THREE-DIMENSIONAL COMPOSITION-PRESSURE-TEMPERATURE PHASE FIELD OF THE INTERMEDIATE ζ-PHASE IN THE SILVER-GERMANIUM SYSTEM

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Phase relation of the Ag-Ge system is investigated by means of measurements of electrical resistance and analyses of X-ray diffraction profiles. A three-dimensional composition-pressure-temperature phase diagram is constructed from the results. An intermediate ζ-phase is stable within a limited region above 1.2 GPa and germanium content between 14-28 mol %.

1. Introduction

An intermediate ζ-phase in the Ag-Ge system is stable under high pressure and temperature. It can be obtained at atmospheric pressure by quenching it from the stable state. Although partial phase diagrams including the ζ-phase have been proposed [1-3], the three-dimensional (3-D) composition-pressure-temperature (C-P-T) phase field of the ζ-phase is unclear because of less experimental data under high pressure. In the present study, we tried to form a C-P-T phase diagram in wide regions of composition, temperature and pressure up to 7 GPa. The results show a characteristic phase field of the ζ-phase.

2. Experimental procedure

Four kinds of strip of silver-germanium alloys with germanium contents of 10, 17, 26 and 50 mol % were prepared by rapid cooling of the melt. These alloys were composed of the terminal phases of Ag-rich side (α)and Ge-rich side (β) at atmospheric conditions. A cubic type

Fig. 1. Schematic drawing of the system on the measurement of electrical resistance around the sample

multi-anvil press [4] was employed for applying the pressure.

Phase boundaries in the isobaric phase diagrams were determined from the measurements of electrical resistance of the alloys. After application of pressure and temperature the phase identification of the alloys was carried out by analysis of X-ray diffraction profiles at atmospheric pressure. Since the sample for the phase identification was quite small, a micro-area X-ray diffraction system with a high power X-ray source was applied for the measurements. A narrow slit of 0.03 mm ϕ was used for the measurement.

The sample assembly and the other experimental conditions are described in detail elsewhere [3, 5].

3. Results and discussion

3.1 Measurements of electrical resistance

In previous works a strip of alloy with serving electrode has been applied for the measurement of electrical resistance [5]. However, this method was unfavorable for applying the sample with a liquid phase. Since a gradient of pressure occurred along the longitudinal direction of the foil, it was difficult to keep the sample within the center of the gasket. Then, a new sample assembly using tantalum electrodes was employed for the measurement of electrical resistance of the alloys [6]. The schematic illustration is shown in Figure1. According to employment of this method we were able to obtain the experimental data on the liquidus of the isobaric phase diagrams of the Ag-Ge system. This method was also advantageous for the measurement of electrical resistance of the Ag-50mol%Ge alloy which had been difficult to keep the continuous form of the foil because of its brittleness.

The electrical resistance of the alloys was measured as a function of temperature in various isobaric pressures up to 7 GPa. Then, we can determine the pressure dependence of
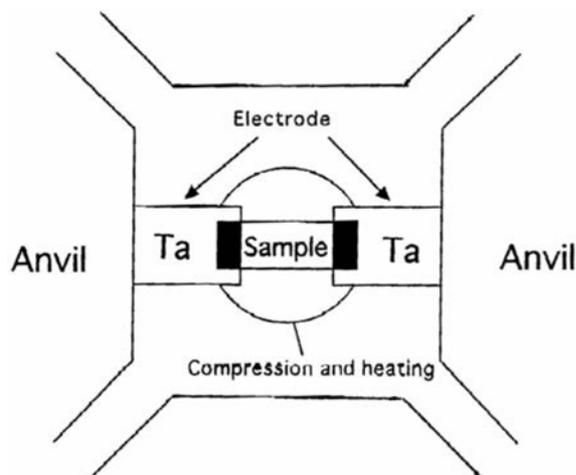
the eutectic, peritectic, eutectoid and liquidus temperatures.
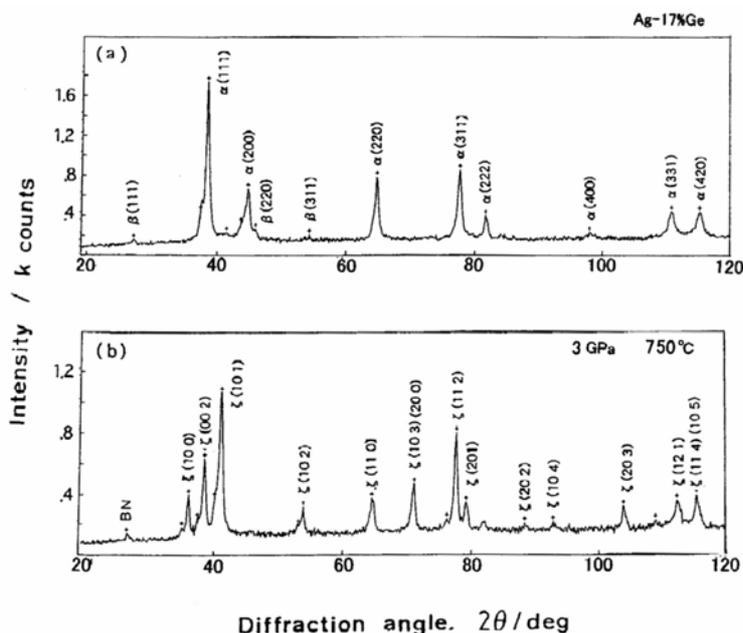

Fig. 2. X-ray diffraction profiles of Ag-17mol%Ge alloy. (a) Initial state with fcc (α) and diamond-type fcc (β) phase, (b) ζ-phase with hcp structure quenched from 750 °C at 3 GPa. The peak of boron nitride (BN) is due to pressure transmitting material

3.2 Analyses of X-ray diffraction

The phase identification of the alloys was carried out in various conditions of pressure and temperature by means of a micro-area X-ray diffraction system. Figure. 2 shows typical X-ray diffraction profiles obtained from the Ag-17mol%Ge alloy. The initial alloy composed of the two terminal phases (a) transforms to the single ζ-phase (b) at the quenched state from 3 GPa and 750 °C.

The maximum solubility of a primary solid solution often depends on the pressure [5,7]. The binary phase diagram of the Ag-Ge system shows the maximum solubility of 9.6 mol % germanium in silver and quite small solubility of silver (0.009%Ag) in germanium at atmospheric pressure [8]. After application of high pressure and temperature we investigated the solubility of the terminal phases by analysis of X-ray diffraction profiles. The solubility of germanium in the α-phase was studied by using the Ag-10mol%Ge alloy. The X-ray diffraction profiles showed the single α-phase near the temperature of peritectic horizontal at pressures between 5 - 7 GPa. This suggests that the maximum solubility of germanium in the α-phase is over 10 mol %, i. e., a little expansion of the phase field occurs in the Ag-rich side as the pressure effect.

The lattice constant of the solid solution has been measured for the determination of the solubility of solute in the terminal phase [5,9]. The solubility of silver in the β-phase was investigated by applying this method. We were not able to detect the difference between the lattice constant of the β-phase and pure germanium within the errors of ±0.0001 nm. The solubility of silver in germanium was not suggested from the measurement of the lattice constant of the β-phase.

Three-dimensional C - P - T phase diagram

Isobaric phase diagrams at 2, 3, 5 and 7 GPa were constructed from the basis of the electrical resistance and X-ray diffraction data. Figure 3 shows a 3-D phase diagram constructed from the isobaric phase diagrams. Four invariant planes (I (eutectic): α+β⇔ liquid (L), II (eutectic): ζ+β⇔ L, III (peritectic): ζ⇔α+L, IV (eutectoid): α+β⇔ζ) are shown in the figure. The minimum pressure (1.2 GPa) of the stable ζ-phase is given from the 3-D phase diagram. Two-dimensional P-T and
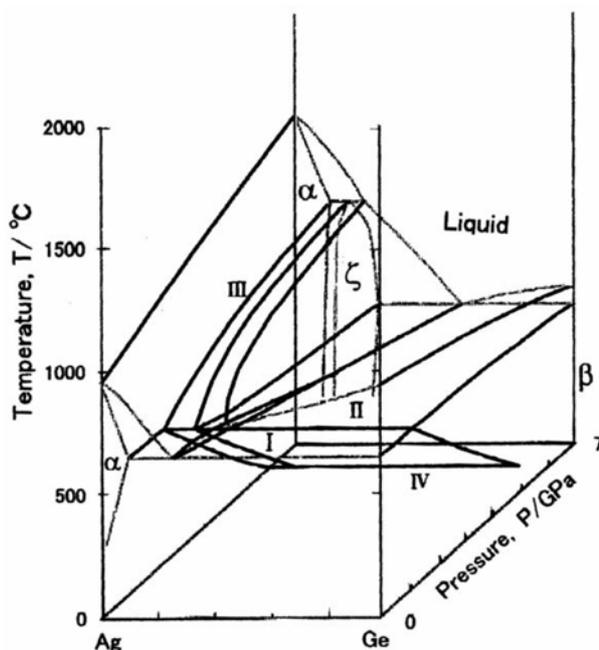

Fig.3. A three-dimensional composition-pressure-temperature phase diagram. The regions indicated by I, II, III and IV are invariant planes

isothermal phase diagrams can be easily obtained from the sections of the 3-D phase diagram.

After originating the ζ-phase the phase field expand as increasing pressure. But the expansion of the composition range is limited between 14-28 mol% of germanium. The ζ-phase is known to be electron phase [12] which is stable within a limited electron atom ratio. The limited composition of the ζ-phase field can be explained by the property of the electron phase.

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