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Microgravity Conditions and Electrical Resistivity of Liquid Alloys with Critical Mixing[1]

T. Itami,[2,3] T. Masaki,[2] K. Kuribayashi,[4] E. Sato,[4] M. Hinada,[4]
M. Yamashita,[4] and K. Kawasaki[5]

The phenomena of two-liquid phase separations are significantly influenced by the gravity on the ground because of the difference in the densities of the constituent components, particularly, in the case of liquid alloys with critical mixing. In this paper, experimental techniques and results are reported for the measurements of the electrical resistivity for typical liquid alloys with critical mixing, such as Bi-Ga, under microgravity by the use of a rocket S520-19 belonging to ISAS (Institute of Space and Astronautical Science, Japan). It was found that the temperature coefficient of the electrical resistivity, on cooling of the homogeneous liquid phase, increases with the approach to the critical temperature. This trend under microgravity by the rocket experiment is more pronounced compared to the trend of the reference experiment on the ground. In addition, the supercooling of homogeneous liquids under microgravity is larger than that on the ground. These differences are explained by the difference in the degree of the growth of concentration fluctuations; the concentration fluctuations are far greater under microgravity than on the ground. Therefore, it is found to be very important to study the process and the critical phenomena of two-liquid phase separations under microgravity. Measurement of electrical resistivity is an effective method to obtain informations about the process, the critical phenomena, and the supercooling of two-liquid phase separations in liquid alloys with critical mixing.

KEY WORDS: critical mixing; electrical resistivity; microgravity; spinodal; supercooling; two-liquid phase separation.

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[2] Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan.

[3] To whom correspondence should be addressed.

[4] Institute of Space and Astronautical Science, Sagamihara 229, Japan.

[5] Nissan Motor Company, Ltd., Tokyo 167, Japan.

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1. INTRODUCTION

An accurate knowledge of electrical resistivity, ρ, in liquid materials is important in technical applications, particularly related to flow control by electromagnetic force in the process of refining and crystal growth of semiconducting materials. Electrical resistivity also plays an important role in the use of the electromagnetic levitation technique. In addition, in the case of liquid alloys with critical mixing, measurements of ρ can be a measure of concentration fluctuations which become appreciable near the critical point in the homogeneous liquid phase. In many cases, liquid alloys with two liquid phases may be composed of constituents, whose electrical resistivity, ρ, differs considerably from each other. Therefore, there may be liquid domains of high ρ and those of low ρ even in the homogeneous liquid phase near the critical point. The appearance of this state with large fluctuations with the approach to the critical point can be detected by the change of electrical resistivity, ρ, its temperature dependence, $d\rho/dT$ (for temperature variation), and its pressure coefficient, $d\rho/dP$ (for pressure variation).

In general, the densities of constituents for liquid alloys with critical mixing are considerably different from each other. As a result, the critical phenomena and the process of two-liquid phase separations may be greatly influenced by the gravity induced convection in a laboratory experiment on the ground. In other words, the essential feature of the critical phenomena and the process of two-liquid phase separations may be clarified only under microgravity conditions with no convection. Also from this point of view, it is very important to measure ρ of liquid alloys with critical mixing as a function of composition, X, accurately under microgravity.

In this paper, experimental results are reported for the temperature dependence (T dependence) of ρ for liquid Bi–Ga alloys on cooling under microgravity conditions in a rocket. The discussion of this T dependence was given in the form $(d\rho/dT)/\rho$. The critical composition, X_c, and the critical temperature, T_c, of this system are Bi–70 at % Ga and 535 K, respectively; the two-liquid phase appears in the concentration range between Bi–38.5 at % Ga and Bi–91.5 at % Ga in the temperature range between 495 and 535 K. In addition to this rocket experiment, the ρ of this system was measured on the ground using the same apparatus as that of the rocket experiment, as a reference experiment.

2. EXPERIMENTAL PROCEDURE

The ρ of liquid Bi–Ga alloys was measured during the cooling process from the homogeneous liquid phase at 573 K to the two-liquid phase below

493 K both under microgravity ($0g_0$) and on the ground ($1g_0$). The microgravity experiment was performed in the S520-19 rocket belonging to the ISAS (Institute of Space and Astronautical Science, Japan) on January 29, 1995. This experiment was conducted as the project ELM-II (Electrical Resistivity of Liquid Metals-II). The level of gravity during the parabolic flight was below $10^{-2}g_0$.

The fundamental design of the present rocket experiment, ELM-II, was almost the same as that of the previous rocket experiment, ELM-I [1], except for some improvements. The experimental assembly [300 mm (length) × 300 mm (width) × 80 mm (depth)] loaded onto the S520-19 rocket was composed of three parts: an electronic circuit (EC), a cell (CELL), and a power supply (PS). Four samples in respective metallic Ti cells were contained in the CELL. Thirty series-connected Ni–Cd batteries were contained in the PS to supply electricity to the EC. The EC is an electronic circuit for measuring resistivities of the four samples, four standard resistances (0.1 Ω), and Pt resistance thermometers by the dc four-probe method. Ohmic voltages of these resistances due to the supplied direct current of both normal and inverse directions were amplified into dc 1- to 5-V signals respectively by the operational amplifiers. The analogue data of these voltages were converted into serial data via an analogue multiplexer and were transmitted as digital data to the operation room on the ground by the telemetry. These real-time data were stored on the ground as serial digital data on magnetic tape and the memory of a microcomputer. The electrical resistivity, ρ, of liquid Bi–Ga alloys was determined from these ohmic voltages by considering that the cell containing liquid Bi–Ga alloy is equivalent to the parallel circuit composed of metallic Ti tube and metallic liquid Bi–Ga sample. Resistance of the empty Ti tube was measured independently before the experiment.

The temperature of the samples was measured with a Pt resistance thermometer, which was placed near the side wall of the cell at the middle position in the long direction. Titanium metal was used as the cell material because of its very low reactivity to liquid Bi–Ga alloys. The cell design is shown in Fig. 1. On one end of the capillary, a diaphragm structure was attached to accommodate the volume change of the sample due to melting, heating, cooling, and solidification processes. The other end was closed by welding after the placement of the sample. Once the samples were solidified, it was difficult to obtain homogeneous liquids in a narrow capillary of the Ti cell by a simple procedure, that is, by melting and keeping the sample at a high temperature. Therefore, the interface of the two solidified phases ("Bi rich" and "Ga rich") in a capillary was kept parallel to the long direction of the capillary so that the interface area was as large as possible. The adoption of this configuration was sufficient

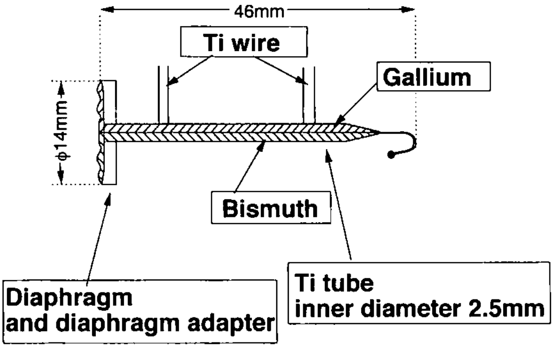

Fig. 1. Schematic diagram of the Ti cell.

to obtain homogeneous liquids in a capillary by keeping samples at 723 K for 1 h.

Until just prior to the launch of rocket, the temperature of the sample was kept at about 773 K for 1 h and the adjustments of thermal insulation condition around cells enabled us to obtain the desired temperature pattern on cooling from the homogeneous liquid at about 583 K to a two-liquid phase below 493 K during the microgravity period (5 min). As can be seen in Fig. 2, the cooling patterns for all four cells were satisfactory. The composition of the four samples loaded on the rocket was, respectively, Bi–58 at % Ga, −62 at % Ga, −71 at % Ga, and −74 at % Ga.

Just prior to the launch of the rocket, the reference data were obtained on the ground by employing the same experimental apparatus as that of the present rocket experiment ELM-II. This experiment on the ground

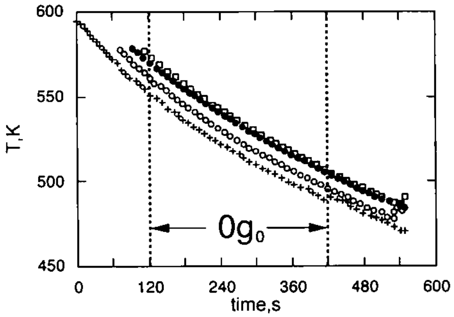

Fig. 2. The temperature variation of four Ti cells containing liquid Bi–Ga alloys during cooling in the rocket experiment, ELM-II. $0g_0$ indicates the duration of microgravity.

plays the role of the reference experiment ($1g_0$), which is compared with the present rocket experiment ELM-II ($0g_0$). Hereafter, this experiment on the ground is referred to as the "reference experiment."

3. RESULTS

The measured values of ρ and $d\rho/dT$ from the reference experiment were in good agreement with the results of precise measurements performed previously in the "laboratory" on the ground by using the glass cell [1], which is referred to as the "laboratory experiment." The differences between the reference experiment and the laboratory experiment were within 3% for ρ and 10% for $d\rho/dT$.

Figure 3 shows a typical example of the change of ρ on the cooling process for the present rocket experiment, ELM-II, and its reference experiment of Bi–71 at % Ga alloy. The ρ itself decreases for both the rocket experiment and the reference experiment with decreasing temperature down to the binodal temperature, T_b. In Fig. 3, the vertical arrow indicates the onset temperature of the two-liquid phase separation, T_{sep}; below T_{sep} on cooling the two-liquid phase separation started. T_{sep} itself was determined to be the temperature from which the deviation of ρ on cooling from the curve of ρ in the homogeneous liquid phase started, as indicated by the vertical arrow in Fig. 3. The value of T_{sep} depended slightly on the adopted forms of ρ as a function of T, which were employed to represent the experimental T dependence of ρ in the homogeneous liquid phase in the high temperature range; in this way T_{sep} was determined within a precision

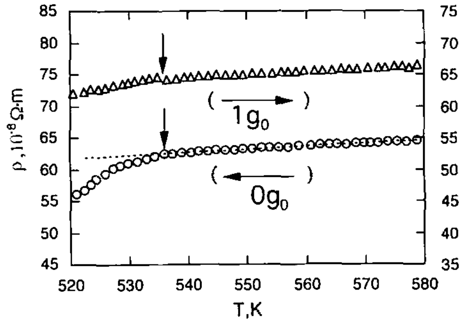

Fig. 3. The electrical resistivity, ρ, of the liquid Bi–71 at % Ga alloy. The vertical arrow indicates the onset temperature of two-liquid phase separations and the horizontal arrow indicates the vertical axis to be referred. $0g_0$, under microgravity (ELM-II); $1g_0$, reference experiment on the ground (Ti cell).

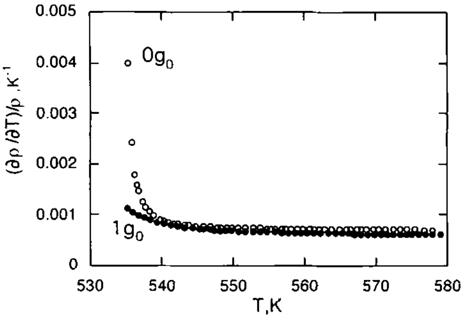

Fig. 4. The temperature dependence on cooling of the ratio, $(d\rho/dT)/\rho$, of the temperature coefficient of electrical resistivity, $d\rho/dT$, to the electrical resistivity, ρ, of the liquid Bi 71 at % Ga alloy. $0g_0$, under microgravity (ELM-II); $1g_0$, reference experiment on the ground (Ti cell).

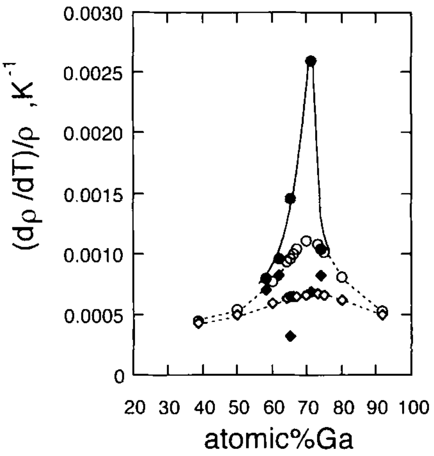

Fig. 5. The concentration dependence of the ratio, $(d\rho/dT)/\rho$, of the temperature coefficient of electrical resistivity, $d\rho/dT$, to the electrical resistivity, ρ, under microgravity by the present ELM-II experiment (Bi 58 at % Ga, −62 at % Ga, −71 at % Ga, and −74 at % Ga), the previous ELM-I (Bi 65 at % Ga) experiment, and the laboratory experiment on the ground (glass cell). (○) Laboratory experiment (glass cell) on the ground at 535 K; (◇) laboratory experiment (glass cell) on the ground at 553 K; (●) rocket experiment under microgravity at 535 K; (■) rocket experiment under microgravity at 553 K.

of 0.2 K. The condition $T_b = T_{sep}$ holds for the liquid Bi–71 at % Ga alloy, whose composition is very close to the critical composition, X_c, though the condition $T_{sep} < T_b$ holds for liquid Bi–Ga alloys around X_c, as described in the next section. In the homogeneous temperature range, $T > T_b$, ρ decreases similarly both for the ELM-II experiment and the reference experiment, and the difference was observed only in the temperature dependence, $d\rho/dT$ [or $(d\rho/dT)/\rho$], as described below.

Figure 4 shows the ratio of the temperature coefficient of ρ, $d\rho/dT$, to ρ itself on the cooling process for the homogeneous liquid phase of Bi–71 at % Ga alloy obtained in the present rocket experiment, ELM-II, and the reference experiment. In this paper, the form $(d\rho/dT)/\rho$ was selected for the discussion of the temperature dependence of ρ instead of the form $d\rho/dT$. This selection is based on the fact that, as described in the previous paper [1], a considerably symmetrical concentration dependence of $(d\rho/dT)/\rho$ was obtained around X_c for the laboratory experiment of liquid Bi–Ga alloys (see also Fig. 5), though the dependence of $d\rho/dT$ itself is unsymmetrical. The $(d\rho/dT)/\rho$ under $0g_0$ is far larger than that under $1g_0$, particularly near T_b. The increasing tendency of $(d\rho/dT)/\rho$ under $0g_0$ starts at a higher temperature on cooling than that under $1g_0$.

4. DISCUSSION

The increase in $(d\rho/dT)/\rho$, namely the increase in decreasing tendency of ρ on cooling, with the approach to T_b (or T_c) in a homogeneous liquid phase may be caused by the growth of fluctuations, in which the size of domains of high ρ (Bi rich) and low ρ (Ga rich) grow even in the homogeneous liquid phase. In principle, the scattering theory of electrons in condensed matter must be applied to analyze this increase of decreasing tendency of ρ with the growth of the size of these domains on cooling down to T_b (or T_c) in a homogeneous liquid phase. However, at present such an analysis is difficult, and only a simple qualitative explanation can be given here. As described above, there exist many domains of high ρ (Bi rich) and low ρ (Ga rich) even in a homogeneous liquid phase near T_b (or T_c) of liquid Bi–Ga alloys. From the view point of percolation theory [2], electrons in such liquid alloys may move on the pass of low resistivity, and as a result, ρ decreases or at least the $d\rho/dT$ [or $(d\rho/dT)/\rho$] increases with the increase in fluctuations in the homogeneous liquid phase. The increase in $(d\rho/dT)/\rho$ on cooling, shown in Fig. 4, may be closely related to this growth of concentration fluctuations. The difference between the behavior of $(d\rho/dT)/\rho$ under $0g_0$ and that under $1g_0$ indicates that the concentration fluctuations in the homogeneous liquid phase (above T_c) grow more stably under $0g_0$ than $1g_0$ because of the lack of convection. The reason for this is given below. These concentration fluctuations finally grow into the two liquid phase separation below T_h (or T_c).

In this paragraph, the two-liquid phase separation is discussed for liquid mixtures with an upper critical point, such as Bi–Ga alloys. In the case of liquid mixtures with a lower critical point, discussions in this paragraph should be inversed, as described in the parentheses. From the thermodynamics point of view, the growth of fluctuations is preferred in the supercooled state and is not preferred in the homogeneous liquid phase. It is well-known that the most concise model for the two-liquid phase separation is the regular solution model [3], whose validity can be confirmed by the Bragg–Williams approximation [4] on the statistical thermodynamics theory from the microscopic point of view. According to this regular solution model, the free energy of mixing as a function of composition, X, shows the minimum at X_c (1:1 composition for this regular solution model) in binary mixtures for $T > T_c (T < T_c)$, that is, for the temperature range of the homogeneous liquid phase. On the other hand, it shows the maximum at X_c and two minima in the concentration ranges $X < X_c$ and $X > X_c$ around X_c for $T < T_c (T > T_c)$, that is, for the temperature range of the two-liquid phase. From a general view point of critical phenomena, the composition, X, corresponds to the order parameter, Φ, in the case of two-liquid (or -solid) phase separation in binary mixtures and a behavior similar to that described above can be assumed for the free energy as a function of Φ [5], that is, one minimum at Φ_c for $T > T_c (T < T_c)$ and one maximum at Φ_c and two minima in the range $\Phi < \Phi_c$ and $\Phi > \Phi_c$ for $T < T_c (T > T_c)$. Therefore, fluctuations in the homogeneous liquid increase the free energy. On the other hand, fluctuations in the supercooled liquids of the composition near X_c decrease the free energy. Inversely, to establish the minimum of the free energy, the presence of collisions among domains due to convection in the liquid near X_c suppresses the growth of concentration fluctuations in the homogeneous liquid phase above (below) T_c. On the other hand, in the supercooled state below (above) T_c, the presence of such collisions enlarges fluctuations and, as a result, accelerates the two-liquid phase separation. In the latter supercooled state, the stability condition works in spite of the presence of the minimum condition of the free energy [2]. By this stability condition, homogeneous liquids at $T < T_c (T > T_c)$ are classified into two categories, the metastable state and the unstable state. Both states are non-equilibrium states and tend to change toward the equilibrium two liquid phase state.

Figure 5 shows the concentration dependence of $(dp/dT)/p$ of the present rocket experiment ELM-II together with that of the previous rocket experiment ELM-I. This figure includes the $(dp/dT)/p$ of the laboratory experiment, in which, as already described, ρ of liquid Bi–Ga alloys was investigated precisely as a function of composition in a laboratory on the ground by using the glass cell. The details of this laboratory experiment were described elsewhere [1]. The concentration dependence of $(d\rho/dT)/\rho$, in Fig. 5, shows the maximum at X_c for both the present ELM-II experiment and the laboratory experiment. In addition, the $(d\rho/dT)/\rho$ of the present ELM-II is well situated on the isotherm of the laboratory experiment on the ground at 553 K, which is a far higher temperature than T_c, and it becomes far larger than that with the approach to T_b, 535 K, particularly near X_c.

The $(d\rho/dT)/\rho$ of the previous ELM-I at 553 K is also well situated on the isotherm drawn by the present ELM-II experiment and the laboratory experiment. A smaller value was found for $(d\rho/dT)/\rho$ of ELM-I at 535 K compared with these experiments. This discrepancy was due to the insufficient accuracy of the ρ measurement for ELM-I and is not distinct at temperatures very close to T_b, such as 535 K, because of the large temperature dependence of ρ. However, this insufficient accuracy brought a larger error at a higher temperature, such as 553 K, into $(d\rho/dT)/\rho$ of ELM-I because of the small temperature dependence of ρ in this temperature range. As already described, $d\rho/dT$ or $(d\rho/dT)/\rho$ is found to be a very good measure for detecting the concentration fluctuations near the critical point. The maximum tendency of $(d\rho/dT)\rho$ at T_c reflects the maximum tendency of the growth of concentration fluctuations near X_c in the homogeneous liquid phase. In addition, the degree of concentration fluctuations is far larger under microgravity than on the ground, particularly near T_c, as discussed in relation to Fig. 4.

As for the behavior of ρ itself, a slight difference appears below T_b (535 K) between the $1g_0$ experiment and the $0g_0$ experiment. In the case of $0g_0$, ρ on cooling decreases continuously down to temperatures considerably below T_b (supercooled state) and then the change of behavior of ρ appears at T_{sep} with the onset of the two-liquid phase separation. On the other hand, ρ, on cooling under $1g_0$, changes the slope at T_b or at a temperature very close to it. The difference between T_{sep} and T_b corresponds to the degree of supercooling of the homogeneous liquid phase. Therefore, the supercooling is almost-zero or very small under $1g_0$. On the other hand, under $0g_0$, a supercooling of a few Kelvins, which is larger than that under $1g_0$, was observed for liquid Bi–Ga alloys except for liquid Bi–71 at % Ga alloy, whose composition is very close to X_c and whose behavior of ρ is shown in Fig. 3.

Greater undercooling under $0g_0$ was obtained for Bi–65 at % Ga alloys in the previous ELM-1 experiment [1]. In the previous ELM-I experiment [1] a cell made of stainless steel was employed. A slight corrosion took place when this cell material (stainless steel) came in contact with the liquid Bi–Ga alloys. Measurements of ρ and $(d\rho/dT)/\rho$ did not suffer from this problem. However, the supercooling is sensitive to this corrosion problem; this sensitivity may be caused by the effect of the surface condition of the cell materials. The wettability of the sample with the wall material of the cell may be increased by the slight chemical reaction. In the case of ELM-II, almost no chemical reaction was detected between the Ti cell and liquid Bi–Ga alloys. Because of this difference, only the data for ELM-II are included in Fig. 6. The difference between the undercooling under $0g_0$ and that under $1g_0$ indicates that the concentration fluctuations near the critical point are more stable under $0g_0$ with no convection than under $1g_0$ with gravitational convection. The gravitational convection below T_c under $1g_0$ accelerates the growth of fluctuations and resulted in two-liquid phase separations, as discussed above.

Figure 6 shows the comparison of concentration dependence of the observed T_b and the observed T_{sep} under $0g_0$ (ELM-II) and $1g_0$ (laboratory experiment and reference experiment). The degree of supercooling is rather large in the concentration range around X_c and almost-zero at X_c for both the $0g_0$ experiment and the $1g_0$ experiment [1]. This concentration dependence of supercooling reminds us that the temperature difference, ΔT, between the binodal temperature T_b and the spinodal

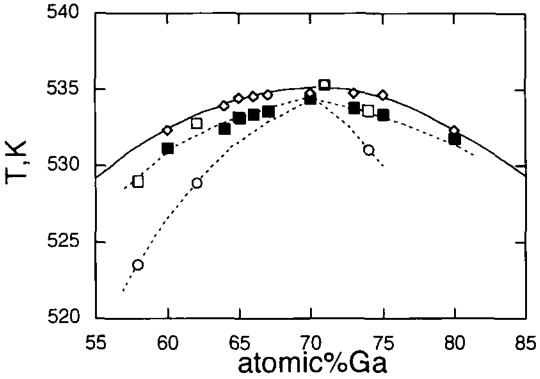

Fig. 6. The concentration dependence of the binodal temperature, T_b, and the onset temperature of two-liquidphase separations, T_{sep}, for liquid Bi Ga alloys. (○) T_{sep} under microgravity (ELM-II); (□) T_{sep} by the reference experiment (Ti cell) on the ground; (■) T_{sep} by the laboratory experiment (glass cell) on the ground; (◇) T_b by the laboratory experiment (glass cell) on the ground.

temperature T_{sp}, also shows a similar concentration dependence, that is, ΔT ($=T_b-T_{sp}$) is zero at X_c and larger in the concentration range around X_c; both T_b and T_{sp} can be predicted theoretically, for example, by the regular solution model [6]. In the temperature range between T_b and T_{sp}, the homogeneous liquid is metastable and the maximum of supercooling can be expected to be ΔT.

This resemblance may indicate that the two-liquid phase separation in liquid Bi–Ga alloys close to X_c may be closely related to the mechanism of spinodal decomposition rather than the nucleation process. This is a rather well-known fact for two-liquid phase separation near X_c [7], though, as far as the authors know, the previous data on supercooling of the homogeneous phase for liquid binary mixtures with critical mixing was taken only in one range of concentrations X, around the critical composition, X_c, that is, $X<X_c$ or $X>X_c$ [8]. There are some features from which the present observation of supercooling by rocket and laboratory experiments may suffer a little from the effect of nucleation; the supercooling seems to be affected by the gravity condition and the surface condition of cell materials. However, no supercooling near X_c may support the mechanism of spinodal decomposition in the range very close to X_c. Microgravity, particularly coupled with the containerless technique, is expected to provide an ideal condition for experimental studies of supercooling in liquids and spinodal process in liquids with critical mixing: such experiments are expected to be free of nucleation. The validity of the supercooling experiment under microgravity conditions was shown by the present experimental fact that the degree of supercooling is larger under $0g_0$ than under $1g_0$.

The role of collision between domains was stressed in the discussion presented above. It is possible to discuss the growth of concentration fluctuations only from the diffusion process in the boundary layer of domains. The presence of convection enhances the mass transport of diffusion and keeps the size of domains small. Under this condition, the gravity condition with gravitational convection suppresses the growth of domain size. At $T>T_c$, the small $(d\rho/dT)/\rho$ can be expected in the $1g_0$ condition. However, at $T<T_c$ in the $1g_0$ condition, greater supercooling can be expected because of the slow growth rate of domains, which is in contradiction with the experiments. The collisions among domains may be important.

Thus, the microgravity condition is expected to be used for study of the critical phenomena, the process of two-liquid phase separation, and the supercooling behavior of liquid mixtures and alloys. In addition, the measurement of ρ and $d\rho/dT$ is a very simple and sensitive method for detecting the concentration fluctuations in liquid alloys with critical mixing, particularly under microgravity conditions.

5. CONCLUSIONS

In this paper, experimental techniques and the results of successful measurements of electrical resistivity under microgravity for liquid Bi–Ga alloys are reported. It was shown that microgravity is a favorable condition for the study of the concentration fluctuations in liquid alloys, which play important roles in the critical phenomena, two-liquid phase separations, and supercooling for liquids with critical mixing. The temperature coefficient of electrical resistivity, $d\rho/dT$, was found to be a good indicator for this concentration fluctuations in liquid alloys with critical mixing, particularly under microgravity. The mechanism of electron conduction in liquid alloys with large fluctuations was discussed in a primitive manner based on the percolation theory. In the future, this must be analyzed in a refined manner based on the scattering theory of conduction electrons. From the experimental point of view, to clarify the supercooling behavior and the mechanism of the two-liquid phase separation, supercooling experiments for liquids with critical mixing must be performed under microgravity conditions, if possible, using the containerless technique.

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