Order-Disorder Transition of Ag₃In

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An order-disorder transition of Ag₃In was investigated by means of specific heat, electrical resistivity and magnetic susceptibility measurements, and X-ray diffraction using an Ag-25at% In alloy. Specific heat vs. temperature curve shows a δ-type anomaly with a maximum at 214°C, and the heat of transition was found to be 220 cal/g-atom. From the X-ray analysis, no difference is found in the axial ratios between the low-temperature and high-temperature phases. From the result of magnetic susceptibility, a minor change in the electronic structure was suggested.

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I. Introduction

The crystal structure of the Ag₃In phase is close packed hexagonal. This phase has a narrow homogeneity range near 25at% In at room temperature, but has a homogeneity range between 25 and 33at% In at higher temperatures (Fig. 1)(1). Weibke and Eggers(2) found a thermal arrest at 187°C in the Ag₃In phase. Hellner and Laves(3) reported by X-ray analysis that there was no difference between the crystal structures of the phases below and above 187°C. On the other hand, Lang(4) measured the temperature dependence of electrical resistivity and elastic modulus of Ag₃In. He concluded from the resistivity measurement that the phase transition occurs at 195°C, and also from the change in the axial ratio (c/a) that this transition is an order-disorder type similar to that of Cd₃Mg. Further, Campbell et al.(5) reported the existence of an ordered structure of Cu₃Au type at 25at% In from X-ray analysis.

Thus, there are some contradictions among the previous results and this phase transition remains unsolved in several respects. Therefore, we carried out the measurements of specific heat, electrical resistivity and magnetic susceptibility and X-ray diffraction for the 25at% In alloy. We determined the transition temperature and the heat of transition and examined the possibility of the changes in crystal and electronic structures with this transition.

II. Experiments

Ag and In used were 99.99 and 99.999% in purity, respectively. Appropriate amounts of Ag(75at%) and In(25at%) were melted together in a fused-quartz tube under a vacuum of 10⁻⁴ Torr. The molten alloy was water-quenched and then annealed at 500°C under a vacuum of 10⁻⁴ Torr. The specimens used for each measurement were annealed at 170°C for 50 hr in a vacuum furnace and furnace-cooled to room temperature.

The specific heat was measured by a Rigaku-Denki specific heat-differential thermal analysis apparatus ('Thermoflex' Type VI). The measurement was performed at temperature intervals of 2°C and at a heating rate of 2 deg/min. The electrical resistivity was measured by the ordinary direct current method using the samples of 2.3ℓ~60mm. The magnetic susceptibility was measured by a Curie-Chenevian type torsion balance, using the sample enclosed in an evacuated quartz cell (7.0ℓ~8mm). The sample was heated at a rate of 1 deg/min, and was kept at each constant temperature for 10 min before both measurements. X-ray diffraction measurement was done by using a 114.6mm Debye-Scherrer camera with nickel-filtered CuKα radiation.

III. Results and Discussion

Figure 2 shows the temperature dependence of specific heat of the 25at% In alloy annealed previously


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Fig. 2 Temperature dependence of specific heat of the alloy of 25 at% In.

Fig. 3 Temperature dependence of electrical resistivity of the alloy of 25 at% In.

at 170°C. The specific heat shows a \( \lambda \)-type curve having a maximum at 214°C, which is due to an order-disorder transition. The heat of transition obtained from Fig. 2 was 220 cal/g-atom, which is nearly equal to the energy in the order-disorder transition of Cd₃Mg alloy (230 cal/g-atom)\(^6\).

Figure 3 shows the temperature dependence of electrical resistivity of the same sample. In a way similar to the change in specific heat, the electrical resistivity begins to increase from 190°C and reaches a steady state above 220°C on heating. On the other hand, it does not show any drastic change on slow cooling, though it decreases slightly at about 200°C. The temperature at which the resistivity falls is somewhat higher than that observed by Lang\(^4\). According to Lang, however, the change in elastic modulus occurs at about 220°C, which agrees well with our result. Lang reported that the elastic modulus of the low temperature (l.t.) phase of this alloy is smaller than that of the high temperature (h.t.) phase, while the temperature coefficient of resistivity is inversely proportional to the elastic modulus\(^7\). If this is the case, it is expected that the temperature coefficient of resistivity of the l.t. phase is larger than that of the h.t. phase. As shown in Fig. 3, however, the experimental result does not agree with this expectation. It is very likely, therefore, that there is the difference in the electronic structure between the l.t. and h.t. phases. The above concept is supported by the result of magnetic susceptibility shown in Fig. 4. This figure shows the temperature dependence of magnetic susceptibility for the alloy annealed previously. The diamagnetic susceptibility of Ag₃In decreases very slightly with increasing temperature, and rapidly rises at about 214°C corresponding to the anomalies observed in the specific heat and electrical resistivity curves. The susceptibility measurement shows that the diamagnetism of the l.t. phase is smaller than that of the h.t. phase; that is, if the valence electron concentration is not affected by the transition, the effective mass of the l.t. phase becomes larger than that of the h.t. phase. However, the change in the electronic structure is very small, for the difference in the magnetic susceptibility between the l.t. and h.t. phases is very small (\( \Delta \chi = 0.26 \times 10^{-8} \) e.m.u./g).

As can be seen from Fig. 3, the phase transition occurs during slow cooling from above the transition temperature. Figure 5 shows the heat of transition vs. annealed time curve obtained by DTA for the samples annealed at 170°C for a varying time. As shown in this figure, the time for completion of the phase

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transition is about 50 hr.

It is supposed that the l.t. phase of Ag$_3$In has the same ordered structure as that of Cd$_3$Mg based on the hcp lattice. From the X-ray diffraction data, however, neither superlattice lines of the Cd$_3$Mg type structure nor the existence of the ordered phase of the Cu$_3$Au type reported by Campbell et al. was detected, because the atomic number of Ag is very close to that of In. Though we could not find such a change in the axial ratio ($c/a$) due to the transition as detected by Lang(4), the lattice parameter of the Ag$_3$In alloy quenched from 250°C was given as $a = 2.954\text{"A}$, $c = 4.791\text{"A}$, and $c/a = 1.621$. This result agrees well with that of Hellner(8).

IV. Summary

Measurements of specific heat, electrical resistivity, magnetic susceptibility and X-ray diffraction of the Ag$_3$In alloy (25at \% In) were carried out. The results obtained are summarized as follows:

1. The order-disorder transition takes place at 214°C, and the heat of transition is determined to be 220 cal/g-atom.

2. From the result of magnetic susceptibility, a small change in the electronic structure with this transition is suggested.

3. No difference is found in the axial ratio between the low-temperature and high-temperature phases.

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