Solid-liquid interfacial energy of $Ni_{40}Pd_{40}P_{20}$ alloy glass

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Based on nucleation theory, the solid-liquid interfacial energy for $Ni_{40}Pd_{40}P_{20}$ is estimated to be 100 ± 2 mJ/m^2 from the nucleation frequency of $Ni_{40}Pd_{40}P_{20}$ alloy glass. The value of the solid-liquid interfacial energy is found to be quite close to that estimated by means of an extension of Turnbull's assumption for alloys.

I. INTRODUCTION

$Ni_{40}Pd_{40}P_{20}$ is an easy glass-forming alloy as the critical cooling rate for glass formation is extremely low.[1] Namely, it is easy to obtain the glass without rapid quenching. Therefore, it is interesting to investigate the dominant factors in controlling the easy glass-forming capability of this alloy. The solid-liquid interfacial energy is known to be one of the most sensitive factors controlling the nucleation of a crystal in a liquid. Several attempts have been made to estimate the solid (crystal) -liquid (supercooled liquid or glass) interfacial energy,[2–4] however, no one has determined this energy in a supercooled liquid at low temperature. Thus, we have suggested a way to estimate the energy.[5] The purpose of the present work is to estimate the solid-liquid interfacial energy of the $Ni_{40}Pd_{40}P_{20}$ alloy during isothermal crystallization above the glass transition temperature.

II. EXPERIMENTAL PROCEDURE

Glass plates of 0.2 mm in thickness were prepared in an Ar-H_2 mixture gas by liquid quenching.[6] The sample piece was dipped into a molten Pb bath that was controlled to within ±1.0 K at the desired temperature above the glass transition temperature. The rapid heating and cooling rates were about 10^4 and 10^3 K/s, respectively.[7] The microstructure change during the isothermal crystallization was monitored by metallographic observations in an optical and scanning electron microscope.

III. NUCLEATION THEORY

For nucleation in glass-forming systems, the following expression has been used for the steady-state nucleation rate:[8]

$$I_v = N_v D a^{-2} \exp(-\Delta G/RT) . \quad (1)$$

Here N_v is the number of unassociated molecules per unit volume, D is the liquid diffusivity for molecular transport across the matrix to the nucleus interface, a is the molecular diameter, R is the gas constant, T is the absolute temperature of this transformation and ΔG is the activation free energy of forming a critical nucleus as follows:

$$\Delta G = 16.2 Q^3/\Delta G_v^2 . \quad (2)$$

Here Q is the solid-liquid interfacial energy 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:[9]

$$\Delta G_v = \Delta S_f (Tm - T) T / V T_m . \quad (3)$$

Here ΔS_f is the entropy change on solidification per mol, T_m is the melting point, and V is the molar volume.

IV. RESULTS AND DISCUSSION

Based on the homogeneous nucleation theory, the solid-liquid interfacial energy is estimated using 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 the liquid metals, D is inversely related to the viscosity v as suggested by Stokes and Einstein.[10] Thus, it is very important to know the viscosity in the supercooled liquid, in which the solute concentration is assumed to be the same as that in front of the interface between the crystal and the supercooled liquid. This viscosity has been expressed by the Fulcher equation.[11] The Fulcher-type viscosity v is calculated from the viscosity (10^{13} mPa s) (Ref. 12) at the glass transition temperature ($T_g = 580$ K),[13] the liquid

TABLE I. Experimental results for nucleation frequency I_v during isothermal crystallization above glass-supercooled liquid transition temperature and solid-liquid interfacial energy Q of $Ni_{40}Pd_{40}P_{20}$ alloy glass.

Temperature	(K)	633	643	653	673	690
$I_v \times 10^{-12}$	(m^{-3}s^{-1})	6.60	14.6	29.6	121	329
Q	(mJ/m^2)	101.4	101.6	101.5	100.2	98.4
K		0.413	0.414	0.414	0.410	0.404

viscosity[14] at the melting point ($T_m=912$ K) (Ref. 1) and the supercooled liquid[14] at the nose temperature ($T_n=0.556T_m+218$) (Ref. 15) of the time-temperature-transformation curve. The supercooled liquid viscosity v (mPa s) is expressed by the following equation:

$$\log_{10}v=-1.497+[1868/(T-451)] . \quad (4)$$

The solid-liquid interfacial energy can be obtained from the enthalpy change on solidification ($\Delta H_f=7.46$ kJ/mol, measured by differential scanning calorimetry,[16] the molar volume (V) extrapolated from the liquid volume [$V=M/p$; p (kg/m^3)$=12.08\times10^3-2.35T$][16] and the nucleation frequency I_v for the $Ni_{40}Pd_{40}P_{20}$ alloy glass (see Table I). Here I_v is statistically estimated by histograms of crystals sizes such as in Fig. 1. The histogram is the summarized results of the scanning electron microscope (SEM) and the optical observations. Figure 2 shows the SEM micrograph of randomly distributed spherical crystals in the cross section of the $Ni_{40}Pd_{40}P_{20}$ alloy glass specimen. The experimentally obtained solid-liquid interfacial energy is 100 ± 2 mJ/m^2 (see Table I). The decrease in the nuclei density at large cluster sizes is due to a difficulty in maintaining a homogeneous sample temperature. The decrease in the nuclei density at small cluster sizes is due to experimental difficulty in resolving the clusters in the SEM micrographs.

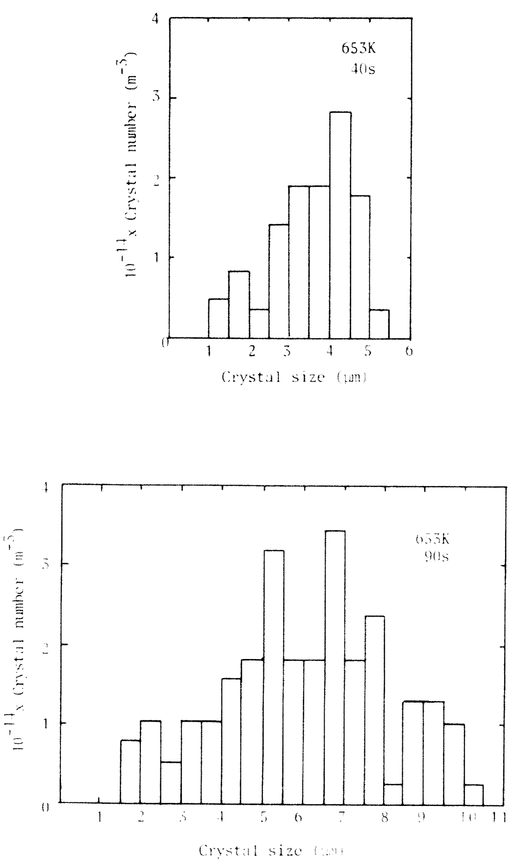

FIG. 1. Histogram of crystal sizes in $Ni_{40}Pd_{40}P_{20}$ alloy glass aged for 40 and 90 s at 653 K.

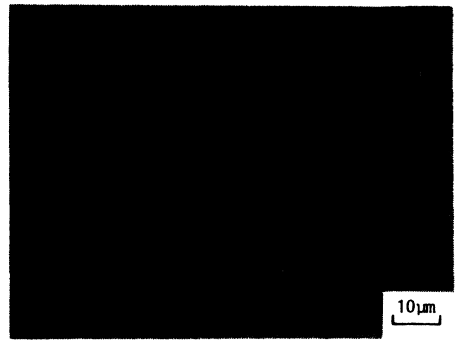

FIG. 2. SEM micrograph of randomly distributed spherical crystals in cross section of $Ni_{40}Pd_{40}P_{20}$ alloy glass specimen aged for 40 s at 653 K.

The following equations of the solid-liquid interfacial energy Q have been suggested by the use of Turnbull's assumption:[3]

$$Q=Q_g/(N^{1/3}V^{2/3}) . \quad (5)$$

Here Q_g is the gram-atomic interfacial energy and is expressed by the following equation:

$$Q_g=K\Delta H_f , \quad (6)$$

Here K is 0.32 (Ref. 3) for covalent bonded elements and is 0.45 (Ref. 3) for metals and N is Avogadro's number.

Figure 3 shows the relation between Q_g and ΔH_f for Ni-Pd-P alloy together with several element[3] and easy glass-forming alloys.[16] The experimental values of these glasses are between a dotted line of the metallic elements ($K=0.45$) and a solid line of the nonmetallic elements ($K=0.32$). Especially, the experimental K ($K=0.409$ ±0.05, see Table I) of the $Ni_{40}Pd_{40}P_{20}$ alloy is quite close to the arithmetic mean K ($K=0.42$) in Eq. (6). Here the arithmetic mean K is estimated for pure elements

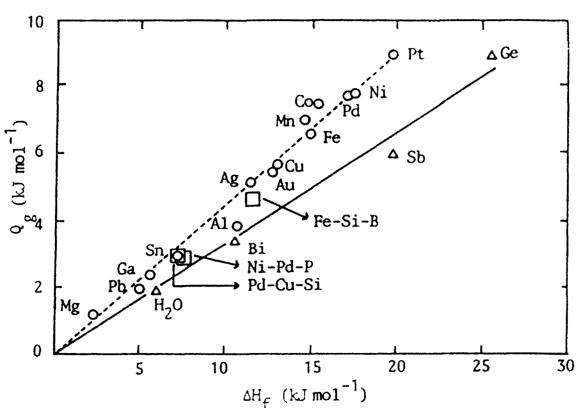

FIG. 3. Relation between gram-atomic interfacial energy and enthalpy change of fusion. Solid line is for covalent bonded materials. Dotted line is for metallic bonded elements.

[$K=0.444$ for pure Pd (Ref. 3), $K=0.450$ for pure Ni (Ref. 3), K for P is assumed to be 0.32 as shown in the solid line in Fig. 3]. This shows that the 20 at.% addition of metalloids to the transition metals seems to transform Pd-Ni metallic alloy into covalent bonded alloy. Since Al, which is clearly a system with metallic bonding, is very near the covalently bonded curve in Fig. 3, this statement seems to be a bit strong on reflection.

It is important to investigate the change in the energy with temperature in supercooled liquid. Some remarkable works are found in this field.[3,17,18] Contrary to these discussions, the obtained values show small changes with aging temperature.

V. CONCLUSION

Based on nucleation theory and an assumed supercooled liquid viscosity, the solid-liquid interfacial energy of $Ni_{40}Pd_{40}P_{20}$ is estimated to be 100 ± 2 mJ/m^2 by the use of the measured nucleation frequency and melting point of $Ni_{40}Pd_{40}P_{20}$ alloy glass. The experimental measurements are important in this work.

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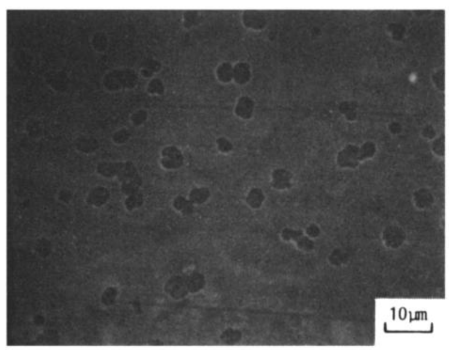

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