

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

Toshio Itami ^{*}, Hirokatsu Aoki, Takeru Shibata, Motoshige Ikeda, Koichi Hotozuka

Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

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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 from high to low temperatures. 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.

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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 homoge-

neous 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

^{*} Corresponding author. Tel./fax: +81 11 706 3532.
E-mail address: itami@sci.hokudai.ac.jp (T. Itami).

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 1–100 nm, 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 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 EARs 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 O_2 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 4 N for Ag, 5 N for Au, and 6 N 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 $\pm 0.0005 \mu\Omega \text{ cm K}^{-1}$, 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

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