X-Ray Diffraction and Electrical Resistivity Study of Ag_2In and High Temperature Ag_3In Phases

By Tsuneo Satow*, Osamu Uemura* and Setsuko Yamakawa*

The phase transition of Ag_2In was investigated by means of X-ray diffraction, measurements of specific heat and electrical resistivity, and the composition dependences of lattice parameter and electrical resistivity of the ζ phase (high temperature form of Ag_3In) were also examined over the range of 25–40 at%In. It was found that (1) the Ag_2In phase transformed from the γ -brass type to hcp structure at 222°C with a heat of transition of 130 cal/g-atom, and that (2) the lattice parameter, and the electrical resistivity and its temperature coefficient changed abruptly at 33.0 at%In in the homogeneous region of ζ phase.

(Received July 25, 1973)

I. Introduction

Weibke and Eggers⁽¹⁾ have investigated the Ag–In system over its entire composition range by means of thermal analysis, photomicrography and X-ray diffraction. Hansen and Anderko⁽²⁾ have corrected the phase diagram in the silver-rich region (25–34 at%In) using the results of micrographic and X-ray investigations by Hellner⁽³⁾ and Hellner and Laves⁽⁴⁾. Campbell et al.⁽⁵⁾ have recently investigated the phase relationships of this system by thermal, photomicrographic and electron microprobe analyses and X-ray powder diffraction. Figure 1 shows the phase diagram by Campbell et al.

There have been conflicting reports in the literature concerning the phase transitions of Ag_3In and Ag_2In . The present authors investigated recently the phase transition of Ag_3In at 214°C by measurements of

electrical resistivity, specific heat, magnetic susceptibility and by X-ray diffraction, and examined the possibility of changes in the crystal and electronic structures with this transition⁽⁶⁾. The purpose of present paper is to investigate the phase transition of Ag_2In (33.2 at%In) by X-ray diffraction, and measurements of specific heat and electrical resistivity. Further, the composition dependences of lattice parameter and electrical resistivity of the ζ phase which has a wide homogeneous region above 300°C are investigated between 25 and 40 at%In.

II. Experimental

Purities of silver and indium used were 99.99 and 99.999%, respectively. The metals were melted together in a fused quartz tube in a vacuum of 10^{-4} Torr. The molten alloy was water-quenched, followed by annealing at 500°C in a vacuum of 10^{-4} Torr.

The X-ray diffraction was carried out by using a 114.6-mm ϕ camera and a 90-mm ϕ high temperature camera with nickel filtered $\text{CuK}\alpha$ radiation.

The electrical resistivity was measured by an ordinary direct current method using samples of $2.3\phi \times 60$ mm. The sample was heated at the rate of about 1 deg/min, and kept at each constant temperature for 10 min prior to the measurement.

The specific heat was measured by a specific heat apparatus (Rigaku-Denki 'Thermoflex' Type VI). The measurement was carried out at temperature intervals of 2°C and at the heating rate of about 2 deg/min.

III. Results and Discussion

1. Phase transition of Ag_2In (33.2 at%In)

X-ray diffraction patterns of 33.2 at%In alloy quenched from 200 and 250°C are given in Photo. 1. The crystal structure at 200°C is the γ -brass type, being consistent with that reported by Hellner⁽³⁾ and Campbell et al.⁽⁵⁾ At 250°C , however, it is a hexagonal close packed structure which will be denoted hereafter as hcp Ag_2In . This is in conflict with the results of Hellner and Laves⁽³⁾⁽⁵⁾, who

Fig. 1 The phase diagram of the Ag–In system by Campbell et al.⁽⁵⁾

* Faculty of Science, Yamagata University, Yamagata 990, Japan.

Photo. 1 X-ray diffraction patterns of 33.2 at%In alloy quenched from (a) 200°C and (b) 250°C.

Fig. 2 The temperature dependence of lattice parameters of 33.2 at%In alloy above 230°C.

Fig. 3 The temperature dependence of specific heat of 33.2 at%In alloy.

reported that the γ -brass type structure remains until about 290°C.

The result of X-ray diffraction of the quenched alloy is confirmed by using the high temperature X-ray camera. Figure 2 gives the temperature dependence of lattice parameters measured above 230°C. As is evident from this figure, the rate of increase in the lattice parameter with temperature changes slightly at 290°C, this temperature may correspond to the transition temperature from the hcp Ag_2In to the hcp ζ phase. However, no difference are found be-

Fig. 4 The temperature dependence of electrical resistivity of 33.2 at%In alloy.

tween these two hcp structures in the X-ray diffraction patterns.

A specific heat curve of this alloy is shown in Fig. 3, where two peaks appears at 222 and 282°C. The heat of transition at 222°C is estimated to be 130 ± 10 cal/g-atom. The heats of structural transitions for $fcc \rightleftharpoons hcp$ and $fcc \rightleftharpoons bcc$ are generally known to be of the order of 20–50 and 200–300 cal/g-atom, respectively. Therefore, the observed value 130 cal/g-atom seems to be reasonable for the transition from the γ -brass type to the hcp structure.

The temperature dependence of electrical resistivity ρ is given in Fig. 4, where a large decrease in ρ appears at 216°C and a small decrease at 286°C. This behavior of ρ is analogous to that of C_p shown above.

From the above results, it is seen that the Ag_2In phase near the stoichiometric composition transforms from the γ -brass type structure to the hcp Ag_2In at about 220°C and then to the hcp ζ phase at about 290°C. Since the nature of the latter transition cannot be well understood yet, further work need to be done. The phase transition at 220°C is not the order-disorder transition as maintained by Weibke and Eggers⁽¹⁾. The transition temperature, 204°C, reported by them is considered to be the eutectoid reaction ζ phase $\rightleftharpoons \gamma$ -brass Ag_2In + liquid.

2. Composition dependence of lattice parameter and electrical resistivity in the ζ phase

As shown in Fig. 5, the lattice parameters of the ζ phase alloys water-quenched from 320°C change abruptly at 33.0 at%In. In the Ag–Ge system, Klement⁽⁷⁾ has found a similar change of the lattice parameters in the homogeneous region of metastable hcp electron compounds prepared by rapid quenching from the melt. Representing the composition in terms of the electron concentration e/a , the homogeneous region of the ζ phase ($e/a=1.5$ –1.9) agrees well with that of the metastable hcp phase in the Ag–Ge system (1.45–1.85). The abrupt change in the lattice parameters is considered to be related to the change in the density of electronic state with the increase of valence electrons.

Figure 6 shows the composition dependence of

Fig. 5 The composition dependence of lattice parameters of the ζ phase quenched from 320°C.

Fig. 6 The composition dependence of temperature coefficient of electrical resistivity of the ζ phase at 320°C.

temperature coefficient of electrical resistivity (ρ_T) of the ζ phase at 320°C. In this figure, ρ_T decreases with In concentration until 32.7 at%In, and increases remarkably at 33.0 at%In. This increase may be due to the increase of p if the change of Q is fairly small, since $\rho_T \propto p^3 Q$, where p and Q are the momentum and the scattering cross section of electrons, respectively. Hence the density of electronic state near the Fermi level is expected to change at this composition. The composition dependence of resistivity ρ at 320°C is shown in Fig. 7, which also shows its abrupt change at 33.0 at%In. It may be concluded therefore that

Fig. 7 The composition dependence of electrical resistivity of the ζ phase at 320°C.

the density of electronic state changes at 33.0 at%In in the ζ phase, though measurements of other properties such as the Hall effect and magnetic susceptibility seem to be necessary for a more detailed discussion.

IV. Conclusion

The results obtained are summarized as follows.

- (1) The phase transition of Ag_2In (33.2 at%In) occurs at 222°C with the heat of transition of 130 cal/g-atom. This transition is not an order-disorder type as proposed by Weibke and Eggers, but is the phase change from the γ -brass type to the hcp Ag_2In .
- (2) The lattice parameters of the alloys quenched from 320°C change abruptly at 33.0 at%In in the ζ phase. A similar change is found in the electrical resistivity and its temperature coefficient, and hence the change in the density of electronic state is proposed at this composition.

Acknowledgment

The authors are grateful to Mr. Y. Sagara for his technical aid.

REFERENCES

- (1) F. Weibke and H. Eggers: *Z. anorg. allg. Chem.*, **222** (1935), 145.
- (2) M. Hansen and K. Anderko: *Constitution of Binary Alloys*, McGraw-Hill, (1958), p. 26.
- (3) E. Hellner: *Z. Metallk.*, **42** (1951), 17.
- (4) E. Hellner and F. Laves: *Z. Naturforsch.*, **2a** (1947), 177.
- (5) A. N. Campbell, R. Wagemann and R. B. Ferguson: *Can. J. Chem.*, **48** (1970), 1703.
- (6) O. Uemura and T. Satow: *Trans. JIM*, **14** (1973), 199.
- (7) W. Klement: *J. Inst. Metals*, **90** (1961-1962), 27.