution function. Harrowell and Oxtoby [35] have suggested a further calculation method, but high quantitative accuracy cannot be expected.

5. Conclusion

Based on homogeneous nucleation theory, the temperature dependence of the crystal nucleation frequency is investigated. By the use of an extension of Turnbull's assumption, the value of the solid–liquid interfacial energy of the alloy is suggested. The suggested equations correlate with an ionization energy and an entropy of fusion for the non-metallic elements.

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