The Structure and the Growth of Guinier-Preston Zones in an Al-6.8at% Zn Alloy*

By Masanori Murakami**, Masahiko Morinaga**,
Osamu Kawano*** and Yotaro Murakami***

A study by means of an X-ray small angle scattering method was carried out on the structure and the growth of Guinier-Preston zones in a binary aluminum-6.8 at% zinc alloy. By the isothermal measurement of scattering intensities of the alloy aged at 40°C, it was found that both models for the structure of G. P. zones proposed by Walker and Guinier⁽¹⁾ and by Gerold and Schweizer⁽²⁾ were not suitable at the early stages of aging, but that the latter model was suitable at the later stages. Moreover, the mechanism of growth of these zones was indicated to be accordant with the diffusion-controlled Ostwald ripening.

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I. Introduction

The studies by X-ray diffraction and electron microscopy gave the evidence that G. P. zones of a binary aluminum-rich zinc alloy were stable when aged at low temperatures after a quench from homogenization temperatures⁽³⁾⁻⁽⁵⁾.

For the structure of G. P. zones two models (Models 1 and 2) have been proposed. They are schematically represented in Fig. 1. Model 1 is the structure of zones

Fig. 1 Two models for the structure of G. P. zones. Model 1 consists of solute-rich zones surrounded by a solute-depleted shell with the rest of the matrix unchanged⁽¹⁾ and Model 2 is a conventional dispersion of zones in a matrix⁽²⁾. C_1 and C_2 are the solute concentrations inside and outside G. P. zones, respectively and C_B is the alloy concentration.

of solute atoms surrounded by a shell denuded in solute with the matrix remaining supersaturated at the original composition of the alloy, which was chosen by Walker and Guinier⁽¹⁾ to explain the appearance of the maximum in X-ray small angle scattering curves in an Al-Ag alloy. This model was also applied to the zones in an Al-Zn system. However, Gerold and Schweizer⁽²⁾ pointed out

that this model was inconsistent with the fact that the integrated intensity calculated from the scattering intensity was constant during the course of isothermal aging. Hence, a new model was given (Model 2): zones of solute concentration C_1 were distributed at random in the matrix of C_2 , where C_1 and C_2 are the solute concentrations determined from the metastable miscibility gap at a given temperature. This model was also known to be suitable even for the early stages of aging. Recently, by measuring the scattering intensity of Al-Zn alloys isothermally aged at -45°C, Bonfiglioli and Guinier⁽⁶⁾ indicated that though Model 2 was suitable for the later stages of aging, it was contradictory at the initial stages of decomposition.

In the present paper, to examine the structure of G. P. zones throughout aging the scattering intensity of an aluminum alloy containing 6.8 at% zinc aged isothermally at 40°C was measured by means of an X-ray small angle scattering method. Although the measured intensity provides a variety of information, by examining the integrated intensity⁽⁷⁾, applying Porod's law⁽⁸⁾ and calculating the short-range order parameter⁽⁹⁾, which were analyzed from the scattering curves, we attempted to indicate the change of solute concentrations inside and outside G. P. zones, to show the gradient of solute concentrations at the interface between zones and matrix and to clarify the distribution of solute atoms in the alloy. (In the present case, the interference function⁽¹⁰⁾ among zones is neglected.)

The initial decomposition of the supersaturated solid solution proceeds either by the spinodal or nucleation and growth mechanism. In a binary Al-22 at% Zn alloy Rundman and Hilliard⁽¹¹⁾ demonstrated that the change of the scattering intensity at 65°C aging coincided with the spinodal theory developed by Hillert⁽¹²⁾

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** Graduate School, Kyoto University, Kyoto, Japan.

*** Department of Metallurgy, Faculty of Engineering, Kyoto University, Kyoto, Japan.

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and Cahn⁽¹³⁾, and the present authors⁽¹⁴⁾, though the calculated spinodal temperature is below 0°C⁽¹¹⁾, estimated the spinodal temperature to be approximately 120°~130°C in an alloy containing 6.8 at% zinc. However, Cook⁽¹⁵⁾ has recently reported that the gradual shift in the intensity maximum during the isothermal aging makes it impossible to describe clustering kinetics. Besides, de Fontaine⁽¹⁶⁾ pointed out that there is no discontinuity either in morphology or in kinetics at the spinodal. Thus, the discussion on the kinetics of the formation of G.P. zones is not given here.

Lifshitz and Slyozov⁽¹⁷⁾ and Wagner⁽¹⁸⁾ established a theory for the growth of particles based on the diffusion equations. The validity of this theory was confirmed experimentally by Ardell⁽¹⁹⁾ in a binary Ni-Al alloy. At stages where the solid solution is completely decomposed to the expected points of metastable miscibility gap, the diffusion coefficient of solute atoms can be evaluated from the slope of a plot of $\bar{R}^3$ ($\bar{R}$: average zone radius) and t (time) by applying this theory to the zone growth. The validity of applicability of this theory to the zone growth will be given in the section of (III-2).

1. Theoretical considerations

(1) Integrated intensity

For the study of the as-quenched state and the time dependence of the solute concentrations inside and outside G. P. zones the investigation of the integrated intensity is utilized.

From the theory of small angle scattering⁽⁷⁾ the integrated intensity Q_0 was given as the function of the local fluctuation of electron density $(\rho - \rho_0)^2$,

$$Q_0 = 2 \pi \int_0^\infty s J(s) ds = \frac{(\rho - \rho_0)^2}{\rho_0} \quad (1a)$$

where $J(s)$ is the observed scattering intensity when the line collimation is used for the primary beam, $s = 2 \sin \theta / \lambda \approx 2\theta / \lambda$ (2θ is the scattering angle and λ is the wavelength of X-ray used) and ρ_0 is the average electron density. Before the decomposition is completed, the value of $(\rho - \rho_0)^2$, i. e. Q_0 , should increase with time t . When the decomposition has been progressed to the points of metastable miscibility gap⁽²⁰⁾, Q_0 should remain constant. In this case eq.(1a) can be rewritten in terms of the solute concentrations inside (C_1) and outside (C_2) G. P. zones⁽²¹⁾,

$$Q_0 = p (C_1 - C_B) (C_B - C_2) \frac{(Z_A - Z_B)^2}{V_a} \quad (1b)$$

where C_B is the solute concentration of the alloy, Z_A and Z_B are the respective atomic numbers of the solute and solvent atoms, V_a is the average atomic volume and p is the fraction of the alloy which has segregated into zones.

(2) Porod's law

To investigate the gradient of the concentration of solutes at the interface of G. P. zones with average electron density $\bar{\rho}$, Porod's equation⁽⁸⁾ can be applied:

$$\lim_{s \rightarrow \infty} s^3 J(s) = \frac{S}{16 \pi^3} (\bar{\rho} - \rho_0)^2 \quad (2)$$

where S is the total surface of G. P. zones per unit mass. According to this equation if there is a sharp interface between the two phases the value of $s^3 J(s)$ should become nearly constant for large s .

(3) Short-range order parameter

The investigation of the short-range order parameter α gives the information on the distribution of solute atoms in the alloy. This parameter is defined by the probability $n_{BB}(x)$ that a pair of atoms separated by a distance x is formed by two Zn atoms as follows⁽⁹⁾:

$$\alpha(x) = 1 - \frac{n_{BA}}{C_A} = 1 - \frac{1 - n_{BB}}{C_A} = \frac{n_{BB} - C_B}{C_A} \quad (3)$$

where

$$n_{BA} = \frac{N_{BA}}{N_{BB} + N_{BA}}, \quad n_{BB} = \frac{N_{BB}}{N_{BB} + N_{BA}},$$

$$C_A = N_{AB} + N_{AA}, \quad C_B = N_{BB} + N_{BA}.$$

N_{AA} , N_{AB} , N_{BB} and N_{BA} are the proportions of the various types of pairs on the vector x . Since the knowledge of the order parameter determines completely the scattering pattern, the order parameter can inversely be determined from the scattering pattern as follows:

$$\alpha(x) = \frac{1}{2 \pi x} \frac{\int_0^\infty I(s) \sin(2 \pi x s) ds}{\int_0^\infty I(s) s^2 ds} \quad (4)$$

where $\alpha(x)$ is normalized as $\alpha(0) = 1$, and $I(s)$ is the scattering intensity after beam height correction.

(4) Growth law

When the solute concentration in the solid solution has almost reached its equilibrium value, the Lifshitz-Wagner theory⁽¹⁷⁾⁽¹⁸⁾ is applicable to spherical G.P. zones dispersed in the matrix.

The theoretical kinetic equation for G. P. zones growth is,

$$\bar{R}^3 - \bar{R}_0^3 = k (t - t_0) \quad (5a)$$

where $\bar{R}$ and $\bar{R}_0$ are the average zone radius at time t and at the onset of coarsening (t_0) respectively. The rate constant k is given by

$$k = \frac{2 \sigma D C_e V_m^2}{\rho_e^2 R T}, \quad (5b)$$

where D is the diffusion coefficient of the solute, V_m is the molar volume of the zone, C_e is the concentration

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of solute in equilibrium with a particle of infinite size, ρ_c is a numerical constant related to the distribution of zone sizes (theoretically $\rho_c = 3/2$), RT has its usual meaning, and σ is the interfacial free energy of the zone-matrix interface.

σ is calculated on the basis of the situations in which G. P. zones and matrix are random solid solutions and the boundary is coherent. The interfacial energy is written by the summation of the structural interfacial energy ΔF^{str} and the chemical interfacial energy ΔF^{chem} . In the case of the coherent zone-matrix boundary $\Delta F^{\text{str}} \approx 0$.

Then,

$$\sigma \approx \Delta F^{\text{chem}} = \Delta H^{\text{chem}} - T \Delta S^{\text{chem}} \quad (6)$$

To calculate the enthalpic component ΔH^{chem} of the chemical interfacial energy, the relationship of Servi and Turnbull⁽²²⁾ can be applied to the zone-matrix boundary when the small misfit across the boundary is ignored:

$$\Delta H^{\text{chem}} = N_s Z_s (C_1 - C_2)^2 \Delta H_m \quad (7)$$

where N_s is the number of atoms per unit area in the plane of the interface, Z_s is the surface coordination number, and ΔH_m is the mixing enthalpy.

The entropic component ΔS^{chem} of the chemical interfacial energy is defined by,

$$\Delta S^{\text{chem}} = S_{mz} - \frac{1}{2} (S_{mm} + S_{zz}) \quad (8)$$

where S_{mm} , S_{zz} and S_{mz} are the positional entropies at the fully coherent matrix-matrix, zone-zone and matrix-zone boundaries, respectively, $\Delta S^{\text{chem}} = 0$ because the juxtaposition of two random solid solution produces an interphase boundary at which the randomness of the bond arrangements is exactly the average randomness at crystallographically identical boundaries within the component phases. Hence,

$$\sigma \approx \Delta H^{\text{chem}}. \quad (9)$$

II. Experimental Procedures

The material used was an aluminum-6.8 at% zinc alloy prepared from 99.99% aluminum and 99.99% zinc. The measurements of X-ray small angle scattering were carried out with the foils of 0.2 mm thick using Ni-filtered $\text{CuK}\alpha$ radiation. The specimens were homogenized at 300°C for one hour and cooled rapidly in a 0°C water bath placed below the furnace. After holding at this temperature for 15 sec, they were further cooled to the liquid nitrogen temperature before aging. The aging was performed in an air furnace kept at 40°C $\pm 0.1^\circ\text{C}$. The heat-up time of the specimens was less than 10 sec. The scattering intensity was counted at liquid nitrogen temperature at $1/8^\circ$ intervals in the scattering angle (2θ) up to $2\theta_0 = 3.75^\circ$ with line collimation. At the angles higher than $2\theta_0$, the $(2\theta)^{-3}$ law was utilized. The counted intensity spectra were corrected for beam height using a technique of the computer

method developed by Schmidt⁽²³⁾. The calculation of Q_0 was carried out by the method developed by Gerold⁽²¹⁾ and the average zone radius was obtained by using Guinier's approximation⁽²⁴⁾ utilizing the slope of a $\log I$ vs. $(2\theta)^2$ plot of X-ray scattering intensity data. In evaluating $\alpha(x)$ of eq. (4), the computer method was also used setting an upper limit $2\theta = 7.5^\circ$.

III. Experimental Results and Discussions

1. Structure of G. P. zones

Representative X-ray small angle scattering curves for specimens which were quenched from 300°C and aged at 40°C for the specified times are shown in Fig. 2. These curves were analyzed by utilizing the integrated intensity, Porod's law and the short-range order parameter.

Fig. 2 X-ray intensities scattered from the alloys quenched from 300°C and aged for the specific times at 40°C.

(1) Integrated intensity

Using eq. (1a) the integrated intensity Q_0 was calculated as shown in Fig. 3. The values of Q_0 in the specimens of the as-quenched state and aged for 1 min cannot be obtained, because the measured intensities were too weak to find the critical value of s , where $dQ_0/ds \approx 0$. After 2 min Q_0 increases as aging proceeds up to the critical time t_0 (~ 6 min) and after t_0 it becomes constant within experimental accuracy. From eq. (1a) this increase suggests the increase in the degree of discrepancy of electron densities inside and outside G. P. zones. At t_0 it is made clear by eq. (1b) that the decomposition has been progressed to the points of the metastable miscibility gap⁽²⁰⁾, that is, the solute concentrations inside and outside G. P. zones have been progressed to C_1 and

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Fig. 3 Change of the integrated intensities of the alloys quenched from 300°C and aged at 40°C.

C_2 respectively, where p is considered to be unity. The constancy of Q_0 after t_0 means that the values of C_1 and C_2 do not change during subsequent aging, although the zone radius increases with aging time.

(2) Porod's law

As given in eq. (2), the plot of $s^3 J(s)$ vs. s^3 gives the qualitative information on the gradient of solute concentration at the interface of G. P. zones. This plot is shown in Fig. 4 for the specimens aged for various times. In the early stages of aging $s^3 J(s)$ increases monotonously, but after 6 min it becomes constant for large s , obeying Porod's law. These results mean that G. P. zones having a sharp interface with the matrix are formed after 6 min and that the interface is not sharp until this critical time. It is interesting to note that this critical time almost coincides with the times when the integrated intensity shows a constant value.

(3) Short-range order parameter

Using eq. (4) the short-range order parameter $\alpha(x)$ can be calculated from the scattering intensities in Fig. 2. From these calculated $\alpha(x)$, the probability $n_{BB}(x)$ that a

Fig. 5 Probability of finding a zinc atom at a distance x from a given zinc atom for the alloys quenched from 300°C and aged at 40°C.

pair of atoms separated by a distance x is formed by two Zn atoms can be obtained as shown in Fig. 5.

The fact that n_{BB} is higher than the average C_B over distances of 20~30Å demonstrates the existence of segregated regions of atoms at this aging temperature. As aging proceeds these regions become larger and it is noted that the regions where n_{BB} is lower than the average value cannot be found even at the initial aging as in the case of the Al-Ag⁽⁴⁾ or Cu-Ni⁽²⁵⁾ system.

(4) New model

It is found that these results cannot be interpreted by supposing the structure of G. P. zones as only Model 1 or 2 throughout aging.

Model 1 is applicable mainly for the initial stages of aging on condition that at the aging times less than t_0 the following conditions are fulfilled: (1) Q_0 is lower than the final value Q_f , (2) Porod's law is not satisfied

Fig. 4 Variation of $s^3 J(s)$ as a function of s^3 for the alloys quenched from 300°C and aged at 40°C.

and (3) the region where n_{BB} is lower than C_B is observed. Though conditions (1) and (2) were satisfied at times less than t_0 , condition (3) was not. Besides, after t_0 all of these conditions were no longer valid. This suggests that Model 1 may not be valid even at the initial stages of aging.

In the case of Model 2, the following conditions are required throughout aging: (1) Q_0 is constant, (2) Porod's law is satisfied and (3) n_{BB} is higher than C_B . As shown in Figs. 3 and 4, at the initial stages ($t < t_0$) though condition (3) was valid, conditions (1) and (2) were not satisfied. However, at the later stages ($t > t_0$) these conditions were shown to be satisfactory. Thus, Model 2 is considered improper at the initial stages, but it may be suitable for the structure of G. P. zones at the later stage.

Therefore, at the later stages Model 2 is considered to be consistent with the present results, but at the initial stages both models are inconsistent. Thus a new model (Model 3) at the initial stage is given in Fig. 6. At this

Fig. 6 Proposed model for the structure of G. P. zones at the early stages of aging.

stage the solute concentration (C_1') inside G. P. zones does not reach the equilibrium value C_1 , the concentration of the matrix is still supersaturated ($C_2 < C_2'$) and the gradient of solute concentration at the interfaces between zones and matrix is not sharp. Recently de Fontaine⁽¹⁶⁾ indicated that this model is the same as the one⁽²⁶⁾ simulated by computer inside spinodal. As aging proceeds, both C_1' and C_2' tend to approach C_1 and C_2 respectively and at t_0 $C_1' = C_1$ and $C_2' = C_2$. The gradient of concentration becomes sharp simultaneously. At t_0 the decomposition is completed and after t_0 these zones grow keeping the solute concentrations both inside and outside the zones constant. This model is not contradictory to the present results.

2. Kinetics of growth of G.P. zones

The law of diffusion-controlled Ostwald ripening is applicable only to the growth of particles whose structures and solute concentrations do not change during aging like the stable precipitates or metallic compounds. Generally, from the viewpoint of stability, G. P. zones are classified as the metastable precipitates. However, Merz and Gerold⁽⁸⁾ revealed that the structure of the zones in the aluminum-rich aluminum-zinc alloys which were formed at room temperature did not change during aging. Besides, the constancy of the integrated intensity

Q_0 as shown in Fig. 3 or in the previous results⁽²⁰⁾⁽²⁷⁾ confirms that the solute concentrations of G.P. zones and the matrix do not change after the aging time of 6 min. Since the G.P. zones may be considered to be the "stable" precipitates from the viewpoint of stability, the Ostwald ripening can be applicable to the growth of G.P. zones and a plot of $\bar{R}^3$ vs. t ($t > t_0$) is given in Fig. 7, where data are found to show the excellent linearity. The diffusion coefficient during coarsening of G. P. zones is

Fig. 7 Time dependence of the average zone radius for the alloys quenched from 300°C and aged at 40°C.

estimated from the slope of the plot according to eq. (5 a). The measured value of k for specimens aged for 6~95 min is 5.069×10^{-22} cm³/sec. Putting $V_m = 9.401$ cm³/g-atom, $T = 313^\circ\text{K}$, and $C_e = 0.00185$ mol/cm³ into eq. (5 b), one obtains

$$D\sigma = 9.47 \times 10^{-11} \text{ erg/sec.} \quad (10)$$

To estimate the value of D from this equation, since the value of σ was not experimentally obtained at such low temperature, the calculated value, $\sigma = 64$ erg/cm², was used by putting $H_m = 232$ cal/mol⁽²⁸⁾, $N_s = 1.5 \times 10^{14}$ /cm² and $Zs \approx 4$ into eqs. (7) and (9). Then, from eq. (10) D is calculated to be 1.5×10^{-12} cm²/sec. Using the values of D obtained above and $D_0 = 0.31 \pm 0.14$ cm²/sec⁽²⁹⁾ which was determined by the use of the radioactive isotope Zn⁶⁵, the activation energy Q_{Zn} for the diffusion of zinc atoms in aluminum is calculated to be 0.70 ± 0.02 eV. From the temperature dependence of the critical time to reach electrical resistivity maximum, Panseri and Federighi⁽³⁰⁾ obtained $Q_{Zn} = 1.13 \pm 0.04$ eV in an Al-4.5 at% Zn alloy. Compared with this value, the one obtained by the present experiment is very low even though there is the difference in alloy concentrations. The origin of this discrepancy is not known, but one of the significant reasons may be due to the difference of solute concentrations in the zones when the measurements were carried out. At the critical times

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when the electrical resistivity measurements were carried out to determine the value of Q_{Zn} , the decomposition seems not to be completed.

IV. Conclusions

The measurements of the scattered intensities of the specimens quenched from 300°C and aged at 40°C by means of the X-ray small angle scattering method gave the information on the structures and the growth of G. P. zones in an Al-6.8 at% Zn alloy.

At the early stages of aging the formerly proposed models for the structures of zones were pointed out not to be consistent with the present experimental results and then an outline of a new structure for zones was given. At the later stages, when the solid solution was

completely decomposed Gerold and Schweizer's model was indicated to be suitable for the structure of G. P. zones.

The kinetics of growth of these zones was proved to follow the Ostwald ripening and also the diffusion coefficient at later stages was calculated to be 1.5×10^{-12} cm²/sec by applying the Lifshitz-Wagner theory to the zone growth.

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