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The estimation of concentration fluctuations in liquid Ag-Si and Au-Si alloys

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Abstract

The specific electrical resistivity was measured for liquid states of Ag-Si and Au-Si with deep eutectic points for which the “electron atom ratio” at the eutectic composition is 1.33 and 1.56 respectively. On lowering the temperature, the specific electrical resistivity deviates from the straight line, which was obtained by extrapolating its behavior in the high temperature to the low one. The concentration dependence of this deviation at the liquidus shows the largest value at the eutectic composition. The analysis based on the effective medium theory tells us that the volume fraction of concentration fluctuation in the homogeneous liquid phase is largest at the eutectic composition. The degree of concentration fluctuation was summarized on one systematic trend among metal-semiconductor eutectic systems. It is concluded that the large concentration fluctuation develops in the homogeneous liquid phase of eutectic systems. The possibility of the poor supercooling tendency of homogeneous liquids at the eutectic composition was revealed with relation to this concentration fluctuation.

PACS codes: 61.20.-p; 61.25.-Mv; 72.15.-v; 72.15.Cz; -81.30.-Bx

1. Introduction

Eutectic alloys have attracted much attentions because of low melting temperatures. Since Hume-Rothery and Anderson [1] presented a famous proposal for the existence of icosahedral units in the liquid state of eutectic alloys, many researchers reported anomalous behaviors of physical quantities, especially the specific electrical resistivity and the viscosity. However, these anomalies were denied by the later studies with the advance of experimental techniques [2]. Since then, it has been considered that the eutectic liquid is not abundant in important physical problems but is only a liquid with low melting temperature. However, recently, Aoki et al. [3] found that the temperature coefficient of specific electrical resistivity for the homogeneous liquid state of eutectic $\text{Ga}_{11.8}\text{Sb}_{88.2}$ changes the sign (from positive to negative) with the approach to the eutectic temperature on a cooling process. No anomalous behaviors of specific electrical resistivity and its temperature coefficient in homogeneous liquid phase were observed at the stoichiometric composition, $\text{Ga}_{0.5}\text{Sb}_{0.5}$, which is a compound semiconductor in the solid state. Similar behaviors were found also for the liquid state of In-Sb [4].

If the essential point for this anomalous behavior is present in the fact that these systems are metal-semiconductor systems, more striking anomaly can be expected for “deep eutectic systems” composed of noble metal element and semiconductor one, such as Au-Ge and Au-Si, whose eutectic temperatures are far lower (“deeper”) than the melting temperatures of constituent elements. Generally, the particular feature of atomic correlations in liquids can be observed weakly at the high temperature because of the increase of atomic thermal energy and entropy effect. It can be easily expected that the anomalous atomic correlations can be conspicuous in low temperature liquids, such as “deep eutectic liquids”.

As for the particular feature of eutectic liquids, Popel [5] showed the indication for the existence of microscopic domains of 1~100nm, which is enriched with one of components, in molten eutectics and monotectics. This appears only after the melting of heterogeneous initial

ingot. In his paper, a small angle neutron scattering (SANS) of M. Carvo-Dahlborg et al. [6] was introduced as an evidence for the existence of such domains. By a study using a high-resolution electron microscopy, Okubo and Hirotsu [7] found a nanoscale atomic ordering of fcc-Pd type in the rapidly quenched amorphous alloy of $\text{Pd}_{82}\text{Si}_{18}$, which is very close to the eutectic composition. With the aid of Reverse Monte Carlo analysis, they presented a model, in which a fcc-cluster region, or a nanoscale phase-separation, is embedded in a dense random packing of Pd and Si. This study may indicate an evidence for the existence of concentration fluctuations derived from a microscopic pre-solidification in the homogeneous liquid phase of eutectic alloys.

In a previous study [8], the specific electrical conductivity was measured for liquid Au-Ge and Ag-Ge alloys. A large negative temperature coefficient of specific electrical resistivity was observed particularly in liquid Au-Ge alloys. However, it has been sometimes mentioned that the negative temperature dependence appears on the condition that the electron atom ratio (EAR), which is a number of conduction electrons per atom, is 2 [9]. The values of EAR at the eutectic composition for Ga-Sb and In-Sb systems are 4.76 and 4.36 respectively, which are far apart from this criterion, $\text{EAR}=2$. However, the EAR for liquid Au-Ge and Ag-Ge alloys are close to this criterion, namely 1.78 and 1.84 respectively. It is important to investigate the temperature dependence of specific electrical resistivity also for liquid Ag-Si and Au-Si alloys, whose EAR's at the eutectic composition are 1.33 and 1.56 respectively. By performing this study, concentration fluctuations can be studied freely from the criterion, $\text{EAR}=2$.

The purpose of this study is to investigate the specific electrical resistivity of liquid Ag-Si and Au-Si alloys around the eutectic composition as a function of composition and to discuss the concentration fluctuations in homogeneous liquids of metal-semiconductor eutectic systems.

2. Experimental

The specific electrical resistivity of liquid Ag-Si and Au-Si alloys, whose eutectic compositions are 89 at.% Ag and 81.4 at.% Au respectively, was measured by a dc-four probes method. The concentration range studied was around the eutectic composition, 80~100 at.% Ag for Ag-Si and 50~100 at.% Au for Au-Si. The specific electrical resistivity was measured by using an U type quartz cell, which was put in an electric furnace of maximum temperature 1903 K. This furnace can rotate. The Ar gas purge enabled us to keep the O₂ concentration of furnace atmosphere low. The U type cell, whose design was described elsewhere [3], was composed of a capillary part (a), two quartz tubes (b) as a sample reservoir part (which is connected by the capillary part (a) like U shape), and sample inlet port (c). Two W electrodes and the small glass tube (d) were inserted into two quartz tubes (b) in terms of the graphite plug. The temperature of sample was measured by two sheathed chromel-alumel thermocouples, which were inserted tightly to the small glass tubes (d). The U type cell enabled us to remove gas bubbles in liquid samples very easily at the high temperature by rotating the furnace. This was very effective to improve the accuracy of measurements. The present configuration of thermocouples, which were immersed in liquid samples in terms of small glass tubes (d), made the temperature measurements of liquid sample very accurate.

Measurements of specific electrical resistivity on cooling down to the liquidus were performed from 1430 K for Ag-Si and from 1480 K for Au-Si respectively. The sample atmosphere was kept to be same as that of the furnace in terms a small leak hole. The metals used were 4N for Ag, 5N for Au, and 6N for Si. Weighed amounts of constituent metals were contained in an alumina crucible and were mixed completely in the liquid state over 1740 K (over the melting temperature of constituent elements), which was measured by a thermocouple of Pt-Pt containing 13 % Rh. The fast cooled sample was supplied with resistivity measurements.

The temperature was determined with an error of less than 0.1 % by adopting the special

design of cell described above and by using the calibration, which was performed by using the melting temperature of Sn, Zn, and Sb. The measurements of specific electrical resistivity and its temperature coefficient were performed with an error within $\pm 0.5\%$ and $\pm 0.0005 \mu\Omega\text{cmK}^{-1}$ respectively judging from the reproducibility of measurements. These error bars are almost same as those in previous similar studies for liquid eutectic alloys [3,4,8].

3. Results

Figs. 1 and 2 show respectively the temperature and the concentration dependence of specific electrical resistivity for liquid Ag-Si alloys. If we magnify this temperature dependence, the specific electrical resistivity at the liquidus around the eutectic composition shows a deviation from the line obtained by extrapolating its linear temperature dependence in the high temperature range to the liquidus, as typically shown in the inset of Fig. 1. This deviation was largest at the eutectic composition (89 at.% Ag). The concentration dependence of specific electrical resistivity for liquid Ag-Si alloys is a smooth function of composition, as shown in Fig. 2. Fig. 3 depicts the concentration dependence of temperature coefficient of specific electrical conductivity for liquid Ag-Si alloys. In this concentration dependence, a minimum of temperature coefficient exists at 83 at.% Ag. Figs. 4 and 5 show respectively the temperature and the concentration dependence of specific electrical resistivity for liquid Au-Si alloys. With the increase of temperature, the specific electrical resistivity decreases a little abruptly for eutectic composition (81.4 at.% Au), as shown in Fig. 4. In Fig.5, with the increase of Au composition the specific electrical resistivity decreases moderately and over the eutectic composition it decreases abruptly. Fig.6 indicates that a minimum exists at the eutectic composition (81.4 at.% Au) in the concentration dependence of temperature coefficient of specific electrical resistivity. The temperature dependence of specific electrical resistivity was well expressed by a fourth order polynomial function of temperature. The root mean square

deviation from this polynomial is very small, $0.063 \mu\Omega\text{cm}^{-1}$ for Ag-Si and $0.004 \mu\Omega\text{cm}^{-1}$ for Au-Si. Thus, the error bar of data in Figs. 1~6 was small and within the size of data points.

4. Discussions

In previous papers [3,4,8], we have revealed that with the approach to the eutectic temperature in the homogeneous liquid phase, the concentration fluctuations appear around the eutectic composition. This fact was found based on the change of the sign of the temperature coefficient of specific electrical resistivity [3]. For liquid $\text{Ga}_{11.8}\text{-Sb}_{88.2}$ (eutectic composition), the specific electrical resistivity decreased on lowering the temperature from 1200 K to 920 K; this behavior is metallic due to a positive temperature coefficient. However, on further cooling, it showed a minimum value and finally it increased even in the homogeneous liquid phase. The appearance of this negative temperature coefficient may imply a new physical phenomenon. The order of specific electrical resistivity is metallic. EAR of $\text{Ga}_{11.8}\text{-Sb}_{88.2}$ is far larger than the special value, 2, for the appearance of negative temperature coefficient. Some of present authors [3] succeeded in explaining this change of sign. The microscopic domains of solid $\text{Ga}_{0.5}\text{Sb}_{0.5}$ (semi-conductive phase) like and solid Sb like were assumed to appear as a concentration fluctuation in a homogeneous liquid near the eutectic point; this concentration fluctuation may be derived from some kind of microscopic eutectic pre-solidification. As can be seen in equation (3) shown later in this section, the enhancement or a negative temperature coefficient of specific electrical resistivity occurs with the decrease of volume fraction of homogeneous liquid phase, which was a result of the growth of concentration fluctuations with the approach to the eutectic temperature.

In Fig. 6 the temperature coefficient at the liquidus of specific electrical resistivity shows a minimum with negative value at the eutectic composition (81.4 at.% Au) for liquid Au-Si alloys. On the other hand, for liquid Ag-Si alloys, as shown in Fig. 3, a minimum can be observed at 83 at.% Ag, which is different from the eutectic composition, 89 at.% Ag. However, here we note

the deviation of specific electrical resistivity at the liquidus from the straight line obtained by extrapolating its behavior in the high temperature range to the low one. This deviation, which was explicitly shown in the inset of Fig. 1, was found to be largest at the eutectic composition for liquid Ag-Si. For liquid Au-Si alloys, it was not always possible to obtain a linear temperature dependence of specific electrical resistivity in the high temperature range because of the experimental limitation of measured temperature range. In such cases, the deviation was estimated as the difference between the specific electrical resistivity at the liquidus and that at the temperature where its temperature coefficient is zero (see the inset of Fig. 4). Strictly speaking, this procedure may cause an error on the estimation of this deviation. However, the discussion given here is rather qualitative and we are forced to accept such estimation. As discussed later, this does not cause a serious error. The deviation of specific electrical resistivity for liquid Au-Si alloys shows a maximum also at the eutectic composition. Similar maximum of deviation at the eutectic composition has been found also for liquid Ga-Sb [3,4], In-Sb [4], Ag-Ge [8] and Au-Ge [8] alloys, in which a minimum of the temperature coefficient of specific electrical resistivity also exists at the eutectic composition. Therefore, the homogeneous liquids at the eutectic composition for Ag-Si and Au-Si systems show an anomalous behavior derived from the concentration fluctuations.

On the analysis of anomaly in the present study, it was assumed that the semi-conductive domain (Si like), 1, and the metallic domain (Ag or Au like), 2, were immersed in the homogeneous liquid phase of metallic character, 3 [3,4,8]. This composite system was analyzed by the effective medium (EM) theory of three phases [3], which was derived by extending the EM theory of two phases [10] into the case of three phases.

The same Laplace equation for the electrostatic potential [10] can be obtained both for the problem of “electrostatic field with no electric charge and the uniform dielectric constant” and that of “stationary current problem with uniform electrical conductivity”. Therefore, it is

possible to replace the latter problem by the former one. If the spherical cavity in the medium, m , with conductivity σ_m is immersed by the medium, 1, with conductivity σ_1 , the electric polarization can be written as $E(\sigma_1 - \sigma_m)/(\sigma_1 + 2\sigma_m)$; E : electrostatic field. Then, we consider that this cavity is immersed by the volume fraction average of mediums 1, 2, and 3. It is possible to consider that there is no difference between this immersed cavity part and the surrounding medium if we observe them from their outside. Then, the condition for “zero polarization” (namely, no difference) [10] reduces to the following equation.

$$\phi_1 \left(\frac{\sigma_1 - \sigma_m}{\sigma_1 + 2\sigma_m} \right) + \phi_2 \left(\frac{\sigma_2 - \sigma_m}{\sigma_2 + 2\sigma_m} \right) + \phi_3 \left(\frac{\sigma_3 - \sigma_m}{\sigma_3 + 2\sigma_m} \right) = 0. \quad (1)$$

In this equation, σ_i and ϕ_i are the specific electrical conductivity and the volume fraction of domain i respectively. We consider that the homogeneous liquid phase 3 (metallic) occupies a far larger volume than the semi-conductive domain 1 and the metallic domain 2; that is concentration fluctuations appear only as a small volume fraction. Then, conditions, $\phi_1, \phi_2 \ll \phi_3$, $\sigma_1 \ll \sigma_m$, $\sigma_2 \approx \sigma_m$, and $\sigma_3 \approx \sigma_m$, are held. By noting the relation $\phi_1 + \phi_2 + \phi_3 = 1$ and by using the conditions described above, following equation can be obtained.

$$4\sigma_m^2 + 2(\sigma_2 - 2\sigma_3\phi_3)\sigma_m - 2\sigma_2\sigma_3\phi_3 = 0. \quad (2)$$

This equation yields the relation, $\sigma_m = \sigma_3\phi_3$, or $\rho_m = \rho_3/\phi_3$.

Rewriting this equation by using the notation $\Delta\rho (= \rho_m - \rho_3)$, we obtain

$$\phi_1 + \phi_2 = \frac{\Delta\rho}{\rho_m}. \quad (4)$$

We can estimate the concentration fluctuation, $\phi_1 + \phi_2$, with the knowledge of experimental specific electrical resistivity (as that of effective medium), and its deviation at the temperature considered.

The estimated concentration fluctuations at the liquidus were shown in Figs. 7 and 8 for liquid Ag-Si and Au-Si alloys respectively. This estimation depends on the drawing of ρ_3 line, as shown in the insets of Figs. 1 and 4. The error of this estimation is 5% for Ag-Si system. It is 10% for Au-Si system judging from the data of 86 at.% Au which is the closest composition to the eutectic one among systems for which a straight line can be drawn as ρ_3 . The concentration fluctuations show a maximum at the eutectic composition for both systems.

It is a little strange that such concentration fluctuations appear within a considerably wider temperature range adjacent to the transition temperature. Generally, an effect of concentration fluctuations in the critical phenomena, for example, relating to two liquid phase separation, appears only in the limited temperature range close to the critical point [11]. Popel [5] have already presented the similar question, though he only stated that the reason for this wide temperature range is not clear. Only we can mention about this is that the change of Gibbs free energy of liquid-solid transition (eutectic solidification) is larger than that of liquid-liquid transition (two liquid phase separation). For liquid Ga-Sb [3], the concentration fluctuation prevails in a considerably wide temperature range (17 K) just above the eutectic temperature. The solid-solid separation tendency may be far larger for eutectic Au-Si system with deep eutectic point than the case of Ga-Sb system. The concentration fluctuations may be observed sensitively by microscopic probes, such as SANS, electrical resistivity, compared with the thermodynamic ones, the specific heat, magnetic susceptibility, etc., which has been adopted conventionally for the study of critical phenomena. In addition, under microgravity, such a concentration fluctuation exists in a considerably wide temperature range [12, 13]. The problem, wider fluctuation range, must be discussed further in future.

In a previous study [8], the appearance tendency of concentration fluctuation was discussed for liquid Ga-Sb, In-Sb, Ag-Ge and Au-Ge systems based on the correlation between $\phi_1 + \phi_2$ at the liquidus for the eutectic composition and the parameter $\Delta T / \Delta x^2$; Δx (“composition distance”) and ΔT (“depth of eutectic point”) are respectively the composition and the temperature difference between the eutectic point and the semiconductor phase in the phase diagram [14]. Estimation of $\phi_1 + \phi_2$ in this study for liquid Ag-Si and Au-Si alloys was also included in this correlation, as shown in Fig. 9. The concentration fluctuations for liquid Ga-Sb, In-Sb, Ag-Ge, and Au-Ge alloys are reliable with an almost same error (below 5 %) [8] to the case of present Ag-Si system. The concentration fluctuations are larger with the increase of the depth of the eutectic point, ΔT , and with the decrease of the composition distance, Δx . In this correlation, Δx^2 was adopted as a role of Δx because of a good correlation. In addition, it was adopted partially by considering a suppressing effect of collision each other of concentration fluctuations on their growth; this effect was found in the microgravity experiment [12].

The concentration fluctuations found for liquid eutectic systems should work as the nucleation site on the solidification of homogeneous liquids. Therefore, there is a possibility that the supercooling of homogeneous liquids is absent or small at the eutectic composition. Up to date, such supercooling experiments have been already performed for Bi-Sn [15] and Sn-Pb [16] if we read data in a little different manner from the original paper. Pezerenko et al. [15] performed the supercooling experiment for liquid Bi-Sn by using the differential scanning calorimetry (DSC), in which sample particles were covered by a fused flux to decrease the effect of heterogeneous nucleation as much as possible. They presented the limiting temperature of homogeneous liquids, T_L , on cooling process. In the present study, the degree of supercooling, $\Delta T (= T_m - T_L$; T_m : the melting temperature), was plotted as a function of composition in Fig.10. Obtained degree of supercooling shows a minimum at the eutectic composition. Similar poor tendency of supercooling at the eutectic composition can be shown also for liquid Pb-Sn alloys [16]. The

error of ΔT may be caused by non-equilibrium character of T_L . The concentration dependence of T_L showed the data scattering within 5K for liquid Bi-Sn [15]. Fig.10 indicates that the liquid eutectic alloys seem to have a low supercooling tendency. The experiments of complete homogeneous supercooling, such as containerless experiments, are important to obtain a further evidence for the existence of concentration fluctuations in eutectic liquids.

5. Conclusions

The existence of concentration fluctuation in the homogeneous liquid phase was clarified near the eutectic point of metal-semiconductor eutectic systems. The concentration fluctuations are larger with the increase of the depth of the eutectic point and with the decrease of the concentration distance from the eutectic point to the semiconductor.

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Captions for Figures

Fig. 1 The temperature dependence of specific electrical resistivity, ρ , for liquid Ag-Si alloys. In the inset, the ρ at the eutectic composition was shown in the large scale together with the extrapolated line, ρ_3 , from the high temperature range. $\Delta\rho$ is the deviation of ρ at the liquidus temperature from ρ_3 . Error bar is within the size of data point (see the text).

Fig. 2 The concentration dependence of specific electrical resistivity, ρ , at the liquidus temperature for liquid Ag-Si alloys. The line is the aide for the eye. Error bar is within the size of data point (see the text).

Fig.3 The concentration dependence of temperature coefficient of specific electrical

resistivity, $d\rho/dT$, at the liquidus temperature for liquid Ag-Si alloys. The line is the aide for the eye. Error bar is within the size of data point (see the text).

Fig. 4 The temperature dependence of specific electrical resistivity, ρ , for liquid Au-Si alloys. In the inset, the ρ at the eutectic composition was shown in the large scale. The line corresponds to ρ_3 , which is drawn as ρ at the temperature where the temperature coefficient of ρ was zero. Error bar is within the size of data point (see the text).

Fig. 5 The concentration dependence of specific electrical resistivity, ρ , at the liquidus temperature for liquid Au-Si alloys. The line is the aide for the eye. Error bar is within the size of data point (see the text).

Fig. 6 The concentration dependence of temperature coefficient of specific electrical resistivity, $d\rho/dT$, at the liquidus temperature for liquid Au-Si alloys. The line is the aide for the eye. Error bar is within the size of data point (see the text).

Fig.7 The concentration dependence of concentration fluctuation, $\phi_1+\phi_2$, at the liquidus temperature for liquid Ag-Si alloys. The line is the aide for the eye. Error bar is indicated by the vertical range attached to data points.

Fig.8 The concentration dependence of concentration fluctuation, $\phi_1+\phi_2$, at the liquidus temperature for liquid Au-Si alloys. The line is the aide for the eye. Error bar is indicated by the vertical range attached to data points.

Fig.9 The concentration fluctuation, $\phi_1+\phi_2$, at the eutectic point as a function of $\Delta T/\Delta x^2$ for

metal-semiconductor eutectic systems; Δx : the composition difference between the eutectic point and the semiconductor phase; ΔT : the temperature difference between the eutectic point and the melting point of semiconductor phase. The line is the aide for the eye. Error bar is indicated by the vertical range attached to data points.

Fig.10 The degree of supercooling $\Delta T (=T_m - T_L)$ as a function of composition for Bi-Sn alloys; T_L : the limiting temperature of homogeneous liquids on cooling process [15]; T_m : the melting temperature. The line is the aide for the eye. Error bar is within the size of data point (see the text).



















