The Effect of Additional Elements on the $\beta' \rightarrow \zeta$ Transformation in Equiatomic AgZn Alloy

By Yoshie Matsuo*

The transformation of a metastable β' -(ordered *bcc*) phase into a ζ -(complex hexagonal) phase on heating was examined for AgZn alloys doped with various kinds of elements, using thermal differential analysis, electric resistivity measurement and high-temperature X-ray diffractometry.

The $\beta' \rightarrow \zeta$ transition temperature falls exponentially with increase of the electron-atom ratio (e/a) of alloys. Furthermore, an anomalous heat accompanied with the transformation was observed. For specimens of $e/a < 1.5$ the anomaly appears as a generation of heat, while for $e/a > 1.5$ as an absorption of heat.

These phenomena were discussed briefly in terms of a reduction of the kinetic energy of electrons due to the Brillouin zone effect.

(Received August 30, 1979)

I. Introduction

An equiatomic AgZn alloy is transformed into a ζ -phase from a disordered *bcc* β -phase by slow cooling, but it undergoes an ordering reaction to a metastable β' -phase with the CsCl-type ordered structure when it is quenched from the β -phase⁽¹⁾. The β' -phase is transformed into the ζ -phase by heating.

Edmunds and Qurashi⁽²⁾ showed that the ζ -phase has a complex hexagonal structure closely related to a *bcc*-type structure and the unit cell contains nine atoms in a partially ordered arrangement. The formation of the ζ -phase is of particular interest because of the uniqueness in equiatomic alloys of noble metals with IIB elements. The crystallographic relation between the β' - and ζ -phases has been already reported by Kitchingman⁽³⁾, and the mechanism of the $\beta' \rightarrow \zeta$ transformation has been discussed by Clark *et al.*⁽⁴⁾ and Brooks and Smith⁽⁵⁾.

Furthermore, the stability of the ζ -phase was discussed by Noguchi⁽⁶⁾, who proposed that the stability of such a ζ -phase structure was caused by a reduction of the Fermi energy according to an interaction between the Brillouin zone boundary and the Fermi surface. Factors which affect the interaction include the

changes in an electron-atom ratio e/a of alloy, in an energy gap at the Brillouin zone boundary and in a degree of distortion of the Fermi surface.

It is essential to study the $\beta' \rightarrow \zeta$ phase transition of multicomponent AgZn-based alloys under the condition of constant or altered e/a , in order to understand the stability of the ζ -phase. In the present study, the equiatomic AgZn alloy is treated as a master alloy, and the transformation is examined by differential thermal analysis, electric resistivity measurement and high temperature X-ray diffractometry when various kinds of third element are added to the master alloy.

II. Experimental Procedures

Ternary alloys (AgZn)_{100-x}M_x with several kinds of element M were prepared from each metal of 99.999% purity. Monovalent metals Cu and Au, divalent metals Mg and Cd and trivalent metals Al and In were chosen as the additional elements M. The composition of the additional element was restricted within the range where the ζ -phase existed at low temperature (less than several atomic per cent of M as shown in III). Predetermined weights of these metals contained in a graphite crucible were melted in a sealed silica tube under an atmosphere of argon. After prolonged homogenization at about 870 K, all alloys were quenched into ice water. From each ingot a

* Department of Physics, Faculty of Science, Nara Women's University, Nara 630, Japan.

number of specimens was prepared for differential thermal analysis, electric resistivity measurement and high-temperature X-ray diffractometry.

The $\beta' \rightarrow \zeta$ transition temperature and the heat anomaly accompanied with the transformation were determined by differential thermal analysis (D.T.A.), using specimens of a cylindrical shape with a diameter of 5 mm and a height of 12 mm. The specimens were held at a desired temperature (670 K in almost all the cases) for one day (86.4 ks) in a sealed pylex tube and then quenched into water. Measurements were carried out with heating and cooling rates of 5.83×10^{-2} K/s.

Variation of the transition temperature was also examined by electric resistivity measurement, using specimens with a dimension of $0.2 \text{ mm} \times 2.0 \text{ mm} \times 15 \text{ mm}$. After copper wires were welded to the specimen as current and potential leads, the specimen were annealed at about 670 K for one day and then quenched into ice water. The resistivity was measured by the usual potentiometric method under temperature variation with a rate of 3.33×10^{-2} K/s.

Finally, the alloy phase was identified by high-temperature X-ray diffractometry. Specimens for X-ray analysis were prepared by filling the ingot at room temperature, annealed for stress-relief at about 670 K in a sealed pylex tube and then cooled slowly, or quenched. Diffraction patterns were recorded under an atmosphere of helium after holding the specimen at each desired temperature for more than 600 s.

III. Experimental Results

The observed phase diagrams are shown in Fig. 1, where (a), (b) and (c) correspond to the alloys doped with monovalent, divalent and trivalent elements, respectively. In the figures, X indicates a phase with an unknown structure which is not analyzed successfully. As seen from Fig. 1, the single phase of ζ exists only when a few atomic per cent of each of the third elements is added.

Like the binary alloy AgZn do, the ternary alloys in β -phase undergo an ordering reaction

to a metastable β' -phase when they are quenched. The β' -phase alloys are transformed into the stable ζ -phase ones by heating. The dotted lines in Fig. 1 indicate the variation of the $\beta' \rightarrow \zeta$ transition temperature T_0 of specimens quenched from 670 K determined by D.T.A. A change in this quenching temperature from 570 K to 770 K brings about only an elevation of less than 10 K to T_0 . The addition of Cu or Au causes a rise of T_0 , while the addition of Mg, Cd, Al or In lowers T_0 .

The results of D.T.A. for some of these alloys are shown in Fig. 2. Figure 2(a), (b) and (c) are the typical patterns of quenched specimens with 0.5 at% Au, Cd and In, respectively. For comparison, the result for a quenched AgZn binary alloy is shown in (d), and also a D.T.A. curve of AgZn on cooling from the β -phase is shown in (e). Although the general feature of the curve is identical in the alloys doped with the element of same valence, there is a marked difference between the alloys doped with the different valence elements. The temperature at which the $\beta' \rightarrow \zeta$ transformation occurs on heating falls with increase of the valence of additional elements. Furthermore, at the transformation the Au doped alloy has a heat generation, the In doped alloy a heat absorption, but the Cd doped and AgZn alloys show a heat absorption followed by a heat generation. No apparent change in the $\zeta \rightarrow \beta$ transition temperature among the different alloys is observed, and a temperature hysteresis between the $\zeta \rightleftharpoons \beta$ transitions with heating and cooling exists also in the ternary alloys as observed in AgZn alloys (see Fig. 2(d) and (e)).

Figure 3 shows a relation between the $\beta' \rightarrow \zeta$ transition temperature T_0 and the electron atom ratio e/a of the doped systems. It is clear that T_0 predominantly depends, among other factors, on e/a of alloy. For the sake of the later discussion, the same relation in the Ag-Zn binary system given by Brooks and Smith⁽⁵⁾ is added in the figure.

Electric resistivity change of specimens quenched from 670 K is shown in Fig. 4 for the same alloys as chosen in Fig. 2. In the figure are plotted the relative values of the resistivity at 473 K. The result shows that the β' -phase has considerably lower resistivity than the ζ -phase,

Fig. 1 Observed phase diagrams of the AgZn alloys doped with monovalent elements (a), divalent elements (b) and trivalent elements (c). X indicates a phase with an unknown structure.

and a critical discontinuity appears at the $\beta' \rightarrow \zeta$ transformation. The transition temperature dependence upon the electron-atom ratio can be seen also in this figure.

IV. Discussion

The results obtained in the present study are summarized as follows: (A) the $\beta' \rightarrow \zeta$ transition temperature T_0 falls exponentially with increase of e/a , and (B) the anomalous heat accompanied

with the transition is a heat generation for values of e/a less than 1.5 and a heat absorption for more than 1.5. Noguchi⁽⁶⁾ discussed the stability of ζ -phase in the Ag-Zn binary system in terms of the Brillouin zone effect. Along his line we shall try to interpret the above results qualitatively.

The free energy of an alloy is expressed as $F = U - TS$, where U is the internal energy, T the absolute temperature and S the entropy. When we consider a cohesive energy as the

Fig. 2 Differential thermal analysis (D.T.A.) of the AgZn alloys doped with 0.5 at% Au, Cd and In, together with that of the binary AgZn alloy.

Fig. 3 Variation of the $\beta' \rightarrow \zeta$ transition temperature T_0 with the electron-atom ratio e/a .

internal energy, it consists of the potential energy and the kinetic energy of conduction electrons; that is $U = U_p + U_k$. In order to

Fig. 4 Temperature dependence of electrical resistivity.

realize the stable ζ -phase at very low temperature, the following relation must be satisfied; $U(\zeta) < U(\beta')$. U_p is composed of various kinds of term, but an electrostatic energy among ions in a sea of conduction electrons plays an important role in the determination of alloy structure. It has a minimum value at a specific ionic distance in the crystal structure with high symmetry, and it increases rapidly with any distortion of crystal lattice. The ζ -phase has a considerably complicated structure with lower symmetry; therefore, $U_p(\zeta) > U_p(\beta')$. Hence, the stability of the ζ -phase should be caused by a reduction of the kinetic energy of electrons, outweighing the rise of potential energy. The process by which U_k is lowered is considered generally to be an interaction between the Fermi surface and the Brillouin zone boundary. The Fermi radius k_f , which is assumed to be spherical surface, and the Brillouin zone boundary can be calculated in the usual way with an electron-atom ratio and lattice parameters obtained experimentally by X-ray diffractometry. They are shown in Fig. 5. The relations for Ag-Zn binary alloys are plotted together⁽⁷⁾. As seen from the figure, two sets of Brillouin zone boundary $\{111\}_\zeta$ and $\{300\}_\zeta$ lie closely to the Fermi surface in the ζ -phase, but only one set $\{110\}_{\beta'}$ does in the β' -phase. The splitting of $\{110\}_{\beta'}$ into $\{111\}_\zeta$ and $\{300\}_\zeta$ may be considered as the origin of the reduction of the kinetic energy. The configurational entropy of ζ -phase alloys is larger than that of β' -phase alloys because of the decrease of a degree of order. Then, even

Fig. 5 Dependence of the Fermi radius k_F and the Brillouin boundary of β' - and ζ -phase alloys upon the electron-atom ratio e/a .

with elevated temperatures, the ζ -phase remains more stable than the β' -phase.

Brookes and Smith⁽⁵⁾ showed that the zinc content in binary Ag-Zn alloys decreases, the $\beta' \rightarrow \zeta$ transition temperature T_0 falls (Fig. 3). This indicates that T_0 rises with increase of the electron-atom ratio e/a , contrary to the present doped systems in which T_0 falls with increasing e/a . As seen from Fig. 5, when e/a increases from 1.46, Fermi radius $k_F(\beta')$ in the β' -phase approaches the $\{110\}_{\beta'}$ set of Brillouin zone boundary, and the degree of reduction of the kinetic energy according to the $\beta' \rightarrow \zeta$ transition may be lowered. This is a reason for the fact that T_0 rises with increase of e/a in a range of $e/a < 1.49$. On the other hand, as e/a increases beyond about 1.49, $k_F(\beta')$ goes away from the $\{110\}_{\beta'}$ set and the effect of interaction becomes less significant. Thus, T_0 is expected to fall as e/a increases in the present ternary systems.

Next, we shall discuss the anomalous heat accompanied with the transition, referring to the results of 0.5 at% Au and 0.5 at% In alloys shown in Fig. 2. The former alloy shows a heat generation, while the latter a heat absorption. The generation of heat comes from a decrease of the internal energy and the absorption comes from an increase of the entropy. Therefore, the effect of a change of internal energy $\Delta U(\beta' \rightarrow \zeta)$ at the transition should surpass that of entropy change $T\Delta S(\beta' \rightarrow \zeta)$ for the Au-doped alloy, while the contrary is true for the In-doped alloy. If we assume that atoms of the additional element do not occupy specific lattice points, then both $\Delta S(\beta' \rightarrow \zeta)$ and $\Delta U_p(\beta' \rightarrow \zeta)$ may be almost the same in the two alloy systems. Neglecting the difference of T_0 between the systems, the magnitude of reduction of the kinetic energy $\Delta U_k(\beta' \rightarrow \zeta)$ plays a predominant role in the difference of heat anomalies between the two systems. The Au-doped alloy ($e/a = 1.4975$) has a Fermi surface which interacts with the two Brillouin zone boundaries $\{111\}_{\zeta}$ and $\{300\}_{\zeta}$, while the In-doped alloy ($e/a = 1.5075$) has the surface which lies near only one $\{300\}_{\zeta}$ (see Fig. 5).

REFERENCES

- (1) M. Hansen: *Constitution of Binary Alloys*, McGraw-Hill, New York, (1958), p. 63.
- (2) I. G. Edmunds and M. Quarashi: *Acta Crystallogr.*, **4** (1951), 417.
- (3) W. J. Kitchingman: *Acta Met.*, **10** (1962), 799.
- (4) H. McL. Clark, E. A. Merriman and C. M. Wayman: *Acta Met.*, **17** (1969), 719.
- (5) M. E. Brooks and R. W. Smith: *Trans. Met. Soc. AIME*, **242** (1968), 31.
- (6) S. Noguchi: *J. Phys. Soc. Japan*, **17** (1962), 1844.
- (7) W. B. Pearson: *Handbook of Lattice Spacings and Structures of Metals and Alloys*, Pergman Press, (1958), p. 307.