

Supercooling of Homogeneous Liquid Phase of Liquid Metals and Alloys— —Poor Supercooling around the Eutectic Composition of Liquid Ni-Nb System—

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To study the supercooling of many liquid metals with high melting temperatures, the investigation was performed for the cooling curves of electrostatic levitation (ESL) experiments, which had been originally obtained for the measurements of many physical properties. The largest supercooling over the literature values was found for liquid Ru (428 K), Ta (721 K), W (601 K), and Ir (438 K), where temperatures in the parentheses mean the supercooling of respective liquid metals. This indicates the validity of ESL for the supercooling experiments of liquid metals and alloys because of being rather free from the heterogeneous nucleation. This ESL was applied to the study of supercooling of homogeneous liquid phase in the composition range from 29 at% Nb to 71 at% Nb of eutectic Ni-Nb system, whose eutectic point is present at 40.5 at% Nb and 1448 K. The experimental result shows a poor supercooling tendency of homogeneous liquid phase around the eutectic composition in spite of large supercooling far apart from this eutectic composition. This characteristic feature was discussed based on the classical nucleation theory coupled with the knowledge recently found, the existence of concentration fluctuations in the homogeneous liquid phase near the eutectic point. [doi:10.2320/matertrans.MAW201025]

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1. Introduction

Supercooling of liquids has been important in the metallurgy and the materials science.^{1,2)} This phenomenon is closely related to the solidification or crystallization.²⁾ In addition, the metallic glass, which has gathered attention of many fields, is prepared, for example, by the rapid quenching method through the supercooled state of metallic liquids.³⁾ Historically the study of supercooling has been the effort to realize the homogeneous nucleation by suppressing the effect of the heterogeneous one. The large supercooling of liquids was found to be obtained with the use of droplet technique, which divides bulk liquid metals into many small droplets.⁴⁾ In this technique, the heterogeneous nucleation sites are restricted only in a few droplets and the large supercooling is established for most of other droplets. Turnbull and co-researchers^{1,2)} studied extensively the supercooling of liquid metals by using this technique of 50 μm size. For the supercooling of many liquid metals, ΔT ($= T_m - T_C$; T_m : melting temperature; T_C : temperature of cooling limit), they found an universal law, $\Delta T = 0.185T_m$ for 17 liquid metals. Perepezko⁵⁾ extended this droplet technique into the emulsion technique (droplets of 10~20 μm diameter in a medium) and obtained more larger supercooling, $\Delta T = 0.3\sim 0.5T_m$, for liquid metals with low T_m (Sn, Pb, Bi, etc.). Devaud and Turnbull⁶⁾ also obtained the supercooling of 0.12~0.34 T_m for liquid Ge droplets of 0.3~0.5 mm diameter in B_2O_3 melts. These dispersion techniques have not been applied to liquid metals with high T_m due to the lack of appropriate containers. The containerless technique is also expected to remove the heterogeneous nucleation sites in addition to the applicability to liquid metals with high T_m . The study of supercooling for liquid metals with high T_m (Ti, Zr, Mo, Rh,

Hf, Ta, and Pt,⁷⁾ W, and Re⁸⁾) was performed during the free fall in the drop tube of high vacuum.^{7,8)} This method has two advantages, containerless technique and microgravity condition. The former may eliminate the heterogeneous nucleation sites and the latter may lead to the absence of collision among embryos each others due to no convection in liquids. With the development of microgravity science, other containerless techniques, the electromagnetic levitation (EML)^{9,10)} and the electrostatic levitation (ESL)¹¹⁻¹³⁾ have been advanced. These techniques have been also applied to the study of physical properties of liquid metals with high T_m . The study of the supercooling of liquid metals and alloys with high T_m is also expected by these levitation techniques.

As described above, there exists a considerable amount of supercooling studies particularly for pure liquid metals with low and intermediate T_m . However, the studies for the supercooling of liquid alloys have not been performed so much.^{14,15)} The supercooling behavior of liquid alloys has been frequently discussed with the relation to the preparation of metallic glass.¹⁶⁾ The composition range around the eutectic composition has been a target to prepare the metallic glass. Therefore, it has been implicitly considered that the liquid alloy of eutectic composition can be easily supercooled. However, one of authors¹⁷⁾ showed that the supercooling of liquid Bi-Sn and Pb-Sn alloys is smallest at the eutectic composition by referring to the previous DSC studies using the emulsions technique.^{18,19)} He also presented the interpretation that the supercooling of homogeneous liquids is suppressed around the eutectic composition due to the existence of concentration fluctuations which may originate from a pre-solidification phenomenon from liquid phase to two solids one.

The purpose of the present paper is to report the experimental result of supercooling behavior for the homogeneous liquid phase around the eutectic composition of Ni-

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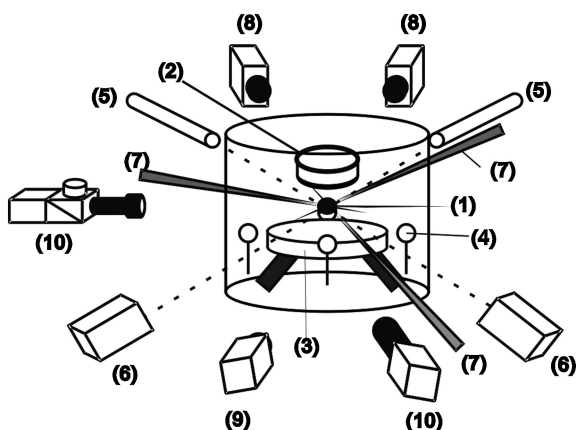


Fig. 1 Schematic view of the electrostatic levitation (ESL) apparatus; (1): sample; (2)(3): vertical electrodes; (4): horizontal electrodes; (5): He-Ne laser for position detection; (6): position sensor; (7): CO₂ laser for heating; (8): pyrometers; (9)(10): CCD cameras.

Nb system with the use of ESL technique, which is one of containerless experimental tools. In the present manuscript, at first, the validity of ESL technique for the study of supercooling of liquid metals was investigated by the survey of cooling curves of many liquid metals with high T_m originally obtained in the experimental studies of many physical properties, such as density, surface tension, viscosity, thermal conductivity, and heat capacity.^{11,12} In the next stage, this ESL technique was applied to the study of the supercooling for the homogeneous liquid phase of eutectic Ni-Nb system whose eutectic point is present at 40.5 at% Nb and 1448 K.²⁰ The particular feature of the result in the present study, a poor supercooling tendency around the eutectic composition, was discussed with the relation to the knowledge recently found,^{17,21–24} the existence of concentration fluctuations in the homogeneous liquid phase near the eutectic point.

2. Experimental

The cooling curve surveyed in this study for pure liquid metals with high T_m had been obtained by the electrostatic levitation (ESL) technique, under almost the same experimental condition as the supercooling experiments for liquid Ni-Nb alloys described below. The purity of respective metals used should be referred elsewhere.^{11,12} The supercooling experiments for the liquid state of eutectic Nb-Ni alloys were performed with the use of the experimental apparatus shown in Fig. 1. The composition range studied was from 29 at% Nb to 71 at% Nb, which includes the eutectic composition, 40.5 at% Nb.²⁰ Metals used were 99.9% grade (Nilako Co. Ltd). Prior to the ESL experiments, spherical samples of 24~28 mg were prepared by melting the weighed amount of Nb and Ni together in an arc furnace followed by solidification. These spherical samples were melted in the ESL by CO₂ laser beam lines (100 W, Synrad Co. Ltd) injected from three directions. These samples, kept at temperatures higher than the liquidus temperature T_L , were cooled down with the cooling rate of 40~70 K·s⁻¹ by cutting the laser beam lines. For the eutectic composition, this

Table 1 The supercooling, ΔT , and the relative supercooling, $\Delta T/T_m$, of liquid metals with high melting temperatures.

	Hofmeister <i>et al.</i> ⁷⁾		Vinet <i>et al.</i> ⁸⁾		Present work	
	ΔT (K)	$\Delta T/T_m$	ΔT (K)	$\Delta T/T_m$	ΔT (K)	$\Delta T/T_m$
Ti	350	0.18			292	0.15
Zr	430	0.20			313	0.15
Nb	480	0.18			413	0.15
Mo	520	0.18			428	0.15
Ru	330	0.13			428	0.17
Rh	450	0.20			431	0.19
Hf	450	0.18			333	0.13
Ta	650	0.20			721	0.22
W			530	0.14	601	0.16
Re			975	0.28	800	0.23
Ir	340	0.13			438	0.16
Pt	380	0.19			377	0.18

keeping temperature before cooling, T_{keep} , was adjusted to be 500 K higher than the eutectic temperature, T_E . The weight loss after experiments was 0.15 mg (0.5%) at the largest. The fine microstructure of samples before and after the levitation was confirmed by the TEM analysis. The vacuum level of levitation chamber was kept to be below 5×10^{-5} Pa. The temperature of sample, which was rotated with a speed of 10 Hz, was measured by the single color pyrometers (Chino Corp). The measured temperature was corrected by referring to the coexisting line of three phases (solid and liquid phases) in the phase diagram.²⁰ Due to the weak radiation loss of heat from the samples, a considerably good constant temperature (coexisting line) was observed in this experiment in spite of small amount of samples (24~28 mg).

3. Results

From the cooling curve for pure liquid metals with high T_m , the supercooling of liquid state, ΔT , was evaluated by the relation, $\Delta T = T_r - T_C$, where T_r is the constant temperature after the recalescence, namely T_m , and T_C the temperature of supercooling limit of liquid phase. Together with literature values,^{7,8} the obtained ΔT was summarized in Table 1. The typical examples of cooling curve for liquid Ni-Nb system are shown in Fig. 2. Figure 2(c) indicates that after the recalescence a constant temperature was able to be observed for the sample of Ni-71 at% Nb. This is derived from the fact that on the recalescence the homogeneous liquid of Ni-71 at% Nb in the supercooled state changed into the coexisting state of three phases, liquid, intermetallic compound (Ni₆Nb₇) and solid Nb.²⁰ Gibbs phase rule²⁾ allows only the unique temperature, 1563 K, under atmosphere pressure for this coexisting state of three-phases. Similarly, as can be seen in Fig. 2(b), the supercooling of homogeneous liquid phase for the eutectic composition (Ni-40.5 at% Nb) provided the eutectic temperature (1448 K) as the constant temperature after the recalescence, which is also derived from the coexistence of three phases, two solid phases, and liquid phase (Gibbs phase rule²⁾). On the other hand, as can be seen in Fig. 2(a), the cooling curve of Ni-35 at% Nb

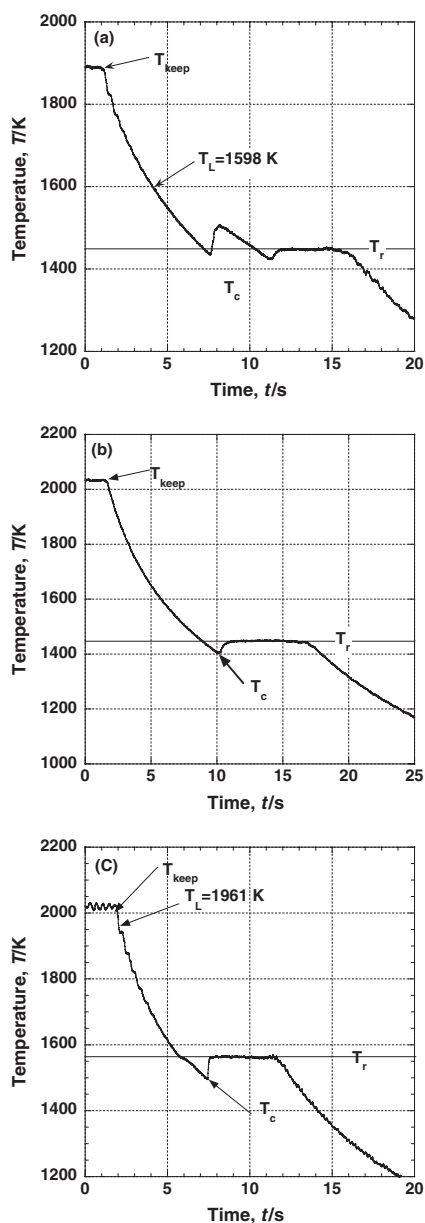


Fig. 2 (a) The typical examples of cooling curve for Ni-Nb system; (a): Ni-35 at% Nb; (b): Ni-40.5 at% Nb (eutectic composition); (c): Ni-71 at% Nb; T_{keep} : keeping temperature before cooling; T_L : liquidus temperature; T_r : constant temperature after recalescence; T_c : cooling limit of homogeneous liquid phase.

showed a prepeak before the constant temperature of eutectic temperature (1448 K). This may be derived from some partial solidification of sample followed by the remelting due to the latent heat on this solidification. On the solidification of liquid sample after the remelting, the recalescence appeared once more and finally the constant temperature of eutectic one (1448 K) was found due to the coexisting state of three phases, two solid phases and one liquid phase. Similar anomalous behaviors of cooling curve were observed rather for Ni rich side. In any cases, the clear supercooling limit of homogeneous liquid phase, T_c , was observed. The supercooling of homogeneous liquid phase, ΔT , was evaluated by the relation, $\Delta T = T_L - T_c$, where T_L is the equilibrium liquidus temperature. The value of T_L was taken from the Ref. 20). In Fig. 3 is shown the concentration dependence

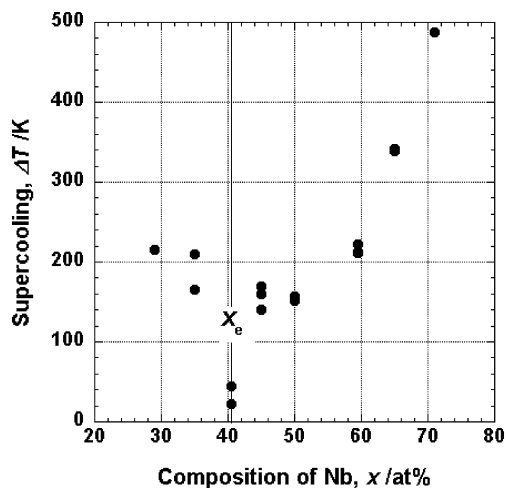


Fig. 3 The composition dependence of the supercooling, ΔT of the homogeneous liquid phase for liquid Ni-Nb alloys. The data points are 1 for Ni-29.0 at% Nb, 2 for Ni-35.0 at% Nb, 3 for Ni-40.5 at% Nb (eutectic composition, x_e), 3 for Ni-45.0 at% Nb, 2 for Ni-50.0 at% Nb, 3 for Ni-59.0 at% Nb, 2 for Ni-65.0 at% Nb, and 2 for Ni-71.0 at% Nb.

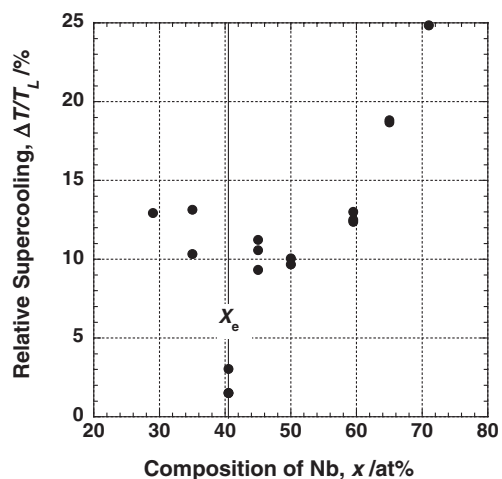


Fig. 4 The composition dependence of the relative supercooling, $\Delta T/T_L$, of the homogeneous liquid phase for liquid Ni-Nb alloys. The data points are 1 for Ni-29.0 at% Nb, 2 for Ni-35.0 at% Nb, 3 for Ni-40.5 at% Nb (eutectic composition, x_e), 3 for Ni-45.0 at% Nb, 2 for Ni-50.0 at% Nb, 3 for Ni-59.0 at% Nb, 2 for Ni-65.0 at% Nb, and 2 for Ni-71.0 at% Nb.

of the supercooling of homogeneous liquid phase, ΔT , for Ni-Nb system. The ΔT is smallest at the eutectic composition, x_e (“V shape”). The relative supercooling, $\Delta T/T_L$, also shows a minimum behavior at the x_e (“V shape”), as shown in Fig. 4.

4. Discussions

The supercooling of the present study in Table 1 shows considerably large values for pure liquid metals with high T_m in spite of the fact that the ESL experiments themselves had been performed for the measurements of many physical properties^(11,12) and in the present study their cooling curves were investigated in detail. Table 1 shows that the largest values of supercooling over the literatures^(7,8) had been

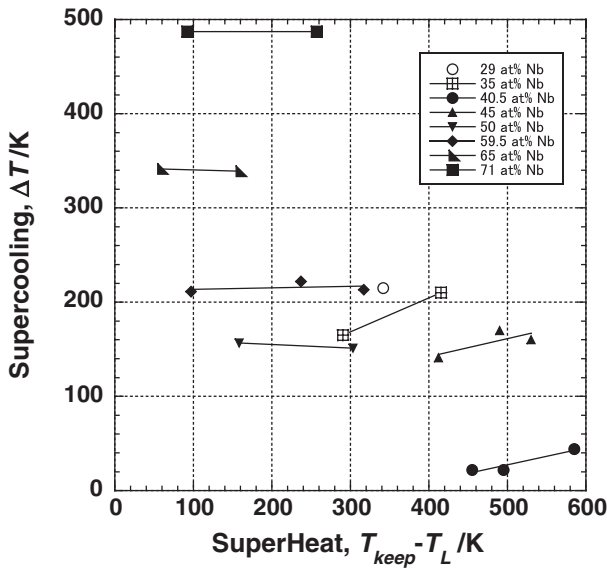


Fig. 5 The superheat, ΔT_{heat} , dependence of supercooling, ΔT , for liquid Ni-Nb alloys. Lines, determined by the least square method, represent respectively the ΔT_{heat} dependence of the ΔT for the same composition.

obtained by the ESL technique, as can be seen in the cases, 428 K (0.17) for liquid Ru, 721 K (0.22) for liquid Ta, 601 K (0.16) for liquid W, and 438 K (0.16) for liquid Ir, in which the values in the parentheses mean the relative supercooling, $\Delta T/T_L$. In addition, the supercooling values of 431 K (0.19) for liquid Rh and 377 K (0.18) for liquid Pt are almost same as the previous drop tube experiments.^{7,8)} These facts indicate that the ESL or the levitation technique is fit to the supercooling experiments and homogeneous nucleation ones.

This validity of ESL for the supercooling experiments of liquid metals with high T_m encourages us to discuss with conviction the experimental results of the supercooling for liquid Ni-Nb system. As can be seen in Fig. 3 the supercooling shows the minimum at the eutectic composition, x_e (“V shape”). In addition, Fig. 4 indicates that the relative supercooling also shows the minimum at the x_e (“V shape”) though, far apart from the eutectic composition, the relative supercooling exceeds over 20%, which is almost same as or a little larger than the standard level of supercooling given by Turnbull.¹⁾ Thus, the suppression of supercooling occurs only around the x_e . We stress that the supercooling experiments for the x_e were performed with a sufficiently high keeping temperature before cooling, as described in the “Experimental”. This poor tendency of supercooling around the x_e was obtained with a good reproducibility, as can be judged from the data points of each composition shown in Figs. 3 and 4 or their figure captions. Figure 5 represents that the ΔT in Fig. 3 decreases with the increase of the superheat, ΔT_{heat} , which is defined by $T_{\text{keep}} - T_L$ (T_{keep} : keeping temperature before cooling; T_L : liquidus temperature). It should be remarked that the supercooling, ΔT , for the same composition keeps rather an invariant tendency or a slightly increasing one with the increase of the superheat, ΔT_{heat} . Therefore, the small ΔT around the eutectic composition may be derived not from the large ΔT_{heat} but from the particular feature of eutectic liquid. In addition, the tendency in Fig. 5 does not support the possibility that the super-

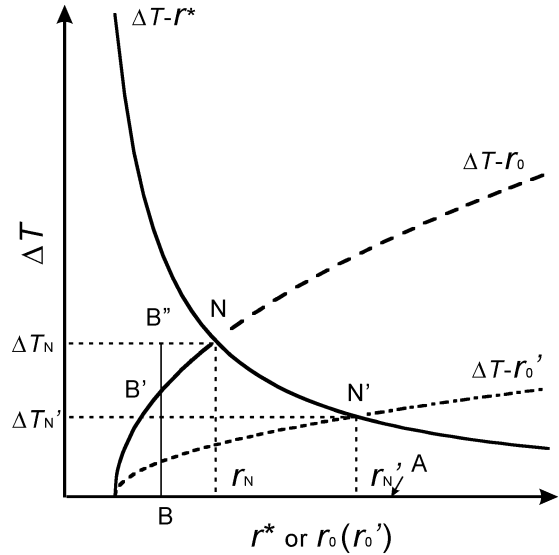


Fig. 6 The schematic figure of the relations, $\Delta T - r^*$, $\Delta T - r_0$ (no concentration fluctuations (case I)), and $\Delta T - r_0'$ (the existence of concentration fluctuations (case II)); ΔT : supercooling of homogeneous liquid; r^* : the critical radius of embryo. In case I: r_0 : the maximum radius of observable embryo; N: nucleation point; ΔT_N : the supercooling at the onset of nucleation; r_N : the radius of embryo at the onset of nucleation. The symbol A corresponds to the situation that the radius of concentration fluctuations, r_{cc} , is greater than r_N in the extreme case of no supercooling. The B-B'-B'' corresponds to the situation that r_{cc} , is close to r_N near the eutectic composition, x_e . In case II, r_0' : the maximum radius of observable embryo; N': nucleation point; $\Delta T_N'$: the supercooling at the onset of nucleation; r_N' : the radius of embryo at the onset of nucleation.

cooling tendencies in Figs. 3 and 4 are derived from the heterogeneous origin remaining on cooling. If such an effect is present, an inverse tendency should be obtained for the $\Delta T - \Delta T_{\text{heat}}$ relation in Fig. 5. Thus, the suppression tendency of supercooling around the x_e may be derived from the essential feature of eutectic liquid. We discuss this supercooling behavior based on the classical nucleation theory.^{1,2)}

Here, we must remember the particular feature of homogeneous liquid phase around the eutectic point. According to the study of one of authors,^{17,21-24)} the concentration fluctuations exist in the homogeneous liquid phase around the x_e . The volume fraction of concentration fluctuation, ϕ_c , which was estimated from the electrical resistivity measurements for many liquid eutectic alloys, shows the maximum at the x_e (“Λ” shape). It was concluded that such concentration fluctuations may correspond to microscopically pre-solidified domain prior to the phase transition from homogeneous liquid phase to two-solids one.^{17,21-24)} This situation for the Ni-Nb liquids around the eutectic composition (Ni-40.5 at%Nb) can be described as the dispersion of solid-like spherical domains of Ni_3Nb and Ni_6Nb_7 ²⁰⁾ in the homogeneous liquid phase even over the liquidus temperature. The volume fraction of these solid-like spherical domains, which may exist as concentration fluctuations, seems to be rather small, for example, 7% at the most.^{17,21-24)} Because spherical shapes were considered for solid-like domains or concentration fluctuations, it is possible to define the radius of domains of concentration fluctuations, r_{cc} , which is important for the discussions for Fig. 6. Some

evidence of such concentration fluctuations in eutectic liquids may be found in the recent TEM study coupled with the reverse Monte Carlo analysis for Pd-Si metallic glass.²⁵⁾ The poor tendency of supercooling of homogeneous liquid phase around the x_e (“V shape”) must be discussed deeply with the relation to these concentration fluctuations coupled with the classical nucleation theory.

Here, for the discussion of poor supercooling tendency of eutectic liquids, we summarize the essential feature of classical nucleation theory by following Chalmers.²⁾ This summary is slightly lengthy but this was done only for clear discussions. The Gibbs free energy change on the formation of atomic aggregation of solid-like with radius r in the liquid^{1,2)} is written as

$$\Delta G = 4\pi r^2 \sigma_{SL} - \frac{4}{3} \pi r^3 \Delta G_{SL}. \quad (1)$$

In this equation, the first term is the energy increase for the formation of interface between the bulk liquid and the solid-like aggregation. The positive contribution of the first term can be evaluated in terms of the solid-liquid interfacial energy, σ_{SL} . The second term expresses the energy decrease due to the appearance of solid-like aggregation with lower energy than the bulk liquid. This negative energy contribution can be evaluated in terms of the ΔG_{SL} , the absolute value of the Gibbs free energy change on the formation of solid-like aggregation of one unit volume in the liquid phase.

ΔG in eq. (1) shows the maximum value, ΔG^* , at r^* as a function of the radius, r . The explicit values of ΔG^* and r^* are written as follows:

$$\Delta G^* = \frac{16}{3} \pi \sigma_{LS}^3 / (\Delta G_{SL})^2, \quad (2)$$

$$r^* = 2\sigma_{LS} / \Delta G_{SL}. \quad (3)$$

The solid-like aggregation with the radius r^* is called as “critical nucleus”. This terminology is derived from the reason that it may grow into crystal if $r > r^*$ and it has a tendency to be decomposed into discrete atoms if $r < r^*$. The atomic aggregation of solid like with the radius r smaller than r^* is called as the “embryo”. By using the supercooling of liquid phase, ΔT , and the heat of fusion per unit volume, L , the ΔG_{SL} can be written as

$$\Delta G_{SL} = L\Delta T / T_m. \quad (4)$$

Equation (3) is easily rewritten as

$$r^* = \frac{2\sigma_{LS} T_m}{L\Delta T}. \quad (5)$$

Thus, the supercooling, ΔT , is inversely proportional to the radius of critical nucleus, r^* , though r^* itself is not always an easily controllable experimental parameter.

As described above, as soon as the radius of embryo exceeds over r^* , the nucleation may occur. However, the nucleation phenomenon must be considered as an event in our measuring time in terms of the nucleation rate. The nucleation rate, I , in unit of $\text{m}^{-3} \cdot \text{s}^{-1}$ is evaluated by the formula,

$$I = ZS^* n^*. \quad (6)$$

In this equation, Z is the rate of migration of atoms across the interface between the liquid and the embryo; S^* and n^* are respectively the surface area and the number density of critical nucleus. By applying the absolute rate theory,²⁶⁾ the nucleation rate can be written, for example, as

$$I = n \frac{k_B T}{h} \exp\{-(\Delta G_{\text{mig}} + \Delta G^*) / k_B T\}. \quad (7)$$

In this equation, n is the number density of atoms; $k_B T / h$ (h : Planck’s constant) is the frequency factor; ΔG_{mig} is the activation Gibbs free energy for the migration of atom from liquid to crystal (embryo) across the interface. The condition of nucleation for the sample of volume V and the observation time, t , is written, for example, as $IVt = 1$.

It is easy to find that for smaller ΔT and larger r^* the nucleation rate is extremely small. Therefore, it is practically impossible to observe the nucleation of such embryos during our observation time, namely $IVt \ll 1$. If the ΔT exceeds over some critical value, the I increases suddenly to a extremely large value. This process is too steeply increasing and the I in this period is almost impossible to be measured ($IVt > 1$). These tendencies can be understood from eqs. (2), (4), and (7). The narrow range of ΔT for this sudden increase of I can be defined as the nucleation (supercooling) temperature.²⁾ The supercooling corresponding to this nucleation (supercooling) temperature is called as the maximum or limiting supercooling. This limiting supercooling has been found to be reproducible for the precise homogeneous nucleation experimnts.

To explain qualitatively the composition dependence of supercooling of Ni-Nb system, we adopt the Chalmers’ discussion for the existence of the nucleation (supercooling) temperature. With the progress of supercooling, ΔT , we can observe embryos of larger size. The r_0 is defined as the maximum radius of such observable embryos. Thus, with the progress of supercooling, ΔT , the value of r_0 may increase. In Fig. 6 is shown the Chalmers’ diagram,²⁾ in which both the relations, $\Delta T - r^*$ (eq. (3)) and $\Delta T - r_0$ (plotted by solid-dotted line), are shown together. The existence of nucleation (supercooling) temperature can be understood concisely from this diagram. In Fig. 6 is also shown another curve, $\Delta T - r_0'$ (plotted by dotted line). However, at first we concentrate our discussion on two curves, $\Delta T - r^*$ and $\Delta T - r_0$ (plotted by solid-dotted line). It should be noted that the relation, $\Delta T - r_0$, is written only for some given experimental condition, such as sample size, cooling rate, and observation time. It should be also noted that this $\Delta T - r_0$ relation contains no effect of concentration fluctuations found for eutectic liquids.^{17,21–24)} The intersecting point of these two relations is $(\Delta T_N, r_N)$, where ΔT_N and r_N are respectively the supercooling and the radius of embryo at the onset of nucleation. In other words, the required condition for the homogeneous nucleation under the given condition is that the radius of embryo is larger than r_N or the ΔT is larger than ΔT_N , depending on the parameters we note.

Here, the domains of concentration fluctuations around the x_e discussed above for liquid eutectic alloys may be considered to play a role of “spontaneous embryo” in the homogeneous nucleation process. Then, it is plausible that the radius of domain of concentration fluctuations, r_{cc} , is the

largest at the x_e with the largest ϕ_c . On the other hand, the r_{cc} may be smaller with the decrease of ϕ_c in the composition range apart from the x_e . In Fig. 6, if r_{cc} is larger than r_N (point A), the condition of nucleation is already established. Therefore, the supercooling may disappear for this r_{cc} in the extreme case. If the r_{cc} is considerably large (line B-B'-B'') in the composition range near the x_e , the condition of nucleation is satisfied only partially. Therefore, the supercooling, ΔT corresponding to B'-B'' in Fig. 6, must be established by the progress of supercooling. Thus, the suppression of supercooling appears. In the composition range far apart from the x_e , there exist almost no concentration fluctuations. The establishment of ΔT_N must be realized only by the progress of supercooling. In this situation, the suppression of supercooling does not appear, as can be seen in the composition range far apart from the x_e , such as Ni-30% and Ni-70% Nb in Figs. 3 and 4. In this way, as a function of composition, the "V shape" of supercooling can be explained by the "Λ shape" of concentration fluctuations. In Fig. 6 the suppression of supercooling can be explained by the introduction of $\Delta T - r_0'$ (plotted by dotted line), which includes the solid like embryos derived from the concentration fluctuations. Because of the effect of concentration fluctuations, the curve, $\Delta T - r_0'$ (plotted by dotted line) is situated in the lower ΔT side compared with the relation, $\Delta T - r_0$ (plotted by solid-dotted line). The nucleation (supercooling) temperature, $\Delta T_N'$, which is obtained as the ΔT of the intersecting point between two relations, $\Delta T - r^*$ and $\Delta T - r_0'$ (plotted by dotted line), is smaller than ΔT_N , which corresponds to the case of no concentration fluctuations. Therefore, the suppression ("V shape") of supercooling may occur due to the existence of concentration fluctuations ("Λ shape").

As described above, the characteristic feature of present experiment, the poor supercooling tendency of homogeneous liquid phase around the eutectic composition was explained by the classical nucleation theory. This seems to give a strong support for the existence of concentration fluctuations in the homogeneous liquid phase around the eutectic composition. Finally we mention the relation between the present poor supercooling tendency of homogeneous liquid phase around the eutectic composition and the traditional selection of the eutectic composition range as the candidate with high glass forming ability.¹⁶⁾ Except for the bulk metallic glass, the preparation of metallic glass has been performed by the rapid quenching method of very fast cooling rate. Under this cooling condition, the effect of the loss of fluidity is more dominant than the nucleation effect. Probably, the effect of poor supercooling of homogeneous liquid phase around the eutectic composition seems to be important for the glass formation by the slower process.

5. Conclusions

The supercooling was found to be very poor for the homogeneous liquid phase around the eutectic composition of Ni-Nb system. This may be a strong evidence for the existence of concentration fluctuation in the homogeneous liquid phase around the eutectic point.

REFERENCES

- 1) D. Turnbull: *J. Appl. Phys.* **21** (1950) 1022–1028.
- 2) B. Chalmers: *Principles of Solidification* (Wiley, 1964).
- 3) D. E. Polk and B. C. Giessen: *Metallic Glasses*, ed. by J. J. Gilman and H. J. Leamy, (American Society of Metals, 1978) pp. 1–35.
- 4) B. Vonnegut: *J. Colloid Sci.* **3** (1948) 563–569.
- 5) J. H. Perepezko: *Mater. Sci. Eng.* **65** (1984) 125–135.
- 6) G. Devaud and D. Turnbull: *Acta Metall.* **35** (1987) 765–769.
- 7) W. H. Hofmeister, M. B. Robinson and R. J. Bayuzick: *J. Appl. Phys.* **49** (1986) 1342–1344.
- 8) B. Vinet, L. Cortella, J. J. Favier and P. Desre: *J. Appl. Phys.* **58** (1991) 97–99.
- 9) G. J. Abbaschian and M. C. Flemings: *Met. Trans.* **14A** (1983) 1147–1157.
- 10) I. Egry, G. Lohöher, I. Sehan, S. Schneider and B. Feuerbacher: *J. Appl. Phys.* **73** (1998) 462–463.
- 11) T. Ishikawa, P.-F. Paradis, T. Itami and S. Yoda: *J. Chem. Phys.* **118** (2003) 7912–7920.
- 12) T. Ishikawa, P. F. Paradis, T. Itami and S. Yoda: *Meas. Sci. Technol.* **16** (2005) 443–451.
- 13) K. F. Kelton and G. D. Gangopadhyay: *Int. Centre for Diffraction Data 2005, Advances in X-ray Analysis* **48** (2005) 1–13.
- 14) M. C. Flemming and Y. Shiobara: *Mat. Sci. Eng.* **65** (1984) 157–170.
- 15) J. H. Perepezko and J. S. Paik: *Rapidly Solidified Amorphous and Crystalline Alloys*, ed. by B. H. Kearns, B. C. Giessen and M. Cohen, (Elsevier Science Publishing Co. Inc., 1982) pp. 49–63.
- 16) H. S. Chen: *Metallic Glasses*, ed. by J. J. Gilman and H. J. Leamy, (American Society of Metals, 1978) pp. 1–35.
- 17) T. Itami, H. Aoki, T. Shibata, M. Ikeda and K. Hotoduka: *J. Non-Cryst. Solids* **353** (2007) 3011–3016.
- 18) J. H. Perepezko, D. H. Rasmussen, I. E. Andersen and C. R. Loper: *Proc. Conf. on Solidification and Casting of Metals*, ed. by A. Hellawell and J. O. Ward (Session3), (Metals Society, London, 1979) pp. 169–174.
- 19) K. P. Cooper, I. E. Andersen and J. H. Perepezko: *Proc. 4th Int. Conf. on Rapidly Quenched Metals*, ed. by T. Masumoto and K. Suzuki, (Japan Institute of Metals, Sendai, 1982) pp. 107–110.
- 20) ASM International Binary Alloy Phase Diagram (on CD-ROM: 2nd ed. Plus Updates Version 1.0), (The Materials Information Society, 1996).
- 21) H. Aoki, T. Shibata and T. Itami: *J. Phys. Condens. Matter* **11** (1999) 10315–10322.
- 22) M. Ikeda, T. Shibata, H. Aoki and T. Itami: *J. Non-Cryst. Solids* **312–314** (2002) 217–221.
- 23) H. Aoki, K. Hotoduka and T. Itami: *J. Non-Cryst. Solids* **312–314** (2002) 222–226.
- 24) Y. Nakagawa and T. Itami: *Mater. Trans.* **46** (2005) 1794–1797.
- 25) T. Okubo and Y. Hirotsu: *Phys. Rev. B* **67** (2003) 09420(1–9).
- 26) S. Glasstone, K. J. Laidler and H. Eyring: *The Theory of Rate Processes*, (McGraw-Hill Book Company Inc., New York, 1941).