Effect of High Pressure on Phase Diagram of Zn–Sn System

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Phase relation of the Zn–Sn system at various pressure up to 7 GPa is investigated by means of isobaric measurement of electrical resistance. Pressure vs. temperature phase diagrams of Zn–91 mol%Sn, Zn–49 mol%Sn and Zn–10 mol%Sn alloys as well as an isobaric phase diagram of the Zn–Sn system at 5 GPa are constructed on the basis of the results. A new eutectoid horizontal caused by the appearance of the high pressure γ phase of tin appears in the phase diagrams. The cross point of the eutectic and eutectoid phase boundaries is 3.9 GPa and 273°C.

An intermediate electron phase with simple hexagonal structure known in many binary alloy systems was not stable in the Zn–Sn system within the present conditions of high pressure and temperature.

In the heating run of temperature vs. electrical resistance curves on the Zn–Sn alloys, a delay of the ending temperature of the reaction at liquidus is observed under high pressures. It is considered to be caused by insufficient interdiffusion of zinc and tin in the liquid phase.

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I. Introduction

The effect of pressure on simple eutectic-type binary phase diagram has been studied with the interest in the change in the eutectic temperature^{(1)–(3)}, eutectic composition⁽⁴⁾ and solubility limit of the terminal phases^{(3)(5)–(7)} as well as the appearance of an intermediate new phase^{(8)–(10)}. The isobaric phase diagram of the Zn–Sn system at atmospheric pressure also has a simple eutectic-type phase relation⁽¹¹⁾. The relation was kept at least up to 3.5 GPa⁽¹⁾. In the case of the Zn–Sn system, however, the terminal element tin forms a triple point of the β -tin, γ -tin (high pressure phase with tetragonal structure) and liquid phases at 3.3 GPa and 310°C⁽¹²⁾. This suggests a notable change in the phase diagram accompanying the phase transformation of the terminal phase in the tin-rich side under high pressure.

Although the Zn–Sn system has no intermediate phase at atmospheric pressure, the phase diagrams of the Cd–Sn, Hg–Sn and In–Sn systems have a stable intermediate phase with the simple hexagonal structure within the electron concentration range (e/a) between 3.82–3.93 at atmospheric pressure⁽¹³⁾. The homology rule for phase transformation⁽¹⁴⁾ also suggests the appearance of an intermediate phase in the Zn–Sn system under pressure.

Most of the phase transformation of alloys in the eutectic-type system occur under interdiffusion of the constituted elements. The diffusion rate is influenced by the pressure⁽¹⁵⁾. Therefore, consideration on the pressure dependence of the phase transformation accompanying the diffusion is important for the construction of the equilibrium phase diagram under high pressure.

In the present study pressure effect on the phase diagram of the Zn–Sn system was investigated up to 7 GPa with the viewpoint of above mentioned problems.

II. Experimental Procedure

The purity of zinc and tin used as the starting material for alloy preparation was 99.998 mass% and 99.999 mass%, respectively. Six kinds of Zn–Sn alloys with tin contents of 10, 30, 49, 70, 91, 95 mol% were prepared by melting them in evacuated quartz ampoules. After alloying they were rolled to thin foils with a thickness of about 30 μm . A part of it was used for electrical resistance measurements and the chemical analysis by means of inductively coupled plasma atomic spectroscopy (AES-ICP) method.

A cubic-type multianvil press was employed for measurement of electrical resistance at high pressure. Leads for measurements of electrical resistance were taken from a pair of side anvils facing each other. The voltage (V) between the leads at a constant current (I (10–30 mA)) was recorded and the electrical resistance was obtained from the ratio V/I . Phase identification was carried out by means of *in-situ* X-ray diffraction method. Other experimental methods were the same as described elsewhere⁽⁴⁾.

III. Results and Discussion

1. Electrical resistance measurements and phase diagrams

The electrical resistance of the Zn–Sn alloys was obtained at various pressures up to 7 GPa as a function of temperature. Figure 1 shows the electrical resistance vs. temperature (R - T) curves of the cooling run from the melt at a pressure of 5 GPa. Kinks in the R - T curves shown with arrows correspond to the phase boundaries of liquidus (c), eutectic (b) and eutectoid (a) in the isobaric phase diagram at the pressure. The eutectoid reaction

Fig. 1 Temperature variation of the electrical resistance at 5 GPa. Arrows indicate the phase boundaries in the isobaric Zn-Sn phase diagram. a: eutectoid horizontal, b: eutectic horizontal, c: liquidus.

is caused by originating the γ -tin phase in Sn-rich side. The kinks due to eutectic and eutectoid reactions are recognized approximately at the same temperature in all of the R - T curves. This means that the eutectic and eutectoid horizontal lines in the isobaric phase diagram expand in the wide composition range from 10 to 95 mol% tin at 5 GPa. The R - T curve of the Zn-91 mol%Sn alloy shows almost zero slope with broad width at the eutectic reaction. This suggests that the eutectic point locates near the composition.

An isobaric binary phase diagram at the pressure was constructed on the basis of the experimental results as shown in Fig. 2. The terminal phase of zinc-rich side is denoted with δ . The eutectic composition with the tin content of 87 mol% was determined from the cross points of the liquidi and the eutectic horizontal. The eutectic composition at atmospheric pressure is 85.1 mol% tin⁽¹⁾. In this system, the eutectic reaction changes from $\delta + \beta \rightleftharpoons \text{liquid (L)}$ to $\delta + \gamma \rightleftharpoons \text{L}$ at about 3.9 GPa. In spite of

the change in the phase relation at the pressure, the eutectic point under pressures was kept around the initial composition up to 7 GPa.

Isobaric composition-temperature sections of the three-dimensional phase diagram of the Zn-Sn system were obtained from the R - T curves at various pressures. Pressure vs. temperature (P - T) phase diagrams of the prepared alloys were given from the result. Examples of the Zn-10, 49, 91 mol% tin alloys are shown in Fig. 3. The phase diagrams of pure zinc and tin are added with light lines in Figs. 3(a) and (c), respectively. A new eutectoid reaction ($\delta + \beta \rightleftharpoons \delta + \gamma$) caused by the appearance of the γ -tin type terminal phase is shown in the figure. The phase identification in the phase field of the alloys was carried out by comparing the phase relation of the Zn-91 mol%Sn alloy with that of tin. The crystal structure of the β , γ and δ phases in the phase fields was confirmed by *in-situ* X-ray diffraction analysis under the pressures.

2. Eutectic and eutectoid slopes in the pressure-temperature phase diagram

In the P - T phase diagrams shown in Fig. 3, the temperature of the eutectic reaction I ($\delta + \beta \rightleftharpoons \delta + \text{L}$) of the Zn-Sn system rises with increasing pressure and the inclination of the slope changes discontinuously at a cross point (C-point) of the eutectic I, eutectic II ($\delta + \gamma \rightleftharpoons \delta + \text{L}$) and eutectoid phase boundaries.

The eutectic and eutectoid temperatures of the prepared alloys were averaged at each pressure. The final form of the phase boundaries of the eutectic and eutectoid in the P - T phase diagram was determined from the result. The C-point given from the P - T phase diagram was 3.9 GPa and 273°C. It was not detected up to 3.5 GPa in a work on the Zn-Sn system by Ozaki and Saito⁽¹⁾. Since the triple point of pure tin is 3.3 GPa and 310°C the C-point corresponding to the triple point of pure tin shifts to high pressure with increasing the zinc content.

Fig. 2 A possible isobaric phase diagram of the Zn-Sn system at 5 GPa.

Fig. 3 Pressure dependence of the phase boundary of the Zn-10 mol%Sn, Zn-49 mol%Sn and Zn-91 mol%Sn alloys. Solid circles are data points. Transition temperatures at atmospheric pressure are employed for the values in the phase diagram at ordinary condition⁽¹¹⁾. Pressure-temperature phase diagrams of the terminal elements are added with light lines. EC: eutectic, ED: eutectoid.

The mean value of the slope of the eutectic temperature curve I (dT/dP)_(0-3.9 GPa) is 18°C/GPa and that of the eutectic curve II (dT/dP)_(3.9-7.0 GPa) is 31°C/GPa. The mean value of the slope of the eutectoid temperature is -37°C/GPa between 3.9-7.0 GPa. The slope of the eutectic temperature curve I was determined by Ozaki and Saito⁽¹⁾ up to 3.5 GPa and estimated by Xiao *et al.*⁽²⁾. The mean values given by the former and the latter were about 20°C/GPa and 25°C/GPa, respectively. Present result is in fair agreement with the value given by Ozaki and Saito.

3. Intermediate phase and terminal phases

In spite of the expectation of the appearance of the high pressure phase, no new intermediate phase was detected in the Zn-Sn system up to 7 GPa. It is thought that the applied pressure for the present experiment was insufficient for such a kind of structural phase transformation on the Zn-Sn system.

The phase boundary of the eutectoid of the P - T phase diagram shown in Fig. 3(c) was compared with the phase boundary between the β and γ phase fields of pure tin. Although the phase boundaries disagree each other at high temperature, they tend to approach as temperature decreases. It is considered that solubility of zinc in the γ -tin type terminal phase decreases at conditions of high pressure and low temperature.

Solubility of solute in the terminal phases of the Zn-Sn system is extremely small (<1 mol%) at atmospheric pressure⁽¹¹⁾. In the present isobaric phase diagram, the eutectic and eutectoid horizontals kept the wide composition range from 10 to 95 mol% tin up to 7 GPa. This means that the solubility of tin in zinc is less than 10 mol% and that of zinc in β and γ phases is less than 5 mol% at the eutectic and eutectoid temperatures of the Zn-Sn system. In a previous study on the Cd-Sn system

pressure dependence of the solubility in the terminal phases was also less notable⁽¹⁶⁾. Pressure effect of the solubility seems to be small in these kinds of tin-alloys.

4. Effect of diffusion for determining the equilibrium phase diagram under high pressure

The R - T curves of the heating (left) and cooling (right) runs on the Zn-91mol%Sn alloy at pressures of 0, 3 and 7 GPa are shown in Fig. 4. The heating and cooling rate was kept between 5-20°C/min. Hysteresis of the R - T measurement of the eutectic reaction was within 20°C, *i.e.* the superheating and supercooling at the eutectic were less for these alloys. The slope of the R - T curve of the heating cycle over the eutectic temperature is different from that of the cooling cycle. The apparent reaction of the melting at the liquidus in the heating cycle is slow and the ending temperature is unclear under pressures. This is considered that the equilibrium at the liquidus is insufficient in the heating cycle for the delay of the interdiffusion in the liquid phase. The solidification reaction in the cooling cycle from the melt may be kept the equilibrium state at the starting temperature because the sufficient interdiffusion occurs between zinc and tin at the melt state. After the beginning of the solidification, of course, the delay of the equilibrium due to insufficient interdiffusion should occur during the cooling run. However, the effect is not important for determining the eutectic horizontal as shown in Fig. 2, where the eutectic temperature approximately locates at the same temperature with that of the heating run. Therefore, the transition temperature from the melt given from the cooling cycle of the R - T curve was used as the liquidus for constructing the present equilibrium phase diagrams. On the other hand, the transition temperatures of the eutectic reactions were given by the middle point of the kinks of the R - T curve of the heating and cooling runs.

Fig. 4 Temperature variation of the electrical resistance in heating (left) and cooling (right) cycles of the Zn-91 mol%Sn alloy at atmospheric pressure, 3 GPa and 7 GPa. A horizontal arrow **a** indicates eutectoid reaction appearing under high pressure.

Hysteresis at the eutectoid temperature was also within 20°C with a measurement of slow temperature variation of 5°C/min. Although the change in the electrical resistance at the temperature was small, it proceeded in the short time within the given cooling and heating rate. The phase transformation is probably a non-equilibrium because within such a short time the equilibrium state may be not completed in the solid reaction accompanying the interdiffusion of zinc and tin. However, the effect is not significant for the determination of the eutectoid temperature of the present equilibrium phase diagram because of the same reason for the determination of the eutectic horizontal.

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