An X-ray Study of the Heusler-type Ordering in AuAgZn₂ Alloy

By Yuichiro Murakami*, Yasuhiro Watanabe** and Sukeji Kachi*

The kinetic behavior of the Heusler(L2₁)-type ordering in the stoichiometric AuAgZn₂ alloy quenched from the CsCl(B2)-type ordered region was studied by X-ray diffraction. The degrees of the B2-type order (S_1) and the L2₁-type order (S_H) and the domain size of the L2₁-type superstructure were measured as a function of annealing time during the isothermal ordering process at 366, 386 and 406 K. The isothermal change of S_H was analyzed by the standard rate equation and the activation energy of the L2₁-type ordering was found to be 46 kJ/mol. The increase of the L2₁-type domain size was proportional to the three-tenth power of the annealing time. The temperature dependence of S_1 and S_H were also studied. S_1 showed a minimum whereas S_H decreased to zero at the critical temperature of the L2₁-type order on heating.

(Received May 17, 1980)

I. Introduction

Noble metal based- β phase alloys such as AuAgZn₂ and AuCuZn₂ have been reported to have two types of superstructure, i.e. the CsCl(B2)-type at high temperatures and the Heusler(L2₁)-type at low temperatures^{(1)~(4)}; The phase diagram of Au_xAg_{50-x}Zn₅₀ alloy is shown in Fig. 1 as an example. The L2₁-type ordering has been treated by the statistical thermodynamics and it was shown that the difference of the critical temperatures (T_{c2}) of the L2₁ lattice between AuAgZn₂ and AuCuZn₂ alloys is due to the difference of the ordering energies between Au-Ag and Au-Cu pairs of the next nearest neighbors⁽⁴⁾. Muldawa has shown that the L2₁-type ordering cannot be suppressed even by quenching from high temperature in AuCuZn₂ alloy, whereas it can be suppressed partially in AuAgZn₂ alloy⁽¹⁾. Then the stoichiometric AuAgZn₂ alloy seems to be appropriate for a study of the kinetic behavior of the L2₁-type ordering.

The kinetics of the ordering in the *bcc* alloy has been studied for the DO₃-type Fe₃Al alloy by many investigators^{(5)~(8)}. The degree of the DO₃-type order and the size of the

ordered domains were measured by X-ray diffraction during the ordering process. For example, Davies⁽⁶⁾ reported that the isothermal DO₃-type ordering proceeded by the nucleation and growth process of the ordered domains, whereas on slow cooling the DO₃-type ordering proceeded by a homogeneous nucleation process. Oki *et al.*⁽⁸⁾ showed that the isothermal DO₃-type ordering is caused by the nucleation and growth of the DO₃-type domain in the B2 matrix and that the activation energy is 155 kJ/mol.

Fig. 1 Critical temperature of the B2-type structure (T_{c1}) and that of the L2₁-type structure (T_{c2}) in Au_xAg_{50-x}Zn₅₀ alloys (after Brooks *et al.*⁽²⁾⁽⁴⁾).

* Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan.

** Graduate School, Kyoto University, Kyoto. Present address: Department of Chemistry, Saitama University, Urawa 338, Japan.

In the L₂₁-type AuCuZn₂ alloy, the degree of the B2-type order S_1 was reported to decrease to zero during the disordering process⁽³⁾. In the stoichiometric L₂₁-type AuAgZn₂ alloy, the temperature dependence of the degree of the L₂₁-type order S_H was reported by Muldower⁽¹⁾ but the information about the kinetic behavior has not been available. Therefore, in this study, the kinetic behaviors of the stoichiometric AuAgZn₂ alloy quenched from the B2 region are investigated by X-ray diffraction during the isothermal ordering process from the B2- to L₂₁-type superstructures, and the isothermal change of S_1 and S_H is analyzed quantitatively using a standard rate equation given by Feder *et al.*^{(7)~(9)}

II. Experimental

The alloy specimens were prepared by melting metals with high purity (99.99% Au, Ag and 99.999% Zn) in an evacuated quartz tube. The specimens were annealed at 873 K for 288 ks and then quenched into salt brine (267 K). The alloy ingot was filed into powders finer than 74 μm . The powdered specimens, sealed in quartz tubes, were annealed at 723 K (in the B2 region) for 3.6 ks and then quenched to 267 K. After this heat treatment, powdered specimens were annealed at temperatures 366, 386 and 406 K, well below T_{c2} (= 588 K) of the L₂₁-type ordering, for a definite period and then quenched to 267 K. Variation of the degree of the B2- and L₂₁-type order, S_1 and S_H , were measured by X-ray diffraction using a filtered CuK α radiation at room temperature. The temperature dependences of S_1 and S_H were also studied using a high temperature X-ray apparatus.

III. Analysis of the Degree of Order

The unit cell of the L₂₁-type superlattice, which consists of three kinds of sublattices, α , β and γ , is shown in Fig. 2. In the completely ordered state, α , β and γ sites are occupied, respectively, by Zn, Au and Ag atoms. In a previous paper⁽⁴⁾, in order to describe the occupation probabilities of the constituent atoms in the three sublattice sites, four kinds

Fig. 2 Unit cell of the Heusler-type(L₂₁) superlattice which consists of three kinds of sublattices, α , β and γ .

of the degree of order were defined as follows:

$$S_1 = 2(A_\alpha - x_A), \quad S_2 = 4(B_\beta - x_B)/3, \\ S_3 = 4(C_\gamma - x_C)/3 \quad \text{and} \quad S_4 = 2(x_A - A_\beta), \quad (1)$$

where x_A , x_B and x_C represent the mole fraction of Zn, Au and Ag atoms and A_α , B_β and C_γ the probabilities of finding a Zn atom on the α site, Au atom on the β site and Ag atom on the γ site, respectively.

The degree of order can be obtained by measuring integrated intensity of the X-ray reflections. The intensity I_{hkl} , from (hkl) plane is given by the following formula:

$$I_{hkl} = cmL(\theta)F_{hkl}^2 \exp(-\gamma \sin^2 \theta), \quad (2)$$

where c is a constant, m the multiplicity factor, $L(\theta)$ the Lorentz-polarization factor, F_{hkl} the structure factor and θ the Bragg angle. γ , the temperature factor, is determined by plotting $\ln \{I_{hkl}/mL(\theta)F_{hkl}\}$ of the fundamental reflections against $\sin^2 \theta$ as suggested by Oki *et al.*⁽⁸⁾

The structure factor F_{hkl} for the ternary *bcc* alloy is given by the following equations:

(i) When h, k, l are all even and $(h+k+l)/2$ is even, i.e. for the fundamental reflections,

$$F_{hkl} = 4x_A f_{\text{Zn}} + 4x_B f_{\text{Au}} + 4x_C f_{\text{Ag}}, \quad (3)$$

where f_i represents the atomic scattering factor of the i -th atom.

(ii) When h, k, l are all even and $(h+k+l)/2$ is odd, i.e. for the B2-type superlattice reflections,

$$F_{hkl} = \{2f_{Zn} - (x_B f_{Au} + x_C f_{Ag}) / (1 - x_A)\} S_1, \quad (4)$$

where S_1 represents the degree of the B2-type order.

(iii) When h, k, l are all odd, i.e. for the $L2_1$ -type superlattice reflections,

$$F_{hkl} = (f_{Au} - f_{Ag}) S_H, \quad (5)$$

$$\text{and } S_H = 3(S_2 + S_3)/4 - S_1/2, \quad (6)$$

where S_H represents the degree of the $L2_1$ -type order.

Each value of the four parameters, S_1, S_2, S_3 and S_4 , in eq. (1) cannot be determined directly by the X-ray measurement. Thereby, in the previous paper⁽⁴⁾, the relations between the probabilities such as $A_\beta = A_\gamma$ and $B_\alpha/x_B = C_\alpha/x_C$ were assumed, which gave simple relations between order parameters in the stoichiometric A_2BC composition as follows:

$$S_1 = S_4 \quad \text{and} \quad S_2 = S_3. \quad (1')$$

In this paper, S_1 and S_H are used as the parameters, because they can be determined directly by an X-ray analysis. In the B2-type lattice, $S_1 = 1$ and $S_2 = S_3 = 1/3$ ⁽⁴⁾, yielding $S_H = 0$. In the $L2_1$ lattice, $S_1 = 1$ and $S_2 = S_3 = 1$, yielding $S_H = 1$. Then the new parameter S_H defined by eq. (6) seems to be appropriate to describe the degree of the $L2_1$ -type order. The parameters, S_2, S_3 and S_4 , can be calculated from S_1 and S_H using eqs. (6) and (1') in the case of the Au-Ag-Zn system⁽⁴⁾.

S_1 and S_H of AuAgZn₂ alloy were determined from the ratio of the integrated intensities of the superlattice and the fundamental reflections, I_{111}/I_{220} and I_{200}/I_{220} , through eqs. (2)~(5) using the measured quantities at room temperature. The temperature dependences of S_1 and S_H were determined, respectively, by comparing the experimental values of (I_{200}/I_{220}) and (I_{111}/I_{220}) at high temperatures with the calculated values of those for the completely ordered state⁽¹⁾, i.e. by $(I_{111}/I_{220})_{\text{exp}} / (I_{111}/I_{220})_{\text{calc}} = S_H^2$ and $(I_{200}/I_{220})_{\text{exp}} / (I_{200}/I_{220})_{\text{calc}} = S_1^2$.

The size of the $L2_1$ -type ordered domain, D , is obtained by using Scherrer's equation:

$$D = \lambda / \beta \cos \theta \quad \text{and} \quad \beta = (B^2 - b^2)^{0.5}, \quad (7)$$

where λ is the wavelength of X-ray, θ the Bragg

angle, B the half width of the (111) reflection, and b the half width due to the instrumental broadening; b is estimated from the half width of the superlattice reflections of the well annealed specimen.

IV. Results and Discussion

1. Variation during isothermal annealing

The degree of order, S_1 and S_H , of the stoichiometric AuAgZn₂ alloy quenched from the B2 phase (723 K) were measured during the isothermal B2-to- $L2_1$ ordering process by an X-ray diffraction. Isothermal changes of S_1 and S_H at 366, 386 and 406 K are shown in

Fig. 3 Isothermal change of the degree of the B2-type order S_1 at temperatures, 366, 386 and 406 K, in the AuAgZn₂ alloy quenched from 723 K measured at room temperature.

Fig. 4 Isothermal change of the degree of the $L2_1$ -type order S_H at temperatures, 366, 386 and 406 K, in the AuAgZn₂ alloy quenched from 723 K measured at room temperature.

Figs. 3 and 4. In the quenched specimen, S_1 is 0.94, that is near to the equilibrium value (1.0 at 293 K). S_H is only 0.60; this result indicates that the L2₁-type ordering is partially suppressed by quenching as pointed out by Muldower⁽¹⁾. During the isothermal annealing, S_1 and S_H increase rapidly with annealing time and become almost constant after annealing over 2.4 ks. Isothermal change of S_H is analyzed by the standard rate equation given by Feder *et al.*⁽⁷⁾⁽⁸⁾:

$$dS_H/dt = (S_H^e - S_H)^n / \tau_n, \quad (8)$$

where S_H^e is the equilibrium value of S_H and τ_n the relaxation time for the n -th order reaction. From eq. (8), change of S_H is shown as a function of annealing time t as follows:

$$\left(\frac{S_H^e - S_H}{S_H^e - S_H^0} \right)^{1-n} = 1 + t(n-1)(S_H^e - S_H^0)^{n-1} / \tau_n$$

$$\text{and } \tau_n = \tau_1(n-1)(S_H^e - S_H^0)^{n-1} / \{\exp(n-1) - 1\}, \quad (9)$$

where S_H^0 is the value of S_H of the quenched specimen (i.e. at $t=0$) and τ_1 the relaxation time of the 1st order reaction⁽⁷⁾. The isothermal change of S_H shown in Fig. 4 can be well explained by this standard rate equation using parameters shown in Table 1.

Activation energy for the L2₁-type ordering is obtained from the Arrhenius plot, i.e. a plot of $\ln \tau_n$ as a function of $1/T$ as shown in Fig. 5. From the slope of a straight line in Fig. 5, the activation energy Q of the L2₁-type ordering was found to be 46 ± 2 kJ/mol, which is considerably smaller than that (155 kJ/mol) of the DO₃-type ordering in Fe₃Al alloy⁽⁸⁾. In the binary β phase alloy such as AgZn and AuZn, the activation energy for the self diffusion has been reported to be 70~138 kJ/mol⁽¹⁰⁾. The activation energy of the

Fig. 5 Relaxation time for the L2₁-type ordering as a function of reciprocal absolute temperature.

L2₁-type ordering obtained here may be smaller than that of the self diffusion in AuAgZn₂ alloy.

The growth of the L2₁-type ordered domains during the isothermal annealing is shown in Fig. 6. The change of the half width of the B2-type superlattice reflection could not be observed. The growth of the domain size D in many alloys has been reported to be described by the following equation⁽⁸⁾⁽¹³⁾:

$$D = kt^n, \quad (10)$$

where k and n are constants. Generally, n is in a range from 0.1 to 0.5⁽¹³⁾. From the slope of the straight lines in $\log D$ -vs- $\log t$ curves in Fig. 6, n is found to be 0.3. This is in agreement with that ($n=0.3$) for the growth of the DO₃-type domains in Fe₃Al⁽⁸⁾. The size of the L2₁-type domains increases with annealing time

Fig. 6 Growth of the antiphase domain size D as a function of the logarithm of annealing time during isothermal L2₁-type ordering.

Table 1 Relaxation time (τ_n) and parameters used to fit a standard rate equation to the isothermal ordering process. τ_1 is obtained directly from the curves of Fig. 4 assuming $n=1$ in eq. (8).

T/K	τ_1/s	τ_n/s	n
366	960 ± 24	932	1.02
386	480 ± 12	440	1.06
406	240 ± 12	208	1.10

even after the saturation of S_H (i.e. after the time longer than $\log(t/s)=3$) as shown in Fig. 6. This is similar to the growth of the DO_3 domains in the B2 matrix in Fe_3Al alloy⁽⁸⁾. These results suggest that the L_{21} -type ordered domains are nucleated in the B2 matrix and they grow by the movement of domain boundaries even after the saturation of degree of order. The existence of antiphase domains in the Heusler alloy AuCuZn_2 has been confirmed by an electron microscopy⁽¹²⁾. For $\log(t/s)$ less than about 2.5 in Fig. 6, experimental points deviate from the straight lines; this may be due to the fact that the domain size has a finite value of about 22 nm even in the quenched specimen (i.e. at $t=0$).

The quenched-in defects in the binary *bcc* alloys such as CuZn and AuCd were studied by many investigators^{(14)~(18)}. By a study of the isothermal annealing process, the activation energy for the migration of vacancies was reported to be 39~60 kJ/mol in these alloys. On the other hand, during the reordering process of the quenched-in disorder in the β - CuZn alloy, the activation energy for the reordering was reported to be 63 kJ/mol by Koczac *et al.*⁽¹⁶⁾, which is close to the summation of the activation energy for the migration of vacancies (39 kJ/mol) and the binding energy of the trapped vacancies (20 kJ/mol) at the antiphase domain boundaries⁽¹⁶⁾⁽¹⁸⁾. The observed activation energy (46 kJ/mol) for the L_{21} -type ordering in AuAgZn_2 alloy is of the same order as that for the migration of vacancies in the β phase alloys⁽¹⁴⁾. Therefore the vacancies are considered to play an important role in the kinetic behavior of the L_{21} -type ordering also in AuAgZn_2 alloy.

2. Variation on heating

In the stoichiometric AuAgZn_2 alloy, the critical temperature (T_{c2}) of the L_{21} -type structure is 587 K⁽²⁾ and that (T_{c1}) of the B2-type structure is 1130 K⁽⁴⁾. The variation of S_1 and S_H of the quenched AuAgZn_2 alloy was measured by using a high temperature X-ray apparatus on the step-wise heating process: temperature was raised at a definite interval and then kept constant during the measurement (averaged rate of heating was

Fig. 7 Variation of the degree of order, S_1 and S_H , in AuAgZn_2 alloy on a heating process.

0.1 K/s). The result is shown in Fig. 7. The experimental values of S_1 and S_H first increase in the temperature range near 360 K, where the ordering reaction is expected to proceed on heating. In the temperature region near T_{c2} , S_H decreases rapidly and becomes zero at T_{c2} . The temperature dependence of S_H just below T_{c2} is very steep compared with that expected from the Bragg-Williams theory. On the other hand, S_1 decreases rapidly at a temperature near T_{c2} and it increases again after passing a minimum at T_{c2} . This result indicates that the diffusion of atoms due to the disordering process of the L_{21} -type lattice destroys partially the B2-type order. Therefore, the diffusion of atoms between the 1st nearest neighbors as well as that between the 2nd nearest neighbors are expected to have an important role in the disordering process of the L_{21} -type lattice, which will be discussed in a following paper⁽¹¹⁾. Experiment above 600 K was very difficult because of the evaporation of Zn atoms.

V. Summary

Kinetic behavior of the AuAgZn_2 alloy quenched from the B2 region was studied by X-ray diffraction. The results are summarized as follows:

(1) The variation of S_H during the isothermal ordering process is well explained by the

standard rate equation and the activation energy of the L₂₁-type ordering is found to be 46 ± 2 kJ/mol.

(2) The isothermal L₂₁-type ordering proceeds by the nucleation and growth of the domains in the B2 matrix. The increase of the L₂₁ domain size is proportional to the three tenth power of the annealing time at a temperature near 400 K.

(3) The temperature dependence of S_1 and S_H were also studied by the high temperature X-ray analysis. S_H becomes zero at T_{c2} upon heating, whereas S_1 showed a minimum at T_{c2} . Diffusion of atoms between the 1st and the 2nd nearest neighbors are shown to play an important role in the ordering process in the Heusler alloy.

Acknowledgment

This work was partly supported by the grant-in-aid for the fundamental chemical research from the Japanese Foundation for Scientific Promotion.

REFERENCES

- (1) L. Muldower: J. Appl. Phys., **37** (1966), 2062.
- (2) M. E. Brooks and R. W. Smith: Scripta Met., **3** (1969), 667.
- (3) Y. Murakami, N. Nakanishi and S. Kachi: Acta Met., **19** (1971), 93.
- (4) Y. Murakami, S. Kachi, N. Nakanishi and H. Takehara: Acta Met., **19** (1971), 97.
- (5) H. J. McQueen and G. C. Kuczynski: Trans. Met. Soc. AIME, **215** (1959), 619.
- (6) R. G. Davies: Trans. Met. Soc. AIME, **230** (1964), 903.
- (7) R. Feder and R. W. Cahn: Phil. Mag., **5** (1960), 343.
- (8) K. Oki, M. Hasaka and T. Eguchi: Trans. JIM, **14** (1973), 8.
- (9) G. E. Poquette and D. E. Mikkola: Trans. Met. Soc. AIME, **245** (1969), 743.
- (10) G. Gupta and D. S. Lieberman: *Ordered Alloys*, Proc. 3rd Borton Landing Conf., Claitor's Publ. Div. (1970), p. 195.
- (11) Y. Murakami, Y. Watanabe and S. Kachi: Trans. JIM, **21** (1980), 714.
- (12) H. Kubo and K. Shimizu: Trans. JIM, **17** (1976), 330.
- (13) P. A. Beck, J. C. Kremer, L. J. Demer and M. L. Holzworth: Trans. AIME, **175** (1948), 372.
- (14) M. S. Wechsler: Acta Met., **5** (1957), 150.
- (15) N. Nakanishi, K. M. Thein and C. M. Wayman: J. Appl. Phys., **34** (1963), 2847.
- (16) M. J. Koczak, H. Herman and A. C. Damask: Acta Met., **19** (1971), 303.
- (17) J. S. Clark and N. Brown: Acta Met., **19** (1971), 291.
- (18) S. G. Cupchall and N. Brown: Acta Met., **19** (1971), 657.