

A STUDY ON THE FORMATION, GROWTH AND  
DISSOLUTION OF GUINIER-PRESTON ZONES  
IN ALUMINUM-ZINC ALLOYS

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A STUDY ON THE FORMATION, GROWTH AND DISSOLUTION  
OF GUINIER-PRESTON ZONES IN ALUMINUM-ZINC ALLOYS

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## CHAPTER 1

### GENERAL INTRODUCTION

#### 1-1. Pre-precipitation Process in Binary Aluminum-Zinc Alloys

There have been numerous previous studies in binary aluminum-rich aluminum-zinc alloy systems, particularly on the clusters of zinc atoms which form at low temperature after quenching from a solution temperature in the single  $\alpha$ -phase region. These clusters of zinc atoms are called "Guinier-Preston Zones" in honour of the names of the first detectors<sup>(1,2)</sup>. However, the general definition of these G.P. zones has not yet given, because it is difficult to find the characters of zones which have a great deal in common with each alloy system. In the binary Al-Zn alloys we call G.P. zones such pre-precipitates that are coherent with the aluminum-rich matrix and that their structure is the same as the matrix.

Several authors have given important results on G.P. zones. First, Guinier<sup>(3)</sup> has shown by X-ray small angle scattering, that the precipitates responsible for the age hardening were very small zinc-rich fcc spherical G.P. zones which were coherent with the aluminum-rich matrix. Panseri and Federighi<sup>(4)</sup>, coincidentally with Turnbull, Rosenbaum and Treafis<sup>(5)</sup>, demonstrated with isothermal resistivity measurements that the kinetics of formation of G.P. zones was controlled by the excess vacancy concentration

that could be retained from the quenching temperature. Gerold<sup>(6)</sup> showed that the concentration of zinc in G.P. zones lies on an extension of the miscibility gap, i.e., that a metastable miscibility exists. Recently Merz and Gerold<sup>(7)</sup> have established the sequence of the transformation of G.P. zones as follows: In the initial stages of aging the small spherical G.P. zones are formed, and at the critical zone radius of about  $35 \text{ \AA}$ , the anisotropy of coherency strains around the spherical G.P. zones lead to the contraction of the lattice spacing along one of the  $\langle 111 \rangle$  -directions inside the zones. These internal rhombohedral lattice deformations give rise to a change of the spherical shape of the zones into an ellipsoidal one. These ellipsoidal G.P. zones are always coherent with the matrix. The coherency strain fields have a rhombohedral symmetry. The typical dimensions of the ellipsoidal G.P. zones are thought to be between  $100$  and  $150 \text{ \AA}$  in the  $(111)$  planes and between  $30$  and  $50 \text{ \AA}$  in the normal direction.

In the present manuscript, the examination of the structure change of G.P. zones during the isothermal aging, the investigations on the kinetics of formation\*, growth\* or dissolution of G.P. zones and the determination of the solvus temperature of G.P. zones were carried out in binary aluminum-zinc alloys by means of X-ray small angle scattering,



electrical resistivity measurements and transmission electron microscopy. Moreover, the effects of addition of small amounts of the third elements or plastic deformation prior to aging on the aging process of G.P. zones were studied. The detailed review of previous work are given in the section of "Introduction" of each chapter.

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\* The words, "formation" and "growth", are distinguished depending on the degree of decomposition of super-saturated solid solution in this paper. "Formation" is used at the stage where there remains still super-saturation in the matrix, and solute rich regions at this stage are called "clusters". After decomposition is completed, that is, solute concentrations inside and outside zones reach the points determined by the miscibility gap of zones, zones grow in radius keeping solute concentrations constant to decrease the surface energy of zones. This process is called "growth process".

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## 1-2. Theory of X-ray Small Angle Scattering

### (a) General Formula

From the theory of the X-ray diffraction the scattering power per unit cell of a small crystal is given by<sup>(8)</sup>,

$$I(\vec{s}) = \frac{F_{hkl}^2}{V_c V} \sum_h \sum_k \sum_l \left| \sum (\vec{s} - \vec{r}_{hkl}^*) \right|^2 \quad (1.1)$$

where  $F_{hkl}$  is the structure factor of the reciprocal for the node  $hkl$ ,

$V_c$  is the volume of the unit cell of the crystal lattice,  $V$  is the volume of the specimen and  $\tilde{r}_{hkl}^* = h\tilde{a}^* + k\tilde{b}^* + l\tilde{c}^*$  ( $\tilde{a}^*$ ,  $\tilde{b}^*$  and  $\tilde{c}^*$  define the reciprocal lattice).  $\Sigma(\tilde{s})$  is the Fourier transform of the form factor  $\sigma(\tilde{x})$  of the crystal given by,

$$\Sigma(\tilde{s}) = \int \sigma(\tilde{x}) \exp(-2\pi i \tilde{s} \tilde{x}) dv_x \quad (1.2)$$

where  $dv_x$  is a small volume situated at the extremity of the vector

$\tilde{r}_{hkl}^*$  and  $\tilde{s} = (\tilde{S} - \tilde{S}_0)/\lambda$  ( $\tilde{S}_0$ ,  $\tilde{S}$  : unit vectors directed respectively along

the incident beam and in the direction of observation,  $\lambda$ : wavelength

X-ray used). A form factor  $\sigma(\tilde{x})$  is a function which is equal to unity

inside the external surface of the real object and equal to zero outside.

In the immediate vicinity of the center of the reciprocal space,

Eq. (1.1) is rewritten,

$$I(\tilde{s}) = \frac{F^2}{V_c V} |\Sigma(\tilde{s})|^2 \quad (1.3)$$

The quantity  $F$  is the structure factor for the unit cell occupying the

volume  $V_c$ . For very small angle,  $F$  is equal to the number of electrons

in the unit cell, so  $F/V_c$  is equal to the average electron density  $\rho$  in

the crystal. Thus the total scattering power is

$$I(\tilde{s}) = I(\tilde{s}) \frac{V}{V_c} = \rho^2 |\Sigma(\tilde{s})|^2. \quad (1.4)$$

We assume that the object contains a large number of identical

particles distributed at random, and that the average volume available for each particle is large compared to the volume of the particle. Under these conditions there is no interference between particles and, as in gas scattering, the intensities diffracted by the various particles simply add. If the particles all have the same orientation, the diffracted intensity per particle is equal to that for an isolated particle; if the particles are oriented at random, the observed intensity is the average intensity diffracted by a single particle for all possible orientations.

In many cases, as in colloidal solutions, for example, the particles are suspended in a homogeneous medium. If  $\rho_0$  is the electron density of the continuous medium, the scattering power of the particle is

$$I(\tilde{s}) = (\rho - \rho_0)^2 |\Sigma(\tilde{s})|^2, \quad (1.5)$$

since the sample can be considered to consist of a medium of uniform density  $\rho_0$  plus particles of density  $\rho - \rho_0$ . As a macroscopic sample of uniform density produces a central peak which is totally unobservable, the observed pattern is therefore correctly given by the above equation.

If the particles are oriented at random, the pattern exhibits symmetry of revolution and the scattering power per particle, as a function of  $s = 2\theta/\lambda$ , is given by

$$I(s) = (\rho - \rho_0)^2 \times \left\{ \begin{array}{l} \text{average value of } |\Sigma(\tilde{s})|^2 \text{ over} \\ \text{the sphere of radius } s = |\tilde{s}| \end{array} \right\} \quad (1.6)$$

The calculation of the pattern for the central peak given by homogeneous particles of given shape can therefore be found from Eqs. (1.5) and (1.6) by a process of integration.

(b) Guinier Approximation

We shall now show that the curvature at the center of the curve is related to a simple geometrical parameter of the particle, whatever the shape of the particle. Let  $S_0$  be the direction of the rays incident on the particle. For very small scattering angles,  $\tilde{s}$  is in the direction  $\tilde{D}$  normal to  $S_0$  and in the plane of the incident and scattered rays, and its modulus is  $s \approx 2\theta/\lambda$ . If  $\tilde{x}$  is any vector in object space,  $\tilde{s} \cdot \tilde{x} = s x_D$  where  $x_D$  is the projection of  $\tilde{x}$  on  $\tilde{D}$ . To calculate the function  $\Sigma(\tilde{s})$ , we have to evaluate the integral

$$\Sigma(\tilde{s}) = \int_V \exp(2\pi i \tilde{s} \cdot \tilde{x}) dv_x$$

This integral can be written as

$$\int \exp(2\pi i s x_D) \sigma(x_D) dx_D \quad (1.7)$$

where  $\sigma(x_D)$  is the cross-section of the particle along a plane normal to  $\tilde{D}$  at the distance  $x_D$  from the origin.

We select the origin  $O$  in object space at the center of gravity of the particle so that

$$\int x_D \sigma(x_D) dx_D = 0$$

and, since  $s$  remains very small within the central peak, we may expand the exponential function of Eq. (1.7) and neglect terms of order higher than  $s^2$ . Then

$$\Sigma(\tilde{s}) = \int \sigma(x_D) dx_D + 2\pi i s \int x_D \sigma(x_D) dx_D - 2\pi^2 s^2 \int x_D^2 \sigma(x_D) dx_D \quad (1.8)$$

The first term is simply the volume  $V$  of the particle ; the second term is zero because of our choice of origin. Let us now set

$$R_D^2 = \frac{1}{V} \int x_D^2 \sigma(x_D) dx_D \quad (1.9)$$

where  $R_D$  is the quadratic average of the distances to the plane ( $\pi_D$ ) normal to  $\tilde{D}$  and passing through the center of gravity  $O$ . This quantity  $R_D$  may be called the average inertial distance along  $\tilde{D}$ .

Then Eq. (1.8) becomes

$$\Sigma(s) = V - 2\pi^2 s^2 V R_D^2$$

We shall adopt as an approximation for  $\Sigma(s)$  the exponential form

$$\Sigma(s) = V \exp(- 2\pi^2 s^2 R_D^2) \quad (1.10)$$

Then the curvature at the origin has the correct value and  $\Sigma(s)$  tends toward zero as  $s$  increases.

From Eqs. (1.4) and (1.10), we now have an approximate formula for the scattering power per particle:

$$I(s) = c^2 V^2 \exp(- 4\pi^2 s^2 R_D^2) = n^2 \exp(- 4\pi^2 s^2 R_D^2) \quad (1.11)$$

For a spherical particle of radius  $r$ , the inertial distance is independ-



ent of the direction  $D$  and is equal to  $R_D = r/\sqrt{5}$ .

(c) Integrated Intensity

If the intensity  $I(s)$  is integrated over the whole region surrounding the origin, Eq. (1.5) gives

$$\int I(s) dv_s = (\rho - \rho_o)^2 \int |\Sigma(\tilde{s})|^2 dv_s$$

and

$$\int |\Sigma(\tilde{s})|^2 dv_s = V$$

Then,

$$\int I(s) dv_s = (\rho - \rho_o)^2 V.$$

If the sample contains identical particles of random orientation, the observed intensity  $I(s)$  is the average value of  $I(\tilde{s})$  for a given value of  $s$ . Thus

$$\int I(\tilde{s}) dv_s = (\rho - \rho_o)^2 V = \int_0^\infty 4\pi s^2 I(s) ds. \quad (1.12)$$

Although  $I(s)$  is not known experimentally up to  $s = 0$ , the extrapolation of  $s^2 I(s)$  can be made with accuracy. Absolute measurements of  $I(s)$  allow the determination of  $V$  if the electron density of the particle is known, or conversely of  $(\rho - \rho_o)$  if  $V$  is known.

Equations (1.5) and (1.12) give the volume of the particle, in terms of relative measurements only :

$$\frac{I(0)}{\int_0^\infty 4\pi s^2 I(s) ds} = \frac{(\rho - \rho_o)^2 V^2}{(\rho - \rho_o)^2 V} = V \quad (1.13)$$

In this case  $I(s)$  can be the diffracted intensity in arbitrary units for a sample of undetermined volume.

The integral of Eq. (1.12) may be applied to the most general case of a heterogeneous sample defined by its electron density  $\rho$ , which varies from point to point<sup>(9)</sup>. If  $\rho_0$  is the average density and  $I(s)$  the scattering power for the sample of volume  $V$ ,

$$\int 4\pi s^2 I(s) ds = V(\rho - \rho_0)^2 \quad (1.14)$$

where  $(\rho - \rho_0)$  is the local fluctuation of the electron density.

#### (d) Porod's Law

The exponential formula Eq. (1.11), is an approximation of the general Eq. (1.4) for the diffracted intensity, which is valid near the center of the curve (small  $s$ ). There is another approximate equation which is valid for the wings of the curve, in the region where the small angle scattering tends to zero. This Porod equation<sup>(10)</sup> is interesting because it provides a geometrical parameter which is different from the radius of gyration.

Let us consider the intensity diffracted by a sphere.  $I(s)$  is written

$$\begin{aligned} I(s) &= \left[ (\rho - \rho_0) \frac{4}{3} \pi r^3 \right]^2 \left[ 3 \frac{\sin 2\pi r s - 2\pi r s \cos 2\pi r s}{(2\pi r s)^3} \right] \\ &= \frac{(\rho - \rho_0)^2}{8\pi^3} \left[ \frac{4\pi^2 r^2}{s^4} + \frac{1}{\pi s^6} - \frac{4r}{s^5} \sin 4\pi r s + \left( \frac{4\pi r^2}{s^4} - \frac{1}{\pi s^6} \right) \cos 4\pi r s \right] \end{aligned} \quad (1.15)$$

The first two terms decrease uniformly with  $s$ , the term in  $s^{-4}$  being the more important, while the other terms oscillate with a decreasing amplitude and with a pseudoperiod of  $s = 1/(2r)$ . Now consider a set of spheres whose radii vary between  $r_1$  and  $r_2$ , the number of spheres of radius  $r_k$  per unit mass being  $g_k$ . The scattering power per unit mass of the sample is then

$$I = \frac{(\rho - \rho_0)^2}{8\pi^3} \left[ \sum g_k 4\pi r_k^2 \frac{1}{s^4} + \dots + \sum \cos 4\pi r_k s [\dots] + \sum \sin 2\pi r_k s [\dots] \right]. \quad (1.16)$$

If  $(2r_1 s - 2r_2 s)$  is much larger than unity, the last two summations are zero since their positive and negative contributions cancel. It is in fact observed that the oscillations disappear from the curve whenever the sample is not absolutely homogeneous. Therefore, if  $s$  is sufficiently large, we are left with the  $s^{-4}$  term. Now  $\sum g_k 4\pi r_k^2$  is the total surface  $S$  of the particles per unit mass, and the asymptotic value of the intensity is given by

$$I_{\text{asympt}} = \frac{(\rho - \rho_0)^2}{8\pi^3} \frac{S}{s^4} \quad (1.17)$$

Porod<sup>(10)</sup> has shown that this equation is valid for any shape of particle, so long as the orientations are random, and so long as none of the particle dimensions are zero ( $sL \gg 1$  for every dimension  $L$  of the particle).

The above asymptotic formula is valid for dissimilar particles and also for particles which are quite close to one another, because interference between particles has little effect on the wings of the curve.

This law has been verified experimentally by Van Nordstrand<sup>(11)</sup> in the case of alumina powders used as catalysts. When  $s$  is not too small, the curves of  $\log I$  versus  $\log s$  are straight lines of slope  $-4$ . He also observed empirically that, for these scattering angles, the scattered intensity is proportional to the total surface of the particles contained in one gram of the powder.

### 1-3. Informations from Experimental Scattering Curves

#### 1-3-1. X-Ray Small Angle Scattering Apparatus

The small angle scattering spectra of polycrystalline quenched and aged specimens were determined on a Rigaku-Denki diffractometer with  $\text{CuK}\alpha$  radiation at 35KV, 15 mA using Ni filter. Figure (1.1) is a photograph of the apparatus, and the slit (Kratky camera<sup>(12)</sup>), specimen and counter positions are shown schematically in Fig. (1.2). The scattering intensity was determined by counting for one minute at the interval of  $1/8^\circ$  of the scattering angle. Also, in Fig. (1.3) the cross-sections of the direct beam of line collimation or point collimation are shown. As the scattering

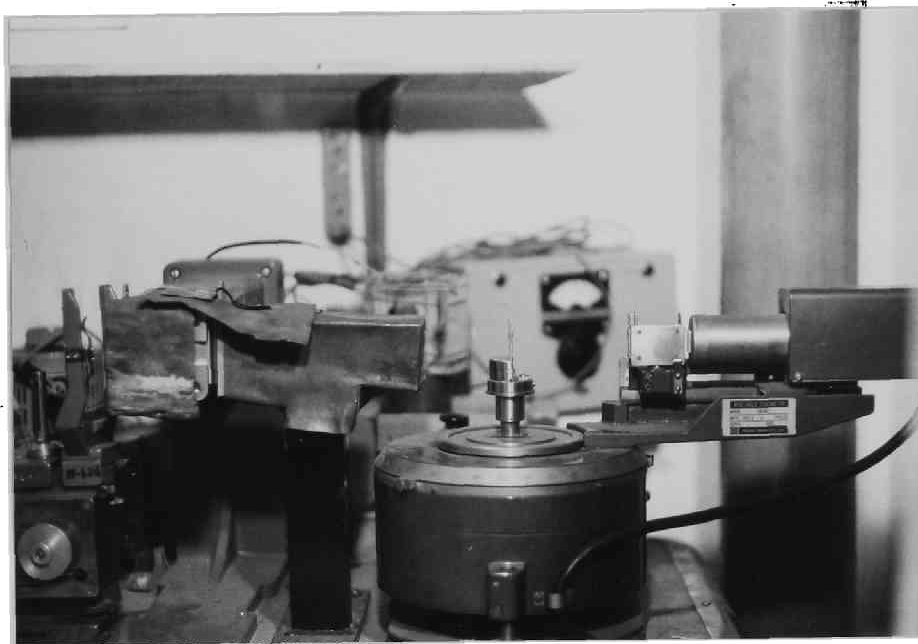


Fig.(1.1). Photograph of a Rigaku-Denki diffractometer.  
K : Kratky camera, S : sample holder,  $S_{1,2}$  : receiving  
slits, C : G.M. counter.

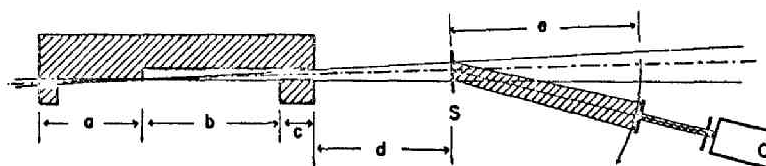


Fig.(1.2). Schematic illustrations of Kratky camera and  
the positions of sample holder (S), receiving slits and  
G.M. counter (C).  $a = 14$  cm,  $b = 8$  cm,  $c = 2$  cm,  $d = 8$  cm,  
 $e = 11$  cm and  $S_1 S_2 = 4$  cm.

intensity using the point collimation is very weak, the line collimation was used in the present studies. Then, the scattering intensity spectra distorted and the correction for the distortion effects of beam height is necessary under a certain circumstances using a computer program developed by Schmidt<sup>(13)</sup>. This correction is described in Appendix. No corrections were made for beam width or receiving slit width since both were small with respect to the spectra and the slit was small with respect to the beam width. The scattering intensities at the position  $s$  using the point and line collimation are denoted by  $I(s)$  and  $J(s)$  respectively. As an example, the scattering curves of  $J(s)$  and  $I(s)$  for alloy containing G.P. zones are shown in Fig. (1.4). From this curve the calculation methods of (a) average zone radius, (b) solute concentrations of zones, (c) zone number, (d) solute gradient at the interface between zones and matrix and (e) short-range order parameter will be given in the next section.

### 1-3-2. Calculation Methods of Zone Radius, Solute Concentrations of Zones, Zone Number, Solute Concentration Gradient at the Interface between Zones and Matrix and Short-Range Order Parameter

#### (a) Average Zone Radius

Average zone radius is obtained by using Guinier approximation

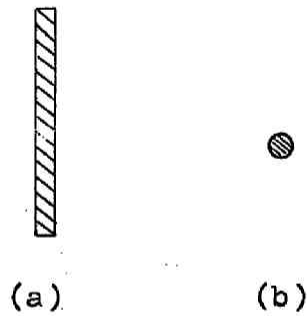


Fig.(1.3). Cross-sections of the direct beams of (a) line collimation and (b) point collimation respectively.

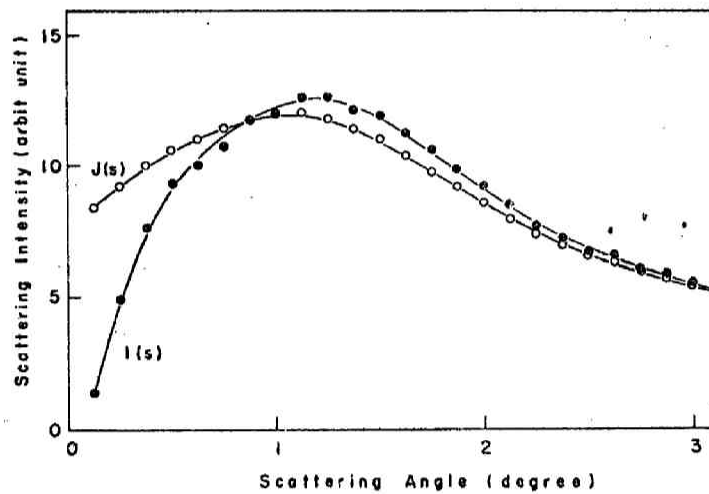


Fig.(1.4). X-ray intensities scattered from an alloy containing small solute-rich regions.  $J(s)$  is the intensity measured by a line collimation and  $I(s)$  is the one corrected for beam height by the method of Schmidt<sup>(13)</sup>.



(Eq. (1.11)), where the true intensity distribution is represented by a Gaussian curve. When the scattering intensity with the point collimation is expressed by a Gaussian distribution with respect to  $s^2$ , the intensity with the line collimation is also indicated to be expressed by a Gaussian distribution (see Eq. (A-2)). That is,

$$J(s) = (\text{const}) \cdot \exp(-4\pi^2 s^2 R_D^2) = (\text{const}) \cdot \exp(-\frac{4}{5}\pi^2 s^2 R^2) \quad (1.19)$$

where  $R_D = R/\sqrt{5}$  ( $R$  : average zone radius). Then, from the intensity curve obtained with the line collimation, the average zone radius is calculated by the slope of  $\log J(s)$  vs  $s^2$  plots.

(b) Solute Concentrations inside and outside Zones

The integrated intensity  $Q_0$  is related by the local fluctuation of electron density as given Eq. (1.14). That is,

$$Q_0 = \int 4\pi s^2 I(s) ds = V \overline{(\rho - \bar{\rho})^2}$$

When the solute concentration in zones is  $C_1$  and that of matrix is  $C_2$ , the integrated intensity is written in terms of  $C_1$  and  $C_2$  as follows,<sup>(6)</sup>

$$Q_0 = p (C_1 - C_0) (C_0 - C_2) \frac{(Z_A - Z_B)^2}{V_a} \quad (1.20)$$

where  $C_0$  is the solute concentration of the alloy,  $Z_A$  and  $Z_B$  are respective atomic number of solute and solvent atoms,  $V_a$  is the average atomic volume and  $p$  is the fraction of alloy which has segregated into zones.

The calculation method of  $Q_0$  from scattering curve obtained by the direct beam of line collimation is given below (see Eq.(A - 4)).

$$Q_0 = \int_0^\infty s^2 I(s) ds = \frac{1}{2} \int_0^\infty s J(s) ds \quad (1.21)$$

It is impossible to measure  $J(s)$  experimentally at large angles, so the asymptotic value of the intensity given by Eq.(1.17), i.e.,  $I = K/s^4$  for point collimation or  $J = \pi K/2s^3$  for line collimation, is used. Then,  $Q_0$  is calculated by the summation of intensities at each angle as follows,

$$Q_0 = \frac{1}{2} \int_0^\infty s J(s) ds = \frac{1}{2} \sum_{s=0}^{s_0} s J(s) \Delta s + \frac{1}{2} s_0^2 J(s_0) \quad (1.22)$$

(c) Zone Number

Zone number  $N$  per unit volume is given, by

$$\frac{4}{3} \pi R^3 N = V_0 \quad (1.23)$$

where  $R$  is average zone radius and  $V_0$  is volume fraction of zones.  $V_0$

is related to solute concentrations by the following equation:

$$V_0 = \frac{C_0 - C_2}{C_1 - C_2} \quad (1.24)$$

When the values of  $R$ ,  $C_1$  and  $C_2$  are obtained, the zone number  $N$  can be

calculated. From the scattering curve of an alloy containing zones,

$R$  is obtained by Eq.(1.19) and  $C_1$  and  $C_2$  are calculated by eqs.(1.20)

and (1.22). Thus, using these values,  $N$  is calculated by Eq.(1.23).

(d) Solute Concentration Gradient at the Interface between Zones

and Matrix

To investigate the gradient of the solute concentration at the interface of G.P. zones with average electron density  $\rho_0$ , Porod's equation can be applied. For the scattering intensity  $J(s)$  of the line collimation, Eq.(1.17) is rewritten (see Eq.(A-3)),

$$\lim_{s \rightarrow \infty} s^3 J(s) = \frac{S}{16\pi^3} (\rho - \rho_0)^2 \quad (1.25)$$

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

(e) Short-Range Order Parameter

The investigation of the short range order parameter  $\alpha$  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 B atoms, as follows<sup>(14)</sup>,

$$\alpha(x) = 1 - \frac{n_{BA}}{C_A} = 1 - \frac{1 - n_{BB}}{C_A} = \frac{n_{BB} - C_B}{C_A} \quad (1.26)$$

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  $\tilde{x}$ . Since the knowledge of order parameter determines

completely the scattering pattern, then, inversely the order parameter can be determined from the scattering pattern as follows,

$$\alpha(x) = \frac{1}{2\pi x} \frac{\int_0^\infty I(s) \sin(2\pi x s) s \, ds}{\int_0^\infty I(s) s^2 \, ds} \quad (1.27)$$

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

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# Appendix : Correction for the Effect of Beam Height<sup>(15)</sup>

The theories developed in Sec. (1-2) is for the direct beam of infinitely small radius i.e., point collimation. However, the scattering intensities with this collimation are too weak to observe, then the beam of the line collimation is used in the present investigation. In order to adapt the theories developed for the beam of point collimation to the present investigation, we must correct for the effect due to a beam which is infinitely narrow but has a certain height along the vertical axis (y - axis) as shown in Fig. (1-5). Let M be the point of observation and let the position of the point R in the direct beam be designated by the coordinate  $y = (2\pi \overline{OR})/\eta\lambda$  ( $\eta$  is the sample-to-film distance and the point O is the central point of the observation). The fraction of the total beam power contained in the segment of dimension  $dy$ , at the ordinate  $y$ , will be denoted by  $i(y)dy$ , where

$$i(y) = \frac{i'(y)}{\int i'(y) dy}$$

If  $I(h)$  is the true scattering distribution ( $i$  is, that obtained with a direct beam of infinitely small radius passing through O), the observed intensity at the point M is

$$J(h) = \int i(y) I(\sqrt{h^2 + y^2}) dy$$

where

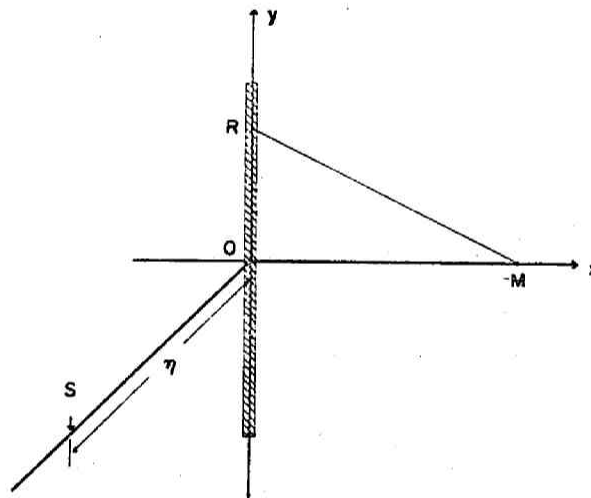


Fig.(1.5). Illustrations of cross-section of the direct beam with line collimation (shaded portion) and the positions of the observation point (M) and sample holder (S).  $\eta$  is the sample-to-counter distance, the point O is the central point of the observation and the point R is the position of the direct beam.

$$h = (2\pi OM)/\eta\lambda = 2\pi s$$

That is,

$$J(s) = \int i(y) I(\sqrt{4\pi^2 s^2 + y^2}) dy \quad (A-1)$$

When the equation of the scattering curve for an incident beam of point-like cross section is known, the scattering curve observed for a beam of infinite height can always be calculated by means of Eq. (A-1).

Several examples are given below.

Example 1 : When the true scattering distribution  $I(s)$  is represented by a Gaussian curve, i.e.,  $I(s) = A_1 \exp(-k^2 s^2)$  (Eq.(1.11)), the observed curve  $J(s)$  is proportional to the real curve ( $A_1, k : \text{const}$ ). This can be seen from the following :

$$J(s) = \left[ \int i(y) \exp(-k^2 y^2) dy \right] A_1 \exp(-k^2 s^2) = (\text{const}) \exp(-k^2 s^2) \quad (A-2)$$

Example 2 : If the asymptotic shape of the intensity curve is of the form of  $I(s) = A_2 s^{-4}$  (Eq.(1.17)), the observed curve varies asymptotically as  $s^{-3}$ . This is seen from the following :

$$J(s) = A_2 \int_{-\infty}^{\infty} \frac{1}{(4\pi^2 s^2 + y^2)^2} dy$$

By making the substitution  $y = 2\pi s \tan \alpha$ ,

$$J(s) = \frac{A_2}{4\pi^3 s^3} \int_0^{\pi/2} \frac{d\alpha}{(1 + \tan^2 \alpha)^2 \cos^2 \alpha}$$



$$= \frac{A_2}{4\pi^3 s^3} \int_0^{\pi/2} \cos^2 \alpha \, d\alpha = \frac{A_2}{16\pi^2 s^3}$$

That is,

$$J(s) = \frac{A_2}{16\pi^2} \cdot \frac{1}{s^3} \quad (A-3)$$

Example 3 : In Eq.(1.14) the integrated intensity  $Q_0$  is expressed by

$A_3 \int s^2 I(s) \, ds$ . In terms of the observed intensity this should be replaced

by the integral  $\frac{1}{2} A_3 \int s J(s) \, ds$ . This can be shown as follows :

$$\int_0^\infty s J(s) \, ds = \int_0^\infty \int_{-\infty}^\infty s I(\sqrt{4\pi^2 s^2 + y^2}) \, ds \, dy$$

By making the change of variables  $y = z \sin \alpha$  and  $s = z \cos \alpha$ , so that,

$$y^2 + s^2 = z^2 \text{ and } ds \, dy = z \, dz \, d\alpha$$

$$\int_0^\infty s J(s) \, ds = \int_0^\infty \int_{-\pi/2}^{\pi/2} I(z) z^2 \cos \alpha \, dz \, d\alpha = 2 \int_0^\infty z^2 I(z) \, dz$$

That is,

$$A_3 \int_0^\infty s^2 I(s) \, ds = \frac{1}{2} A_3 \int_0^\infty s J(s) \, ds \quad (A-4)$$

Example 4 : Other cases are corrected by the computer method developed

by Schmidt<sup>(13)</sup>. The program is given below.

```

C      SLIT HEIGHT CORRECTIONS IN SMALL ANGLE X-RAY SCATTERING
1      DIMENSION F(150,20),FT(150),R(100),XR(100,20),S(100),
      1G(100),WX(100),BNB(100),BX(100)
2      READ(5,100)NA,LA,N,MA,CA,CB
3      100 FORMAT(13,5X,13,5X,13,5X,13,5X,F10.5,5X,F10.5)
4      READ(5,200)((F(2*I,J),I=1,NA),J=1,LA)
5      200 FORMAT(5F10.3)
6      NB=2*NA
7      FNA=FLOAT(NB)
8      DO 1 J=1,LA
9      F(1,J)=0.5*(3.0*F(2,J)-F(4,J))
10     DO 2 I=1,NA-1
11     K=2*I
12     F(K+1,J)=0.5*(F(K,J)+F(K+2,J))
13     2 CONTINUE

```

```

14      DO 3 JD=(NB+1),N
15      FJD=FLOAT(JD)
16      F(JD,J)=(FNA**3)/(FJD**3)*F(NB,J)
17      3 CONTINUE
18      1 CONTINUE
19      H=3.1416/(16.0*180.0)
20      P=225.0*3.1416/8.0
21      DO 4 M=1,LA
22      WRITE(6,500)
23      500 FORMAT(1H1,10X,1HR,25X,2HXR)
24      PZP=FLOAT(M)
25      WRITE(6,600)PZP
26      600 FORMAT(1H0,3X,F7.1)
27      DO 5 J=1,NB
28      R(J)=FLOAT(J)
29      L=2*J
30      AJ=FLOAT(L)
31      B=AJ**2*P*H
32      Z=AJ*SQRT(2.0*AJ+1.0)*F(L,M)
33      DO 6 I=1,N-L
34      AI=FLOAT(I)
35      AE=(I**2+2*I*L)
36      AG=(I+1)**2+2*(I+1)*L
37      AQ=(I-1)**2+2*(I-1)*L
38      D=H*(2.0*SQRT(AE)-(SQRT(AG)+SQRT(AQ)))
39      T=(AJ+AI)*D*EXP(-(P*H/1.7725)**2*AE)
40      FT(I)=T*F(T+L,M)/H
41      6 CONTINUE
42      SA=0.0
43      DO 7 I=1,N-L
44      SA=SA+FT(I)
45      7 CONTINUE
46      XR(J,M)=(Z-SA)/B
47      IF(J.GT.(NA+1)) GO TO 5
48      WRITE(6,400)R(J),XR(J,M)
49      400 FORMAT(1H0,5X,E12.5,13X,E12.5)
50      5 CONTINUE
51      4 CONTINUE
52      DO 13 M=1,LA
53      WRITE(6,700)
54      700 FORMAT(1H1,14X,2HBX,26X,3HBNB,26X,2HWX)
55      DO 8 J=1,NB
56      S(J)=XR(J,M)*R(J)**2
57      8 CONTINUE
58      V=0.5*S(1)
59      VX=0.0
60      DO 9 L=1,NB-1
61      VZ=0.5*(S(L)+S(L+1))
62      VX=VX+VZ
63      9 CONTINUE
64      VU=VX+V
65      DO 10 I=1,MA
66      BX(I)=FLOAT(I)
67      C=0.008901*BX(I)
68      E=SIN(C*R(1))*R(1)*XR(1,M)*0.5
69      DO 11 J=1,NB
70      G(J)=XR(J,M)*R(J)*SIN(C*R(J))

```

|    |     |                                          |
|----|-----|------------------------------------------|
| 71 | 11  | CONTINUE                                 |
| 72 |     | $Q=0.0$                                  |
| 73 |     | DO 12 KL=1,NB-1                          |
| 74 |     | $QH=0.5*(G(KL)+G(KL+1))$                 |
| 75 |     | $Q=Q+QH$                                 |
| 76 | 12  | CONTINUE                                 |
| 77 |     | $W=E+Q$                                  |
| 78 |     | $WX(I)=W/(VU*C)$                         |
| 79 |     | $BNB(I)=CA*WX(I)+CB$                     |
| 80 |     | WRITE(6,800)BX(I),BNB(I),WX(I)           |
| 81 | 800 | FORMAT(1H0,5X,E18.8,10X,E18.8,10X,E18.8) |
| 82 | 10  | CONTINUE                                 |
| 83 | 13  | CONTINUE                                 |
| 84 |     | STOP                                     |
| 85 |     | END                                      |

## CHAPTER 2

### DETERMINATIONS OF THE FORMATION AND SOLVUS TEMPERATURES FOR G.P. ZONES

#### 2-1. Introduction

In this chapter the determinations of both the formation temperature below which zinc-clusters cannot be formed and the solvus temperatures above which G.P. zones can not exist, were carried out by means of X-ray small angle scattering, electrical resistivity measurements and transmission electron microscopy.

Previous works<sup>(1,2)</sup> have revealed that the kinetic of clustering of zinc atoms is controlled by the point defects of vacancy type. Thus, the formation temperature is expected to be influenced by the amounts of quenched-in vacancies which can be changed by the various quenching temperatures. Panseri and Federighi<sup>(1)</sup> found that zinc-clusters were formed at temperatures around  $-100^{\circ}\text{C}$  for an Al-4.4at.% Zn alloy. In this study, to determine the formation temperature for binary aluminum-zinc alloys containing various zinc concentrations from 4.4 - 12.4at.%, the changes of X-ray scattering intensities were measured while quenched specimens were heated slowly from liquid nitrogen temperature to room temperature.

On the other hand, it has been well known that the solute concentrations both inside and outside these zones are determined by the solvus curve for G.P. zones and the existence of this curve was first found by Borelius<sup>(3)</sup> by means of calorimetric measurements. Theoretically, the free energy of a system containing a composition fluctuation allowing for the elastic strain due to coherency was given by Cahn<sup>(4)</sup>, and by using his thermodynamic method, Lašek<sup>(5)</sup> evaluated the curve delineating the solvus for coherent precipitates in aluminum-zinc alloys. The good agreement between this calculated curve and the experimentally determined one was obtained by the electrical resistivity measurement. Recently the theoretical treatment of de Fontaine<sup>(6)</sup> has suggested that it is valid to use the reversion experiment to determine the curve. When an alloy containing zones formed at low temperature is quickly raised to a temperature above the solvus curve, they must completely dissolve, since the free energy surface contains no valley above this curve. However, if this system is raised to a temperature below the curve, these zones partially dissolve and partially survive. Then, to determine the solvus temperature the reversion experiment was utilized.

## 2-2. Theoretical Consideration

## 2-2-1. Determination of the Formation Temperature

From Eq.(1.5) the scattering power of the specimen containing local solute-rich regions of the average electron density  $\rho$  in the homogeneous medium ( $\rho_0$ ) is given by,

$$I(s) = (\rho - \rho_0)^2 |\Sigma(s)|^2 \quad (1.5)$$

where  $\Sigma(s)$  is a function of  $s$ . When the fluctuation of solute atoms is small,  $\Sigma(s)$  is considered to be constant at a given  $s$ . Then at the initial stages of the decomposition, the increase of the intensity is attributable to the increase of the degree of decomposition.

To determine the formation temperature  $T_f$  of zinc-clusters, the quenched specimen is heated slowly from liquid nitrogen temperature. It is expected that at a certain temperature ( $T_f$ ) the zinc-clusters will be formed, which contributes the increase of the difference of the local average electron densities in the specimen. Thus, when the measurements of the scattering intensities are carried out at a given scattering angle, the temperature, at which the increase of the intensity is observed, is determined to be the formation temperature.

## 2-2-2. Determination of the Solvus Temperature

To determine the solvus temperature  $T_c$  through the reversion experiment, the specimens were first aged at the low temperature to

stabilize G.P. zones and then reverted at various temperatures. When these specimens are reverted at the temperatures above  $T_c$ , the following results in each method are expected.

(a) X-ray Small Angle Scattering Method

From Eq.(1.20) the integrated intensity  $Q_o$  is given by,

$$Q_o = p(C_1 - C_o)(C_o - C_2) \frac{(Z_A - Z_B)^2}{V_a} \quad (1.20)$$

When the alloy has decomposed completely at a given temperature,  $C_1$  and  $C_2$  are determined by the solvus curve and  $p$  is considered to be unity.

The reversion process most likely involves "down-hill" diffusion of solute from zones into the matrix, creating more-or-less random solid solution. Thus as the reversion temperature increases, the decrease of  $C_1$  and the increase of  $C_2$  occur simultaneously, and above  $T_c$  (the solvus temperature for G.P. zones of the alloy whose average solute concentration is  $C_o$ )  $C_2 = C_o$ . So it is expected from Eq.(1.20) that  $Q_o$  decreases with reversion temperature and that at a temperature of  $T_c$ ,  $Q_o$  is nearly zero.

(b) Electrical Resistivity Measurements

It is well accepted that the electrical resistivity of an alloy containing G.P. zones is determined mainly by the solute concentrations inside and outside zones and zone radius. At the stages where the both

solute concentrations remain constant, the zone radius dependence of resistivity was given by Panseri and Federighi<sup>(1)</sup> and the plot of resistance and zone radius will be given in the later chapter. From the previous results the resistivity of the alloy aged for 100 min at room temperature was smaller than the value of solid solution ( $\rho_o$ ). Then when the alloy containing zones is reverted at high temperatures, the values of resistivity at a given time will monotonically increase with temperature. In the case that the reversion temperature is higher than  $T_c$ , the resistivity will be expected to increase up to the value of  $\rho_o$ . The value of  $\rho_o$  of an Al-6.8at.% Zn alloy is extrapolated to be  $1.68 \times 10^{-6}$  ohm-cm from the resistivities of pure aluminum ( $0.247 \times 10^{-6}$  ohm-cm)<sup>(7)</sup> and of the solid solution in an Al-3.4at.% Zn alloy ( $0.99 \times 10^{-6}$  ohm-cm)<sup>(7)</sup> measured at liquid nitrogen temperature by utilizing the Nordheim's law<sup>(8)</sup> as illustrated in Fig.(2.1)

### (c) Transmission Electron Microscopy

G.P. zones formed at low temperature aging were observed to be homogeneously distributed in the matrix. Graf and Lenormand<sup>(9)</sup> suggested that these zinc-rich clusters act as centres for  $\alpha'$  formation via a rhombohedral distortion which precedes  $\alpha'$ . In their words, the equilibrium precipitates can form directly from the original G.P. zones in a



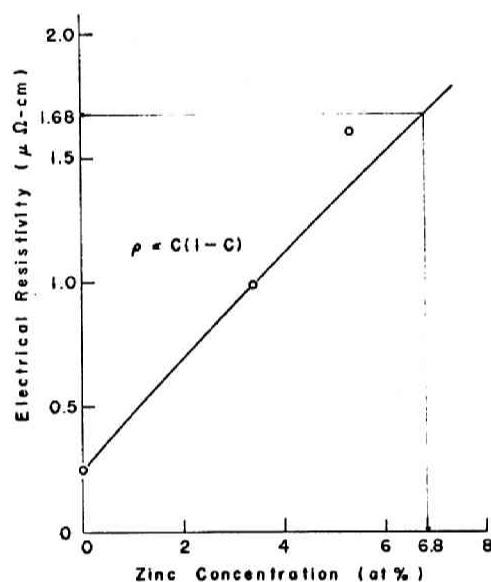


Fig.(2.1). Values of the electrical resistivities at liquid nitrogen temperature for Al-Zn alloys in the random solid solution state. The curve was drawn to fit two points of a pure aluminum and an Al-3.4at.% Zn alloy<sup>(7)</sup> using the Nordheim's law<sup>(8)</sup>. From this curve  $\rho_0$  of an Al-6.8at.% Zn alloy was extrapolated to be  $1.68 \times 10^{-6}$  ohm-cm.

sequential manner during lower temperature aging. On the other hand, at high temperature aging the precipitates of the equilibrium, close-packed hexagonal zinc-rich phase, were observed to nucleate only upon dislocations or at grain boundaries<sup>(10)</sup>.

Thus, if the solvus temperature for G.P. zones determined by the above two methods is correct, it is expected from the results of transmission electron microscopy that the equilibrium precipitates formed at temperatures below  $T_0$  are homogeneously distributed in the matrix and that those of above  $T_0$  are heterogeneously nucleated on the dislocations or grain boundaries.

### 2-3. Experimental Procedures

An aluminum-zinc alloy containing 4.4, 6.8, 9.7 and 12.4at.% Zn in the form of foils of 0.2mm thick was prepared from 99.99% aluminum and 99.99% zinc. For the study of the determination of the formation temperature, the specimens were homogenized at 450°C and 300°C for one hour in an air furnace, dropped rapidly into -70°C ethyl alcohol in a container beneath furnace. The specimens were held at this temperature for 5 sec and then cooled further to the liquid nitrogen temperature. From this temperature the specimens were heated to room temperature at

the constant rate of  $2^{\circ}\text{C}/\text{min}$ . While the specimen is heated, the change of the scattering intensity was measured at the fixed scattering angle of  $2\theta = 2/3^{\circ}$  using a low temperature camera as shown in Fig.(2-2).

This angle exists nearly on the position of the intensity maximum.

Though at this angle the interparticle interference function<sup>(11)</sup> has large effect on the measured intensity, it may not change abruptly.

For the study of the determination of the solvus temperature, the alloy containing 6.8at.% Zn were solution-treated at  $300^{\circ}\text{C}$  for one hour, then dropped rapidly into a water bath of  $0^{\circ}\text{C}$  beneath the furnace, held at this temperature for 15 sec and cooled further to liquid nitrogen temperature. They were pre-aged at room temperature ( $22^{\circ} \pm 3^{\circ}\text{C}$ ) for 100 min before reversion. (The change of zone radius and electrical resistivity during isothermal aging at this temperature will be shown in the later chapter) Then, they were reverted at each temperature in an air furnace which was kept the temperature within  $\pm 1^{\circ}\text{C}$  of the desired temperature. The X-ray intensities of these specimens are counted at  $1/8^{\circ}$  intervals in scattering angle using a Kratky camera in a low temperature camera at liquid nitrogen temperature. The measurement of electrical resistivity was also carried out with same foils at liquid nitrogen temperature.

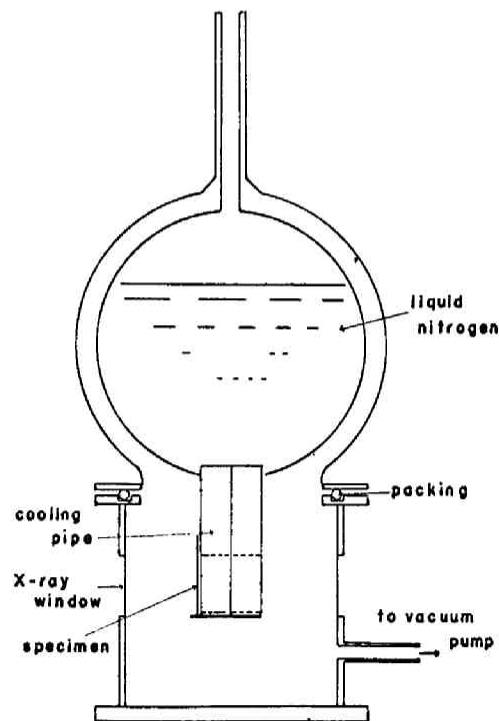


Fig.(2.2). Apparatus of a low temperature camera.

## 2-4. Experimental Results and Discussions

### 2-4-1. Determination of the Formation Temperature

The change of scattering intensities of the alloys of various zinc concentrations quenched either from  $450^{\circ}\text{C}$  or  $300^{\circ}\text{C}$  are measured during heating from liquid nitrogen temperature to room temperature at a constant heating rate of  $2^{\circ}\text{C}$  per min. They are illustrated in Fig.(2.3). That the intensities do not change below the temperatures shown by arrows means that the clustering which is expected to reflect the increase of scattering intensities do not exist at such low temperatures. Above these temperatures the increase of intensities is observed in each specimen, which is attributable to the formation of solute rich clusters. Thus, the temperatures shown by arrows illustrate the formation temperature for G.P. zones. These temperatures are listed for various alloys in Table (2.1). The formation in the specimens quenched from  $450^{\circ}\text{C}$  starts at the temperature range of  $-90^{\circ} \sim -60^{\circ}\text{C}$ , while in specimens quenched from  $300^{\circ}\text{C}$  the formation begins at  $-30^{\circ}\text{C}$ .

It is considered that for the specimens quenched from  $450^{\circ}\text{C}$  the zone formation process is enhanced by the higher quenched-in vacancies compared to the specimens quenched from  $300^{\circ}\text{C}$ .

The intensities which are observed at as-quenched state, that is,

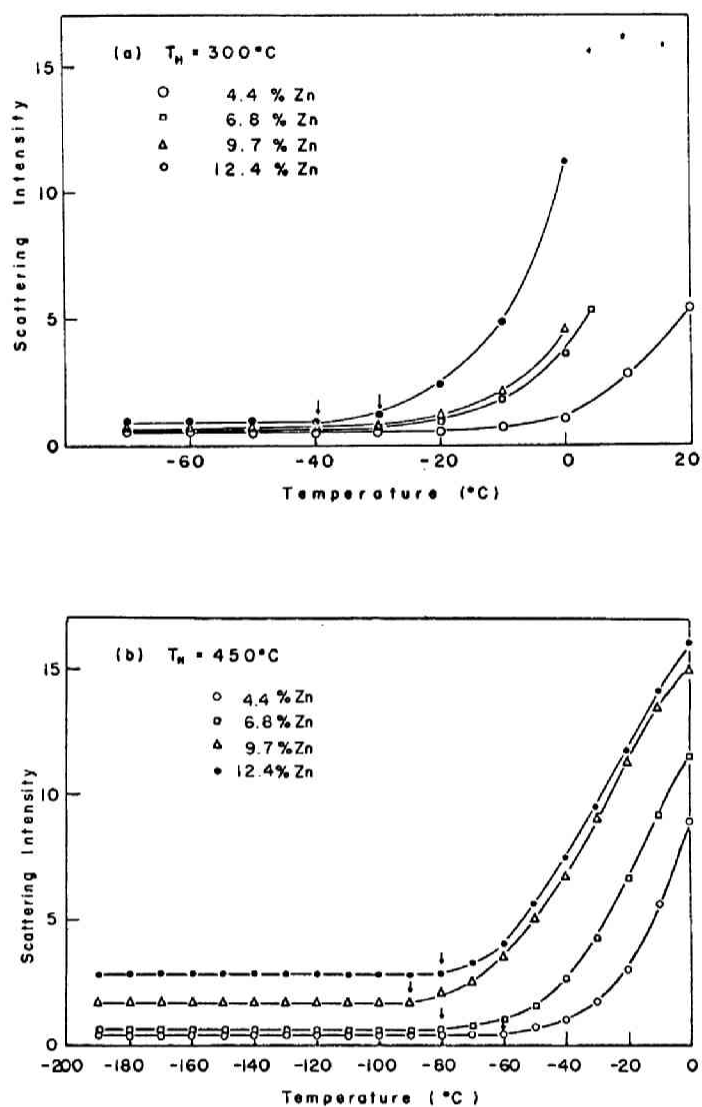


Fig.(2.3). Change of the scattering intensities measured at the fixed angle ( $2\theta = 2/3^\circ$ ) for Al-Zn alloys containing various zinc contents. The specimens were quenched from  $300^\circ\text{C}$  (a) or  $450^\circ\text{C}$  (b) and heated at the constant rate of  $2^\circ\text{C}$  per min. The arrows show the temperature at which the increase of the scattering intensities is observed.

those of at  $-196^{\circ}\text{C}$  are considered to be due to clusters formed during quenching. It is obvious that these intensities are higher for the alloy of higher zinc concentration.

## 2-4-2. Determination of the Solvus Temperature

### (a) X-ray Small Angle Scattering Method

The profiles of X-ray intensities versus scattering angle for these specimens pre-aged at room temperature for 100 min and reverted for 100 min at each high temperature are illustrated in Fig.(2.4), where it is shown that these intensities decrease monotonically with reversion temperature. Those of  $170^{\circ}\text{C}$  and  $180^{\circ}\text{C}$  were the same as the one of  $160^{\circ}\text{C}$  within experimental accuracy, then they were not plotted in this figure.

From these curves the integrated intensities  $Q_0$  are calculated by the method developed by Gerold<sup>(12)</sup> and the results are shown in Fig.(2.5). The change of  $Q_0$  with reversion temperature shows approximate linearity in the regions of lower temperatures than  $150^{\circ}\text{C}$ , although there is no reason why linearity should be maintained throughout this region. The values of  $Q_0$  for the specimens reverted above  $160^{\circ}\text{C}$  are not calculated exactly by the present method, because these intensities are too weak to find the critical value of  $(2\theta)$ , where  $dQ_0/d(2\theta) \simeq 0$  ( $2\theta$  : scattering angle). So using the  $(2\theta)^{-3}$  law (Eq.(A-3)) at higher scattering angle

Table (2.1). Temperature at which the increase of the scattering intensity is observed in the specimens quenched either from 300°C or 450°C.

| Quenching Temperature<br>( °C ) | Zinc Concentration (at%) |     |     |      |
|---------------------------------|--------------------------|-----|-----|------|
|                                 | 4.4                      | 6.8 | 9.7 | 12.4 |
| 3 0 0                           | -30                      | -30 | -35 | -30  |
| 4 5 0                           | -61                      | -80 | -90 | -80  |

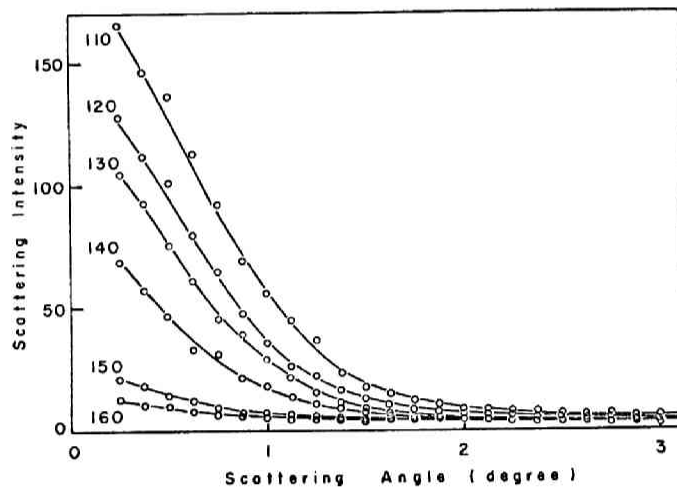


Fig.(2.4). X-ray intensities scattered from Al-6.8 at.% Zn alloys quenched from 300°C, pre-aged at room temperature for 100 min and reverted at each temperature (shown in this figure) for 100 min.



than one degree, the values of  $Q_0$  for these specimens were obtained and also plotted in this figure. However, the calculated values of these specimens are not due to the clustering of solute atoms.

The change of the integrated intensities during reversion is shown in Fig.(2.6). From this figure it is indicated that the holding time of 100 min at each reversion temperature is sufficient, as the isothermal changes of  $Q_0$  at this temperature have shown that during the initial stages of reversion  $Q_0$  decrease with time and that within 100 min  $Q_0$  becomes constant during subsequent reversion. This suggests from Eq.(1.20) that the solute concentrations both inside and outside zones reach the respective point on the solvus curve within 100 min at the given temperature.

It is noted that there exists the discontinuity at the temperature of approximately  $155^{\circ}\text{C}$ . As explained by the previous section, this temperature can be identified with the solvus temperature for G.P. zones in this alloy.

#### (b) Electrical Resistivity Measurements

The changes of the electrical resistivity, measured at liquid nitrogen temperature, during isothermal reversion at each temperature for the specimens pre-aged at room temperature for 100 min are shown

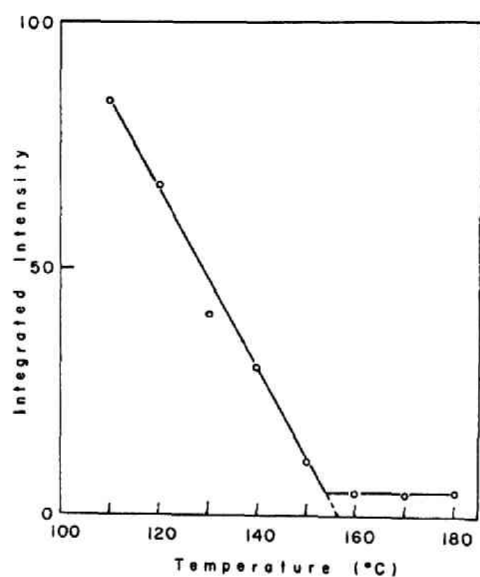


Fig.(2.5). Integrated intensities for Al-6.8at.% Zn alloys quenched from 300°C, pre-aged at room temperature for 100 min and reverted at each temperature for 100 min.

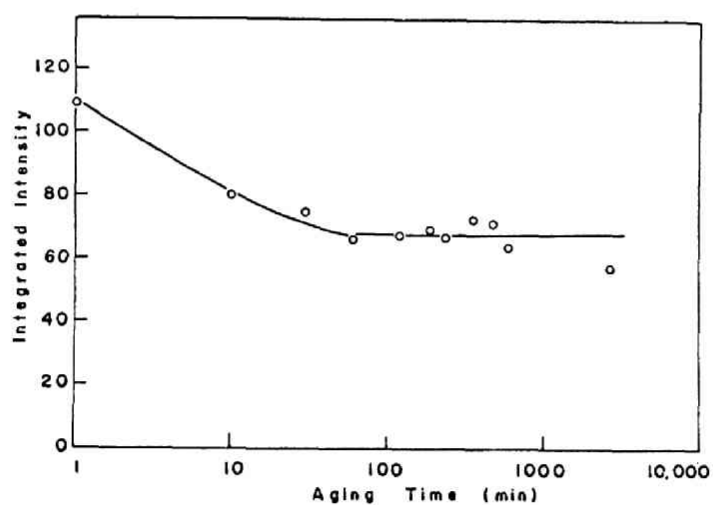


Fig.(2.6). Change of the integrated intensity during reversion at 120°C for an Al-6.8at.% Zn alloy quenched from 300°C and pre-aged at room temperature for 100 min prior to reversion.

in Fig.(2.7).

The resistivities for the specimens reverted below 140°C first increase, pass the maxima and then decrease, but although those of 160°C and 200°C increase during initial stage of reversion, they show almost no change during subsequent reversion. The rate of increase, as revealed by the resistivity value corresponding to 10 sec reversion at each temperature, is greater for the specimens reverted at higher temperature. The initial increase is considered to be due to the dissolution of G.P. zones formed at room temperature and the subsequent decrease is due to the formation and growth of G.P. zones stable at high temperatures.

The maximum resistivity of each specimen is plotted in Fig.(2.8). They increase continuously with reversion temperature up to 160°C and above this temperature they stay constant. The resistivities of the alloys reverted at temperatures above 160°C are approximately  $1.77 \times 10^{-6}$  ohm-cm. This value is about 5% higher than the one of the random solid solution obtained by using the Nordheim's law<sup>(8)</sup>. This difference may be due to the errors in measuring the sizes of the specimen. (If there are 2% error in the each measurement of the length, width and thickness of the specimen, the error of resistivity is about 6%.) Then allowing for these errors, the resistivity of the alloys reverted above 160°C

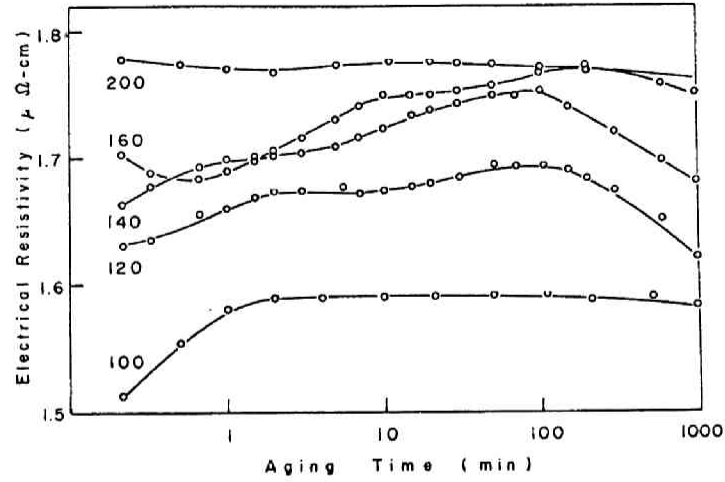


Fig.(2.7). Change of electrical resistivity during reversion at each temperature in Al-6.8at.% Zn alloys quenched from 300°C and pre-aged at room temperature for 100 min prior to reversion.

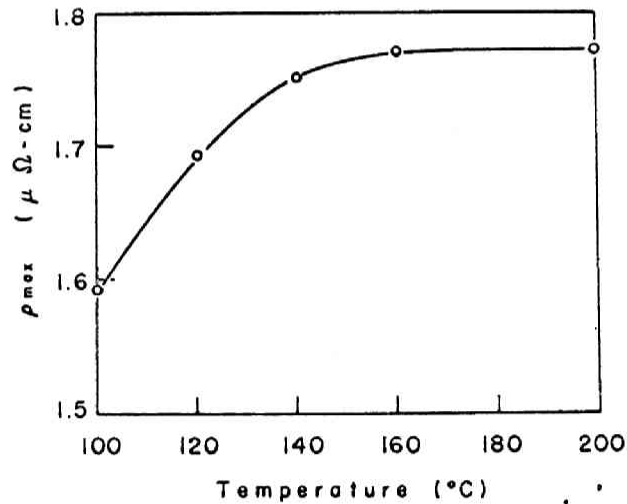


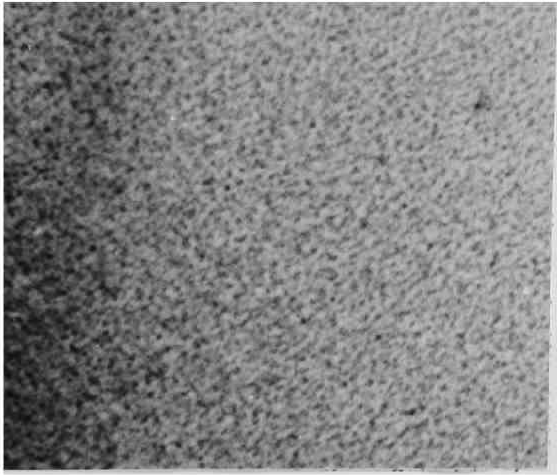
Fig.(2.8). Plot of electrical resistivity maxima and reversion temperatures for Al-6.8at.% Zn alloys reverted at each temperature. Data were deduced from Fig.(2.7).

is almost the same as the one of the random solid solution, that is, above  $160^{\circ}\text{C}$  there is no contribution of G.P. zones to resistivity. This means that G.P. zones do not exist above this critical temperature.

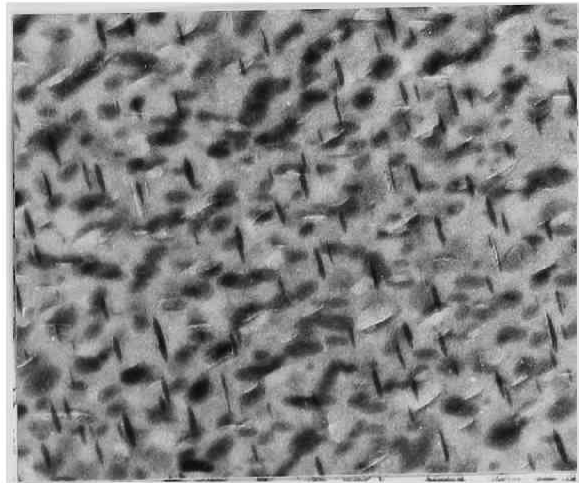
Thus, the solvus temperature determined by the present method is  $160^{\circ}\text{C}$ , which coincides with the one determined by the X-ray small angle scattering method.

#### (c) Transmission Electron Microscopy

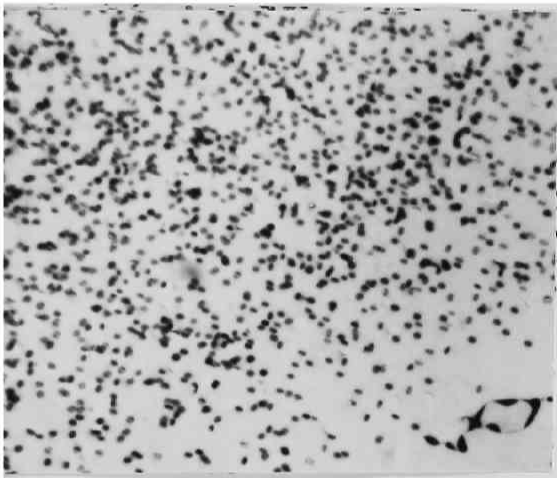
By the observation of transmission electron microscopy, the morphology of particles which were formed at the aging temperature below or above  $T_c$ , that is,  $120^{\circ}\text{C}$ ,  $140^{\circ}\text{C}$  or  $160^{\circ}\text{C}$ , was investigated. The micrographs for the specimens which were water quenched and aged at each temperature for a long time are shown in Fig.(2.9). (The morphology was the same as those pre-aged at room temperature prior to reversion.) In these micrographs it is observed that the difference in morphology between particles formed at  $140^{\circ}\text{C}$  and  $160^{\circ}\text{C}$  are remarkable : the particles of  $140^{\circ}\text{C}$  aging are formed homogeneously in the matrix and their shape is disk, on the other hand, those of  $160^{\circ}\text{C}$  are formed heterogeneously only on the dislocations. Referring to the earlier results<sup>(9, 13)</sup>, the particles formed at  $140^{\circ}\text{C}$  are the partially coherent precipitates  $\alpha'_R$  and those of  $160^{\circ}\text{C}$  are incoherent precipitates  $\beta$ .



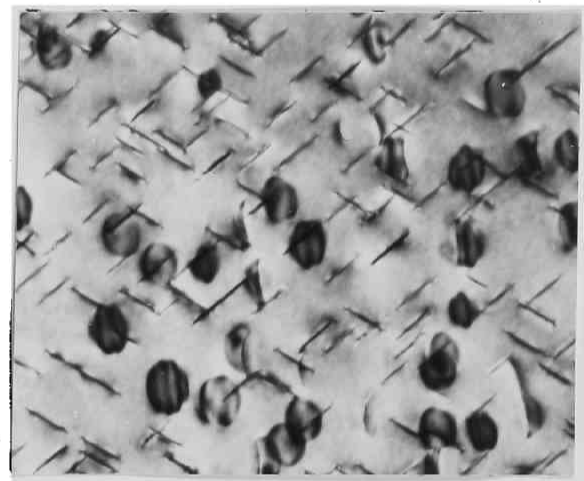
120°C 2880 min. x 60,000



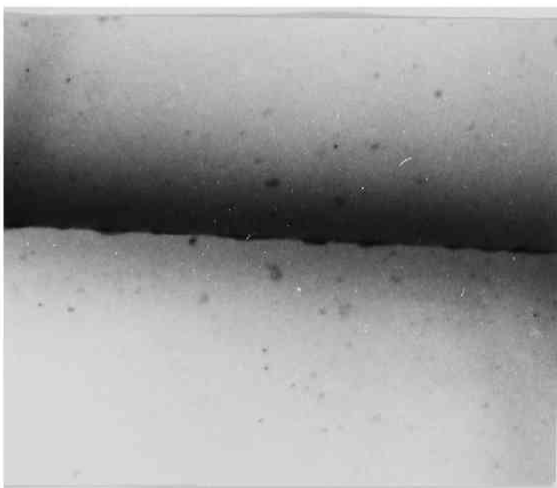
120°C 45,000 min. x 60,000



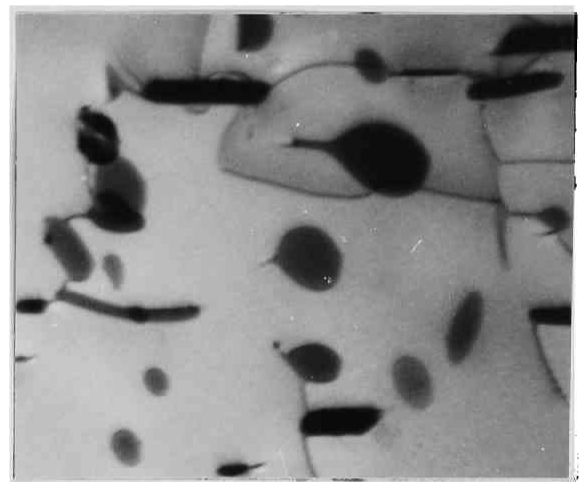
140°C 1230 min. x 30,000



140°C 11,580 min. x 30,000



160°C 900 min. x 30,000



160°C 20,000 min. x 30,000

Fig.(2.9). Transmission electron micrographs for Al-6.8at.% Zn alloys quenched from 300°C and aged at 120°, 140° or 160°.

Hence, the solvus determined by previous method is verified even by the present method.

(d) Comparison with Other Results

The solvus curve for coherent precipitates (G.P. zones), which is calculated by Lašek<sup>(5)</sup> using thermodynamic data<sup>(14)</sup> on the basis of Cahn's equation<sup>(4)</sup>, is illustrated in Fig.(2.10)(here  $C_0 = 0.068$ ).

The point determined by the present experiment is plotted in this figure and it is found that this point falls precisely on this solvus curve.

Also, the points obtained in earlier work by the diffuse X-ray study<sup>(13)</sup>, hardness<sup>(15)</sup>, electrical resistivity<sup>(5)</sup> and X-ray small angle scattering method<sup>(16, 17)</sup> are plotted on this curve, and they are found to be just on this solvus, though the alloy composition used in each experiment is different. This means that the determination of the solvus curve is not much influenced by the prior treatments, that is, quenching temperatures and the pre-aging times at room temperature. However, recent results suggest that this solvus curve is influenced by the plastic deformation in the as-quenched state as shown a later chapter.

2-5. Summary

The formation temperature and solvus temperature for G.P. zones in

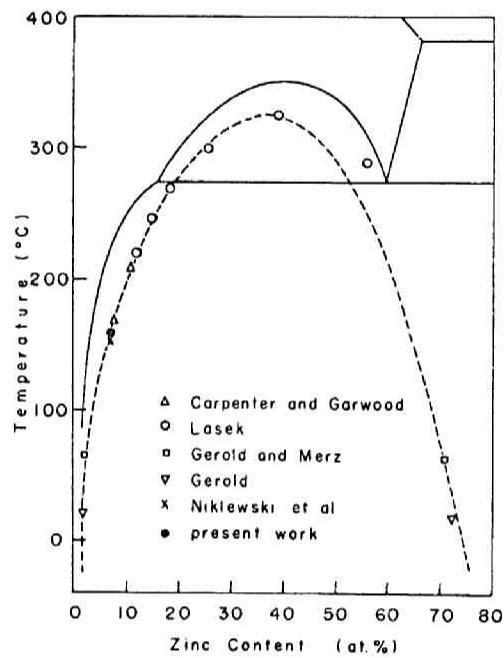


Fig.(2.10). Calculated solvus curve (dashed line) for coherent precipitates in an Al-6.8at.% Zn alloy using the thermodynamic equation given by Lašek<sup>(5)</sup>. It is noted that the points obtained by the present experiment or other authors fall on precisely on this curve.



binary aluminum-zinc alloys were determined by means of X-ray small angle scattering method, electrical resistivity measurements and transmission electron microscopy. It was found that the formation temperature for G.P. zones in quenched alloys have been influenced by both the quenching temperature and alloy concentration. As an example for an alloy containing 6.8at.% Zn  $T_f = -30^{\circ}\text{C}$  when the specimen was quenched from  $300^{\circ}\text{C}$  and  $T_f = -80^{\circ}\text{C}$  when quenched from  $450^{\circ}\text{C}$ . It was also indicated that in this alloy at the temperatures above approximately  $155^{\circ}\text{C}$ , zones which were formed at room temperature aging were found to almost completely dissolve and this critical temperature was concluded to be the solvus temperature for G.P. zones in this alloy. Moreover, this temperature was shown to coincide with the calculated one by using the thermodynamic equation given by Lašek.

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## CHAPTER 3

### STRUCTURE OF G.P. ZONES

#### 3-1. Introduction

For the structure of G.P. zones various models have been proposed to explain the experimental results of X-ray diffraction. They are schematically illustrated in Figs(3.1) and (3.2). These models are divided into two groups. The first group Fig.(3.1) postulates a periodic variation of composition about the mean composition  $C_0$  with a wave length much greater than the mean interplaner spacing in the direction of the fluctuation. This structure is called to be "modulated" by the composition fluctuation. The second group Fig.(3.2) postulates the existence of the isolated fluctuation of composition distributed randomly in the saturated matrix.

On the modulated structure of G.P. zones, Daniel and Lipson<sup>(1,2)</sup> (Fig.(3.1a)) first used a sinusoidal modulation of the crystal structure with respect to lattice spacing in the  $[100]$  direction in order to explain the anomalous diffraction from a Cu-Fe-Ni alloy. Comparison of calculated intensities of the satellite peaks for such a model and those measured on X-ray powder patterns showed some serious discrepancies which could only be accounted for by using an arbitrary correction for extinction. Hargreaves<sup>(3)</sup>, studying the same alloy, proposed a square-wave model

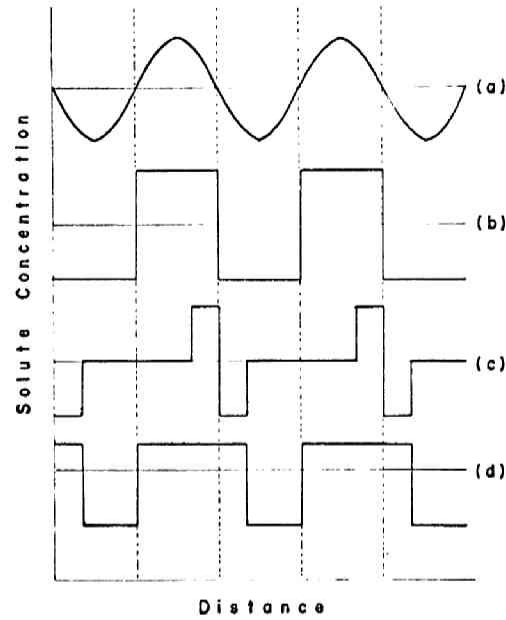


Fig.(3.1). Models of the modulated structures of G.P. zones. They postulate a periodic variation of the fluctuation. The detailed interpretations are given in the text.

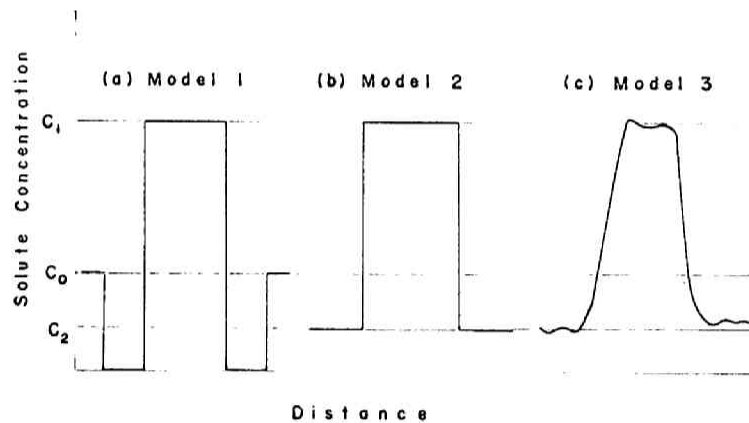


Fig.(3.2). Models of the isolated structure of G.P. zones. Model 1 consists of solute-rich zones surrounded by a solute-depleted shell with the rest of the matrix unchanged<sup>(7)</sup>, Model 2 is a conventional dispersion of zones in a matrix<sup>(8)</sup> and Model 3 is the result of calculation allowing for the elastic strain between zones and matrix<sup>(10)</sup>.  $C_1$  and  $C_2$  are the solute concentrations inside and outside G.P. zones respectively and  $C_0$  is the alloy concentration.

(Fig. (3.1b)) on the assumption that the metastable cubic solid solution transforms eventually into two coherent, slightly tetragonal pre-precipitation. To calculate the resulting diffraction pattern by using approximate formulae, the substantially same result as the sinusoidal fluctuation was given. There seemed to be no improvement in this treatment. Hargreaves<sup>(3)</sup> then proposed a more "flexible" model Fig.(3.1c) which illustrated an  $\alpha'$  pre-precipitate nucleating an adjacent  $\beta'$  phase. With the help of the additional parameter (the amount of supersaturated matrix) chosen in such a way as to give the best possible fit, Hargreaves was able to obtain reasonable agreement between the calculated and measured intensities. However, it was pointed out by Biedermann<sup>(4)</sup> that Hargreaves' formulae were oversimplified and that calculations based on better approximations would actually predict higher intensities for second rather than first-order satellites, which is never seen in practice. It was further shown independently by Balli and Zakharova<sup>(5)</sup>, Tiedema, Bouman and Burgers<sup>(6)</sup> and Biedermann<sup>(4)</sup> that above models (a - c) would only apply to alloys of mean composition located in the central region of the miscibility gap. However, in the case where the fraction of clusters is much greater than the fraction of matrix, an asymmetrical model as sketched in Fig.(3.1d) would be more likely. Such a model gives

rise to an asymmetrix distribution of satellite peaks about the main reflection.

These models of modulated structures were not satisfactory to explain the experimental results of X-ray diffraction. Thus, the models of the isolated zones which are distributed at random in the matrix have been proposed below. First, Walker and Guinier<sup>(7)</sup> (Fig.(3.2a)) proposed the structure of zones of solute atoms surrounded by a shell denuded in solute with the matrix remaining supersaturated at the original composition of the alloy 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<sup>(8)</sup> 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 the isothermal aging. Hence, a new model was given (Fig.(3.2b)) : 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 indicated to be suitable even for the initial stages of aging. Recently, by measuring the intensity scattered from Al-Zn alloys isothermally aged at  $-45^{\circ}\text{C}$ ,

Bonfiglioli and Guinier<sup>(9)</sup> indicated that though Gerold's model was suitable for the later stages of aging, it was contradictory at the initial stages of decomposition. Recently de Fontaine<sup>(10)</sup> illustrated a completely new model which was different from above two models as shown in Fig.(3.2c). Cahn and Hilliard<sup>(11)</sup> developed the theory of the free energy of inhomogeneous solid solution and modified the classical diffusion equation by considering the coherency term. By applying this modified diffusion equation to zone formation, de Fontaine<sup>(10)</sup> showed the composition variations in Al-Zn alloys inside the spinodal at each aging time. His calculation result showed that the modulation was fairly periodic at all times. (However, in the present figure the composition profile of an isolated zone for an Al-Zn alloy is shown). The different points of this model compared with the above two models are that the gradient of concentration of solute atoms at the interface between zones and matrix is not sharp as Gerold's model and that there exist no denuded regions of solute atoms around zones as Walker and Guinier's model.

In the present study, to examine the changes of the structure of G.P. zones during formation, growth or dissolution the scattering intensity of an aluminum alloy containing 6.8at.% zinc was measured by means of X-ray small angle scattering method. Though the measured



intensity includes total informations, by examining the integrated intensity (Eq.(1.14)), applying Porod's law (Eq.(1.25)) and calculating the short-range order parameter (Eq.(1.27)), which were analysed from the scattering curves, we attempted to indicate the change of the solute concentrations inside and outside G.P. zones, to show the gradient of solute concentration 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<sup>(12)</sup> among zones is neglected.)

### 3-2. Experimental Procedures

The material used was an aluminum-zinc alloy containing 6.8at.% Zn prepared from 99.99% aluminum and 99.99% zinc. The measurements of X-ray small angle scattering, using Ni-filtered  $\text{CuK}_\alpha$  radiation, were carried out with the foils of 0.2 mm thick. The specimens were homogenized at  $300^\circ\text{C}$  for one hour, then dropped rapidly into a water bath of  $0^\circ\text{C}$  beneath the furnace, held at this temperature for 15 sec and cooled further to the liquid nitrogen temperature before aging.

For the study of formation and growth, the aging was performed at the temperature of  $40^\circ\text{C}$  and for the study of dissolution the specimen pre-aged at  $40^\circ\text{C}$  for 60 min was reverted at  $160^\circ\text{C}$  in an air furnace keeping the desired temperature within  $\pm 1^\circ\text{C}$ . As the solvus temperature

of G.P. zones in this alloy was determined to be  $155^{\circ}\text{C}$  in the previous chapter, the adoption of the temperatures of  $40^{\circ}\text{C}$  and  $160^{\circ}\text{C}$  as the formation and dissolution temperature respectively was justified. The scattering intensity was counted at liquid nitrogen temperature at  $1/8^{\circ}$  intervals in the scattering angle  $(2\theta)$  up to  $2\theta_0 = 3.75^{\circ}$  with line collimation. At the higher angles than  $2\theta_0$ ,  $(2\theta)^{-3}$  law was utilized. The counted intensity spectra were corrected for beam height using a technique of the computer method developed by Schmidt (see Appendix of Chap. 1). The calculation of  $Q_0$  was carried out by the method developed by Gerold (Eq.(1.22)) and the average zone radius was obtained by using Guinier's approximation (Eq.(1.19)) utilizing the slope of a  $\log I$  vs.  $(2\theta)^2$  plot of X-ray scattering intensity data. In evaluating  $\alpha(x)$  of Eq.(1.27), the computer method was also used setting an upper limit  $2\theta = 7.5^{\circ}$ .

### 3-3. Experimental Results and Discussions

#### 3-3-1. Structure Change of G.P. Zones during The Formation and Growth Processes

Representative X-ray small angle scattering curves for specimens which were quenched from  $300^{\circ}\text{C}$  and aged at  $40^{\circ}\text{C}$  for each time were

shown in Fig.(3.3). These curves were analyzed by utilizing the integrated intensity, Porod's law and the short-range order parameter as follows.

(a) Integrated Intensity

Using Eq.(1.22) the integrated intensity  $Q_0$  was calculated and these results were shown in Fig.(3.4). The values of  $Q_0$  in the specimens of the as-quenched state and aged for a minute can not be obtained, because the measured intensities were too weak to find the critical value of  $s$ , where  $dQ_0/ds \simeq 0$ . After 2 min  $Q_0$  increase as aging proceeds up to the critical time  $t_0$  (~ 6 min) and after  $t_0$  they show constant within experimental accuracy. From Eq.(1.14) this increase suggests the increase in the degree of discrepancy of electron densities inside and outside G.P. zones. At  $t_0$  it is certified by Eq.(1.20) that the decomposition has been progressed to the points of the metastable miscibility gap<sup>(13)</sup>, that is, the solute concentrations inside and outside G.P. zones progressed to  $C_1$  and  $C_2$  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, though as shown later the zone radius increase with aging time.

(b) Porod's Law

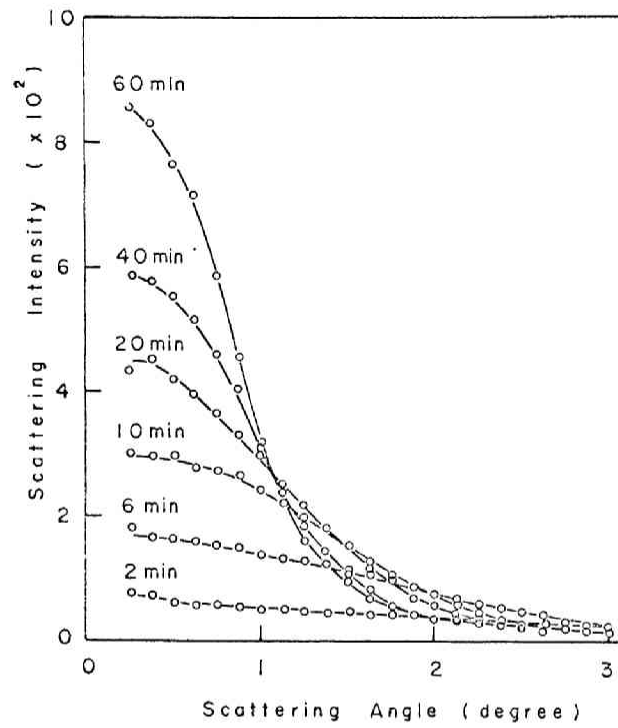


Fig.(3.3). X-ray intensities scattered from an Al-6.8at.% Zn alloy quenched from 300°C and aged for the specific times at 40°C.

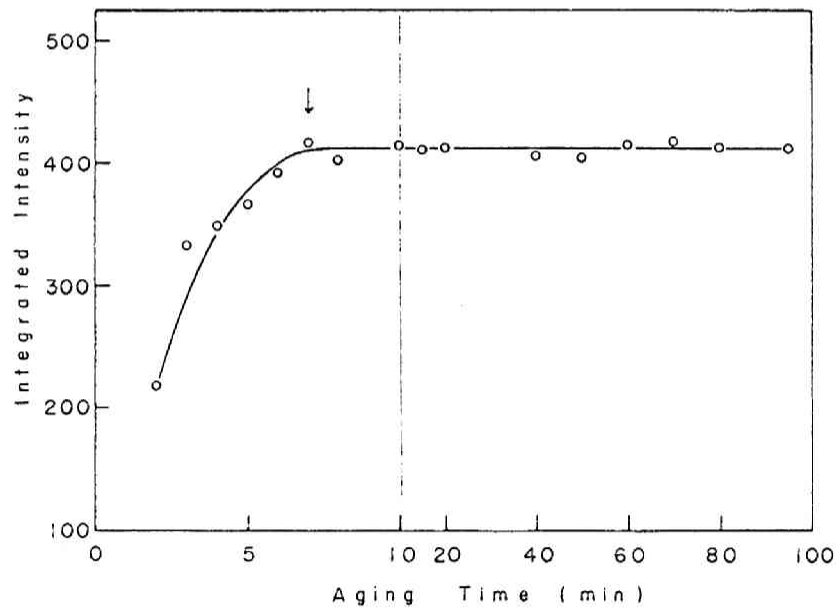


Fig.(3.4). Change of the integrated intensities of an Al-6.8at.% Zn alloy quenched from 300°C and aged at 40°C.

As given in Eq.(1.25), the plot of  $s^3 J(s)$  vs.  $s^3$  gives the qualitative information of the gradient of solute concentration at the interface of G.P. zones. This plot was shown in Fig.(3.5) for the specimens aged for various times. In the early stages of aging  $s^3 J(s)$  increase monotonously, but after 6 min they show constant for large  $s$ , namely, that Porod's law is satisfied. These results mean that G.P. zones with sharp interface between matrix are formed after 6 min and that the interface is not sharp until this critical time. It is interesting that this critical time almost coincides with the times when the integrated intensity shows the constant value.

(c) Short-Range Order Parameter

Using Eq.(1.27) the short-range order parameter  $\alpha(x)$  can be calculated from the scattering intensities of Fig.(3.3). From these calculated  $\alpha(x)$ , the probability  $n_{BB}(x)$  that a pair of atoms separated by a distance  $x$  is formed by two Zn atoms, can be obtained, and they are shown in Fig. (3.6).

The fact that  $n_{BB}$  is higher than the average value  $C_0$  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

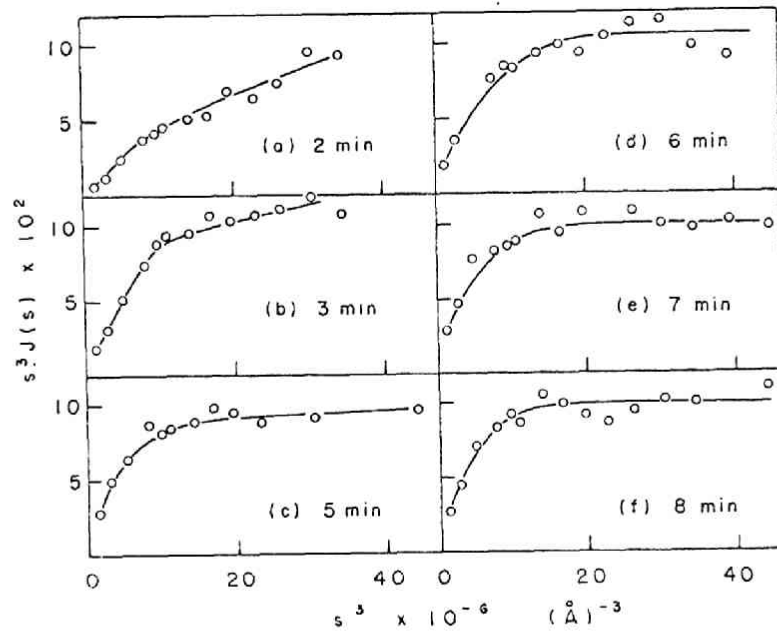


Fig.(3.5). Variation of  $s^3 J(s)$  as a function of  $s^3$  for an Al-6.8at.% Zn alloy quenched from  $300^\circ\text{C}$  and aged at  $40^\circ\text{C}$ .

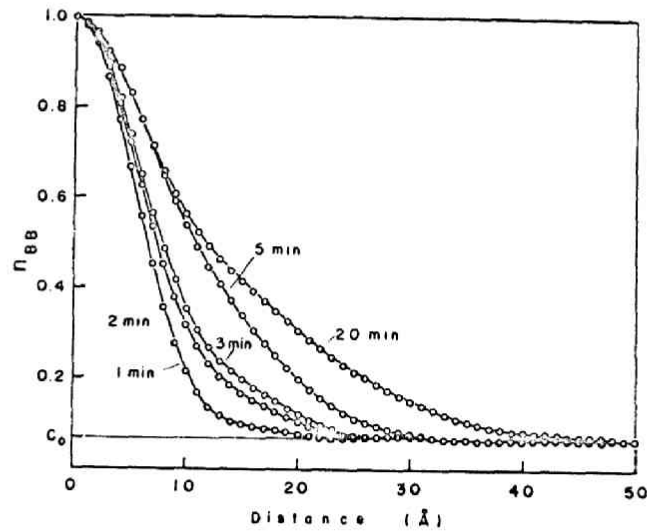


Fig.(3.6). Probability of finding a zinc atom at distance  $x$  from a given zinc atom for an Al-6.8at.% Zn alloy quenched from  $300^\circ\text{C}$  and aged at  $40^\circ\text{C}$ .

average value can not be found even at the initial aging as Al-Ag<sup>(7)</sup> or Cu-Ni<sup>(14)</sup> system.

(d) Model of G.P. Zones during Formation and Growth Processes

It is found that these results can not be interpreted by supposing the structure of G.P. zones as only Model 1 or 2 of Fig. (3.2) throughout aging.

Model 1 was given mainly at the initial stages of aging, thus at the aging times less than  $t_0$  the following conditions should be required :

(1)  $Q_0$  is lower than the final value  $Q_f$ , (2) Porod's law will not be satisfied and (3) regions where  $n_{BB}$  is lower than  $C_0$  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 more 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  $C_0$ . As shown in Figs. (3.4 ~ 3.6), 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 stages.

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 at the initial stages is given in Fig. (3.7). At this stages the solute concentration ( $C'_1$ ) inside G.P. zones does not reach the equilibrium value  $C_1$ , the concentration of matrix is still supersaturated ( $C_2 < C'_2$ ) and gradient of solute concentration at the interfaces between zones and matrix is not sharp. Recently de Fontaine<sup>(10)</sup> indicated that this model is the same as the one simulated by computer inside spinodal, which is shown in Fig. (3.2c). As aging proceeds both  $C'_1$  and  $C'_2$  tend to  $C_1$  and  $C_2$  respectively and at  $t_0$   $C'_1 = C_1$  and  $C'_2 = C_2$ . Also the gradient of concentration becomes simultaneously sharp. At  $t_0$  the decomposition is completed and after  $t_0$  these zones grow keeping the solute concentrations both inside and outside zones constant. This model is not contradictory to the present results.

### 3-3-2. Structure Change of G.P. Zones during Dissolution Process

The X-ray small angle scattering curves of the specimens which were quenched from 300°C, pre-aged at 40°C for 60 min and then reverted at



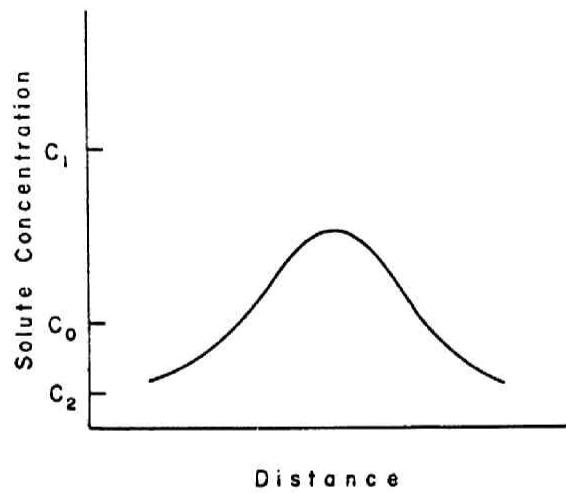


Fig.(3.7). Proposed model for the structure of G.P. zones at the early stages of aging.

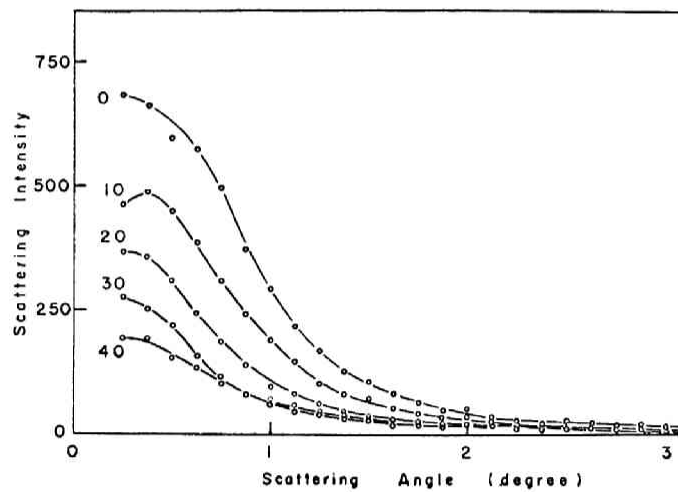


Fig.(3.8). X-ray intensities scattered from an Al-6.8at. % Zn alloy quenched from  $300^\circ\text{C}$ , pre-aged at  $40^\circ\text{C}$  for one hour and reverted at  $160^\circ\text{C}$  for each time (0, 10, 20, 30, 40 sec).

160°C are shown in Fig. (3.8). As is evident from this figure, the scattering intensities decrease monotonously with reversion times.

(a) Integrated Intensity

To investigate the difference of solute concentrations inside and outside zones, the integrated intensities of the specimens reverted for various times were calculated from Fig. (3.8). It has been already shown that the decomposition of the supersaturated solid solution completes within 6 min at the aging temperature of 40°C (Fig. (3.4)), thus before reversion it is concluded that the solute concentrations in zones or in matrix have reached the expected points of the metastable miscibility gap of G.P. zones. The change of the integrated intensities with reversion time is shown in Fig. (3.9), in which it is evident that  $Q_0$  decreases monotonously with the reversion time. From Eq. (1.14) the decrease of  $Q_0$  is attributable to the decrease of the difference of solute concentrations inside and outside zones.

(b) Porod's Law

In Fig. (3.10) the values of  $s^3 J(s)$  are plotted against  $s^3$  for the specimens reverted at 160°C. In the early stage of dissolution,  $s^3 J(s)$  show constant for large  $s$ , namely that Porod's law is satisfied and after about 20 ~ 30 sec ( $t_c$ ), they increase monotonously. These results mean

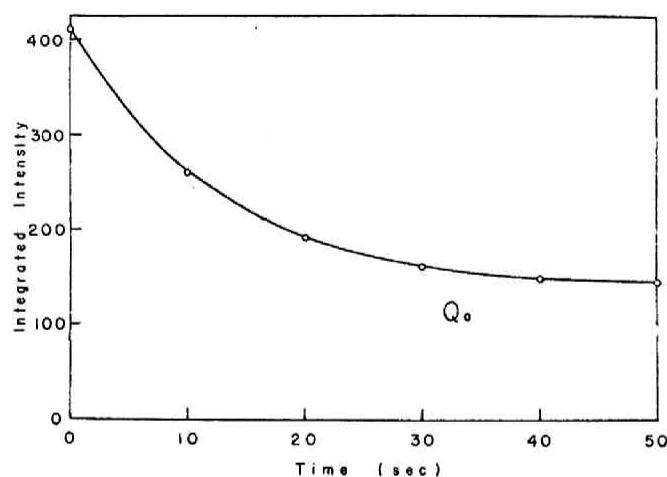


Fig.(3.9). Change of the integrated intensities of an Al-6.8at.% Zn alloy quenched from 300°C, pre-aged <sup>at</sup> 40°C for one hour and reverted at 160°C.

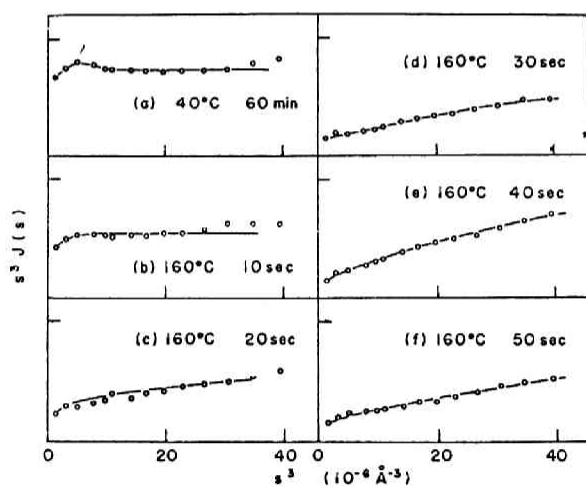


Fig.(3.10). Variation of  $s^3 J(s)$  as a function of  $s^3$  for an Al-6.8at.% Zn alloy quenched from 300°C, pre-aged at 40°C for one hour and reverted at 160°C for each time.

that the interface between zones and matrix is definite until the reversion time of  $t_0$  and after this critical time the interface becomes gradually unclear. It is noted by comparing Figs. (3.7) and (3.10) that the change of the interfacial appearance during reversion is completely the reverse of that of during formation and growth.

(c) Model of G.P. Zones during Dissolution Process

From the results of changes of the gradient of the solute concentration at the interface and the solute concentrations in the zones or in the matrix with reversion times, the model of the structure of dissolving G.P. zones is proposed as illustrated in Fig. (3.11). As the initial average zone radius of  $33.5\text{\AA}$  (which will be shown in the later chapter) prior to reversion is smaller than the critical radius of  $35\text{\AA}$  at which the shape of zones was reported to change from sphere to ellipsoid, the shape of zones before dissolution may be considered to be almost spherical. Thus, during reversion the zones will dissolve keeping the shape spherical. Also, as long as the zone-matrix interface remains almost sharp, the solute concentration in the zones may be equal to the initial value  $C_1$  which is determined by the metastable miscibility gap. These morphological change of spherical G.P. zones during dissolution is approximately the reverse of that of during formation and growth.

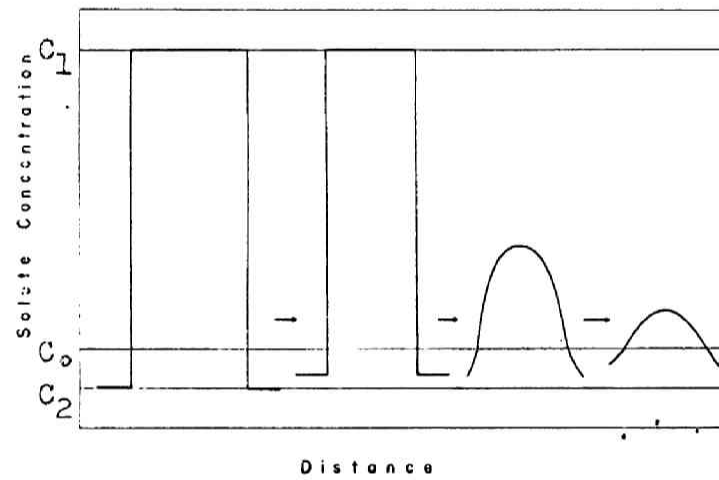


Fig.(3.11). Morphological change of G.P. zones in an Al-Zn alloy during dissolution.

#### 3-4. Summary

The measurements of the scattered intensities of a binary Al-6.8 at.% Zn alloy by means of the X-ray small angle scattering method gave the informations on the structure changes of G.P. zones during the formation, growth or dissolution process.

At the initial stages of the zone formation the formerly proposed two models for the structures of zones (i.e., Walker and Guinier's model and Gerold and Schweizer's model) were pointed out not to be consistent with the present experimental results and then an outline of a new structure for zones was given. This new model was indicated to be approximately coincided with de Fontaine's model. At the later stages of the zone growth when the solid solution was completely decomposed Gerold and Schweizer's model was shown to be suitable. Also it was confirmed that during dissolution the structure change of zones was the reverse of that of the formation and growth processes.

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## CHAPTER 4

### KINETICS OF THE FORMATION OF G.P. ZONES

#### 4-1. Introduction

It is well known that from the supersaturated solid solution there are two possible sequences of the formation of the solute-rich clusters, that is, nucleation-growth and spinodal decomposition. A line between these two mechanisms are drawn by the locus of points satisfying the following equation,<sup>(1)</sup>

$$\left( \frac{\partial^2 f}{\partial C^2} \right)_{T,V} = 0 \quad (4.1)$$

where  $f$  being the Helmholtz free energy,  $C$  the atomic fraction of the second component and  $V$  the volume. This locus is illustrated in Fig. (4.1) by a dashed curve on the phase diagram of a system containing a simple miscibility gap. The decomposition of supersaturated solid solution proceeds by the spinodal mechanism inside this dashed curve ( $f'' < 0$ ) and outside it ( $f'' > 0$ ) the decomposition by the nucleation-growth is expected.

The change  $\Delta f$  in  $f$  for the system, when one mole of composition  $C'$  is formed from a solution of composition  $C_0$ , is written as follows,<sup>(2)</sup>

$$\Delta f = \frac{1}{2} (\Delta C)^2 f''(C_0) \quad (4.2)$$

where  $\Delta C = (C_0 - C')$ . If the initial composition  $C_0$  lies outside the



spinodal, an infinitesimal fluctuation increases the free energy and the system is therefore metastable. However, inside the spinodal any fluctuation decreases the free energy and the system is unstable.

Moreover, these two mechanisms are classified by the diffusion mode<sup>(3)</sup>, that is, the normal diffusion down the solute concentration gradient and the uphill diffusion up the solute concentration gradient. The latter case is expected on the composition within the spinodal and the former outside the spinodal. The proposed possible sequences<sup>(3)</sup> of the change of solute concentration by the normal or uphill diffusion are illustrated in Fig.(4.2).

Theories of both nucleation-growth and spinodal mechanisms have been established by several authors. Volmer and Walker<sup>(4)</sup>, Borelius<sup>(5,6)</sup>, Becker<sup>(7)</sup> and Hobstetter<sup>(8)</sup> have developed the nucleation-growth theory on the assumption that there exist the definite interfaces between two phases. They obtained the critical values of particle size and solute concentration of the particle at which the increase of free energy due to formation of particles was maximum. However, the evidence of existence of these critical values have not yet been given experimentally<sup>(9)</sup>.

While, the kinetics of the spinodal decomposition has been treated theoretically by solving the diffusion equation and several proofs of

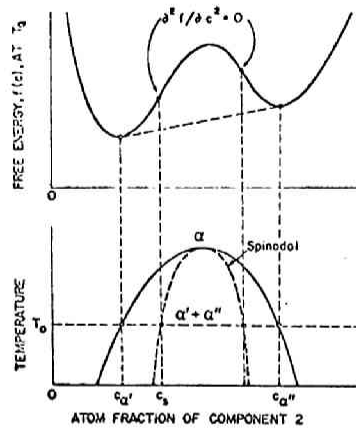


Fig.(4.1). The chemical spinodal is defined by the locus of temperatures ( $T_0$ ) on the phase diagram at which  $f'' = 0$ . Inside the spinodal  $f''$  is negative and outside it is positive.

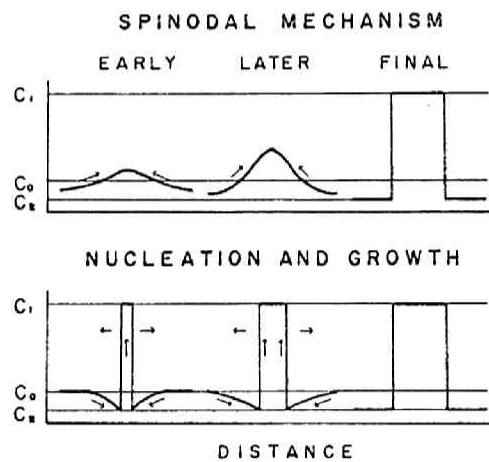


Fig.(4.2). Schematic evolution of concentration profiles to illustrate the difference between the spinodal mechanism and nucleation and growth.

the validity of theories have been given. Both Hillert<sup>(10,11)</sup> and Cahn-Hilliard<sup>(12)</sup> have proposed that a correction must be applied to Fick's laws for chemical diffusion if the penetration distances are small. Hillert's treatment<sup>(10)</sup> was based on the calculation of the free energy of a one dimensional composition variation in a discrete lattice. He assumed that there were only nearest-neighbour interactions and that the entropy of mixing was ideal. (These assumptions correspond to the use of a regular-solution model for the volume free energy.) He thus obtained a flux equation for one-dimensional diffusion in terms of the differences in compositions of the atomic planes and the interaction energy between nearest neighbors. He solved this flux equation numerically to obtain the time dependence of the composition variation. Also, Cahn and Hilliard<sup>(12)</sup> took into account the strain energy associated with a composition variation in a coherent lattice containing atoms of different sizes on basis of the continuum model for the thermodynamic of inhomogeneous systems. The detailed Cahn's treatment will be given later.

Recently eliminating the regular-solution assumption of Hillert and the continuum approximation of Cahn, an expression for diffusion is derived in the form of a differential-difference equation, and a simple analytic solution is obtained for the limiting case of small composition

fluctuations<sup>(13)</sup>. This solution is then used to determine the kinetics and morphology at the early stages of both clustering and ordering as described by the time dependence of Fourier spectrum of the composition variation. It is found that many of the characteristics of ordering are the inverse of those for clustering. Experimentally several verifications of the validity of above theories have been demonstrated by measuring the change of X-ray scattering intensities.<sup>(14 ~ 17)</sup>

For binary Al-Zn alloy Rundman and Hilliard<sup>(14)</sup> have calculated the coherent spinodal curve and confirmed the occurrence of the spinodal decomposition below this curve through the facts that the experimentally obtained functional dependence of amplification factor on the wavenumber, the ratio of the critical wavenumber to the maximum wavenumber and the existence of a unique crossover point at critical wavenumber were in accord with the theories. Bonfiglioli and Guinier<sup>(18)</sup> have also suggested that the changes of the integrated intensities during initial decomposition at  $-45^{\circ}\text{C}$  may be due to the spinodal decomposition.

In the present paper, in order to obtain an additional evidence of occurrence of the spinodal decomposition in Al-Zn alloy, the analysis of the integrated intensity and the examination of the applicability of Porod's law were performed. These studies provide the informations

of the fluctuation of electron density in the specimen and the gradient of concentration of solutes at the interface between the clusters and matrix. According<sup>19</sup> to the Cahn-Hilliard theory of the spinodal reviewed in the next section, the estimation of the spinodal temperature was also carried out through the investigation of the temperature dependences of the maximum and the critical wavenumbers which were determined from the magnitude of the amplification factor<sup>(19)</sup>.

Moreover, though the theory of kinetics above the spinodal has not yet been established by the diffusion mechanism, the examinations of the changes of the scattering intensities for specimens isothermally aged in the vicinity of the spinodal or above the spinodal were carried out.

#### 4-2. Review of Cahn-Hilliard Theory of the Spinodal

The interdiffusion flux  $\tilde{J}$  of two species ( $\tilde{J} = J_A = -J_B$ ) is proportional to the gradient of chemical potential difference ( $\mu_A - \mu_B$ )<sup>(20)</sup>:

$$-\tilde{J} = M \nabla (\mu_A - \mu_B) \quad (4.3)$$

This equation can be considered as a phenomenological definition of the diffusion mobility  $M$  ( $> 0$ )<sup>(3)</sup>. For a homogeneous system,

$$\mu_A - \mu_B = \frac{\partial f}{\partial C_A} \quad (4.4)$$

where  $f(C)$  is the free energy of  $N_v$  molecules of homogeneous material of composition  $C$  ( $N_v$  is the number of molecules in a unit volume of homogeneous material of composition  $C_0$ ). The quantity  $f$  is thus a free energy of that number of lattice points in the crystal which initially occupied a unit volume. Substituting Eq. (4.4) into Eq. (4.3) we obtain:

$$-J_A = M \frac{\partial^2 f}{\partial C_A^2} \nabla C_A \quad (4.5)$$

and defining the interdiffusion coefficient  $\tilde{D}$  by

$$-\tilde{J} = -J_A = \tilde{D} \nabla C_A \quad (4.6)$$

we may identify  $\tilde{D}$  with  $M \partial^2 f / \partial C_A^2$ . Since  $M$  is never negative,  $\tilde{D}$  takes its sign from the sign of  $\partial^2 f / \partial C^2$ .  $\tilde{D}$  is negative within the spinodal.

The above derivation of the diffusion equation is valid for concentration gradients that are so small that, for all practical purposes, each atom finds itself in surroundings similar to that which it would have in a homogeneous material of the same composition. If, however, concentration gradients are so large that within the range of interaction of an atom the average concentration has changed appreciably, the atom will be aware of its inhomogeneous environment. This leads to a change in its chemical potential and for fluids :

$$(\mu_A - \mu_B) = \frac{\partial f}{\partial C_A} - 2KV^2 C_A \quad (4.7)$$

The new term was originally derived from a variational formula<sup>(12)</sup> of the free energy of an inhomogeneous system. Its basis may be understood by considering Fig.(4.3) in which we depict a region in which the composition of A has a positive curvature. Any atom in such a region will **sense** more A atoms in its environment than the local composition would indicate and the greater its range of interaction, the greater the average A concentration among its neighbours. Thus an A atom will have fewer unlike neighbors and with a positive interaction energy will have a lower chemical potential than in homogeneous material of the same composition. The change in  $\mu$  is proportional to the curvature in composition and to the parameter K. For a simple solution model the gradient energy coefficient K is the product of the interaction energy and square of the interaction distance, since the longer this distance is, the greater the change in environment that the atom senses. For a real solution K may be considered a phenomenological coefficient to be determined experimentally. Its magnitude may be parameterized by defining an interaction distance  $\phi$  such that<sup>(3)</sup>:

$$K = N_V k_B T_C \phi^2 \quad (4.8)$$

where  $T_C$  is the critical unmixing temperature which in turn is a measure of the interaction energy and  $k_B$  is the Boltzman constant.

Substitution of Eq. (4.7) into the diffusion equation yields for fluids<sup>(19)</sup>:

$$-\tilde{J} = M \frac{\partial^2 f}{\partial C^2} \nabla C - 2MKV^3 C \quad (4.9)$$

and by taking the divergence, we come to the diffusion equation that one encounters in spinodal decomposition<sup>(21)</sup>:

$$\frac{\partial C}{\partial t} = M \frac{\partial^2 f}{\partial C^2} \nabla^2 C - 2MKV^4 C + \text{non-linear terms} \quad (4.10)$$

For solids, the elastic strains resulting from coherency must be added to Eq. (4.10). Neglecting the non-linear terms yield,

$$\partial C / \partial t = M \{ (f'' + 2\eta^2 Y) \nabla^2 C - 2KV^4 C \} \quad (4.11)$$

in which primes denote derivatives with respect to the atomic fraction,  $\eta$  the fractional change in lattice parameter per unit change in  $C$ , and  $Y$  a function of the elastic constants. For an isotropic solid

$$Y = E / (1 - \nu) \quad (4.12)$$

where  $E$  is Young's modulus and  $\nu$  is Poisson's ratio. The mobility,  $M$ , is related<sup>(22)</sup> to the tracer diffusivities by,

$$M = \{ C(1 - C) / kT \} [ CD_1^* + (1 - C) D_2^* ] . \quad (4.13)$$

If  $f''$  and the other parameters are assumed to be independent of  $C$ , then Eq. (4.11) has the solution<sup>(19)</sup>:

$$C(\vec{r}, t) - C_0 = \int_{\beta} A(\vec{\beta}, t) \exp(i\vec{\beta} \cdot \vec{r}) d\vec{\beta} \quad (4.14)$$

in which  $C_0$  is the average composition,  $\vec{r}$  is the position vector,  $\vec{\beta}$  is



a vector in Fourier space whose magnitude is the wavenumber, and  $A(\tilde{\beta}, t)$  is the amplitude of the Fourier component of wavenumber  $\tilde{\beta}$  at time  $t$ .

The latter is related to the amplitude,  $A(\tilde{\beta}, 0)$ , at time zero by :

$$A(\tilde{\beta}, t) = A(\tilde{\beta}, 0) \exp [R(\tilde{\beta}) \cdot t] \quad (4.15)$$

where  $R(\tilde{\beta})$  is an "amplification factor" defined by :

$$R(\tilde{\beta}) = -(M/N_V)(f'' + 2\eta^2 Y + 2K\beta^2) \beta^2$$

This factor can also be written in terms of the interdiffusion coefficient,  $\tilde{D}$ ; substituting for  $M$  from Eq. (4.13) we obtain :

$$R(\tilde{\beta}) = -(\tilde{D}/f'')(f'' + 2\eta^2 Y + 2K\beta^2) \beta^2 \quad (4.16)$$

For a solution that has undergone a perfect quench into the spinodal region, the initial amplitude distribution,  $A(\tilde{\beta}, 0)$ , will be that corresponding to the equilibrium distribution<sup>(23)</sup> at the homogenizing temperature. Whether a particular Fourier component grows or decays depends on the sign  $R(\tilde{\beta})$ . Thus for growth :

$$f'' + 2\eta^2 Y + 2K\beta^2 < 0 \quad (4.17)$$

This condition can be satisfied only inside the coherent spinodal and then only for those components having wavenumbers less than a critical value given by :

$$\beta_c^2 = -(1/2K)(f'' + 2\eta^2 Y) \quad (4.18)$$

The dependence of  $R(\tilde{\beta})$  on  $\tilde{\beta}$  is shown schematically in Fig. (4.4) both

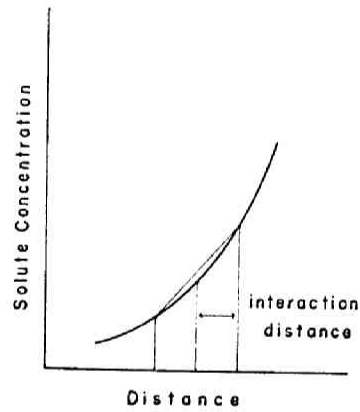


Fig.(4.3). Average composition profile in the neighbourhood of an atom. This average composition is altered if the composition profile has curvature, which affects the chemical potential of the atom.

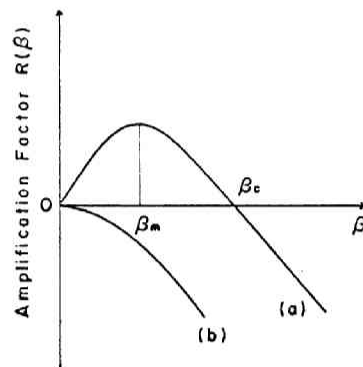


Fig.(4.4). Profiles of the amplification factor  $R(\beta)$  inside spinodal (a) and outside spinodal (b).

inside and outside the spinodal. For the temperatures inside the spinodal

it is zero at  $\tilde{\beta} = 0$  and at  $\tilde{\beta} = \tilde{\beta}_0$  and has a maximum at a wavenumber,

$\tilde{\beta}_m$ , given by

$$\tilde{\beta}_m = \tilde{\beta}_0 / \sqrt{2} \quad (4.19)$$

Because of the assumption that the parameters in Eq. (4.11) are independent of composition, the solution given by Eqs. (4.14) and (4.15) is an approximation which is valid only at small amplitude, that is, in the early stages of the decomposition.

# Determination of $R(\tilde{\beta})$ by X-ray Diffraction<sup>(14)</sup>

With respect to the approximate solution, we note that the right-hand side of Eq.(4.14) is the Fourier transform of the amplitude spectra.

It therefore follows that :

$$A(\tilde{\beta}, t) = \int_V [C(\tilde{r}, t) - C_0] \exp(-i\tilde{\beta} \cdot \tilde{r}) d\tilde{r} \quad (4.20)$$

in which the integration is over  $V$ , the volume of the specimen. Let us now consider the X-ray spectra from a specimen containing a composition fluctuation. The amplitude,  $A(\tilde{s})$ , of the diffracted radiation at a point  $\tilde{s}$  in reciprocal space is given by the well-known expression :

$$A(\tilde{s}, t) = \int_V \rho(\tilde{r}, t) \exp(-2\pi i \tilde{s} \cdot \tilde{r}) d\tilde{r} \quad (4.21)$$

in which  $\rho(\tilde{r}, t)$  is the electron density at point  $\tilde{r}$  and time  $t$ . If  $f_A$  and  $f_B$  are the scattering factors of the A and B atoms, then :

$$\rho(\tilde{r}, t) = \rho_0 + (f_B - f_A) [C(\tilde{r}, t) - C_0] \quad (4.22)$$

in which  $\rho_0$  is the average electron density. At small angles, the scattering factors can be assumed to be independent of angle. Thus, on substituting  $\rho(\tilde{r}, t)$  in Eq. (4.21) we obtain for  $\tilde{s} > 0$ ,

$$A(\tilde{s}, t) = (f_B - f_A) \int_V [C(\tilde{r}, t) - C_0] \exp(-2\pi i \tilde{s} \cdot \tilde{r}) d\tilde{r} \quad (4.23)$$

Substituting  $\tilde{\beta} = 2\pi\tilde{s}$  and noting that the diffracted intensity,  $I(\tilde{s})$ , is equal to  $A(\tilde{s}) A^*(\tilde{s})$ , we obtain from Eqs. (4.1), (4.20) and (4.23),

$$I(\tilde{\beta}, t) = I(\tilde{\beta}, 0) \exp[2R(\tilde{\beta}) \cdot t] \quad (4.24)$$

in which  $I(\tilde{\beta}, 0)$  is the scattered intensity at time zero.

#### 4-3. Experimental Procedures

The material used was the aluminum-zinc alloy containing 6.8at.% Zn prepared from 99.99% aluminum and 99.99% zinc. The measurements of X-ray small angle scattering, using Ni-filtered  $\text{Cu K}_\alpha$  radiation, were carried out with the foils of 0.2 mm thick. The specimens were homogenized at  $300^\circ\text{C}$  for one hour, then dropped rapidly into water bath of  $0^\circ\text{C}$  beneath the furnace, held at this temperature for 15 sec and cooled further to the liquid nitrogen temperature before aging. The aging was performed in an air furnace keeping the temperature within  $\pm 1^\circ\text{C}$  of the desired temperature. The heat up time of the specimens was less than 10 sec.

For the studies of the integrated intensity and Porod's law the intensities were counted at liquid nitrogen temperature at  $1/8^\circ$  intervals in the scattering angle. The calculation of  $Q_0$  was carried out by the method developed by Gerold (Eq.(1.22)). For the study of the analysis of  $R(\tilde{\beta})$ , the intensities were counted every 30 sec of aging time at a given scattering angle with the specimen placed in high temperature camera shown in Fig. (4.5).

#### 4-4. Experimental Results and Discussions

##### 4-4-1. Decomposition inside the Spinodal

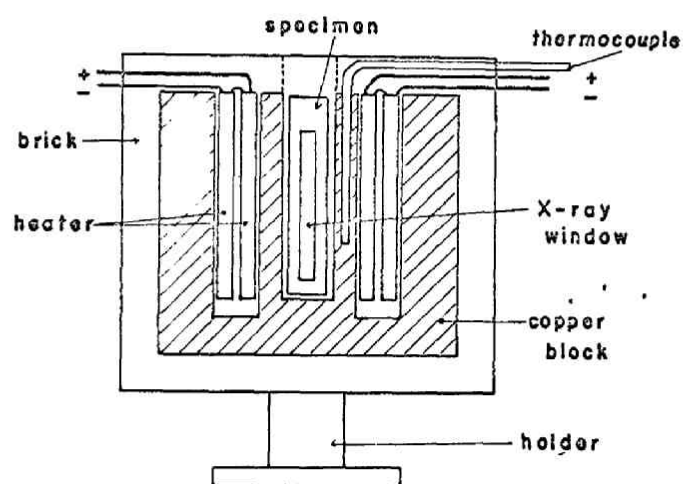
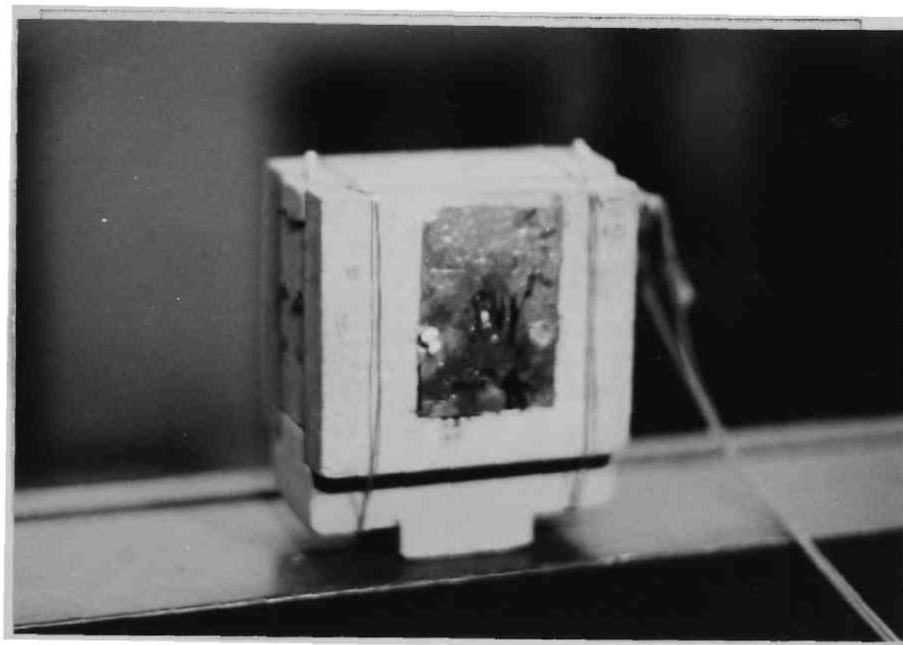


Fig.(4.5). Apparatus of a high temperature camera.

If the decomposition of the supersaturated solid solution proceeds in accordance with the Cahn-Hilliard theory of the spinodal, the following results will be expected :

- (1) The solute concentration in the clusters is lower than that determined by the miscibility gap at the initial stages of decomposition (see Fig. (4.2)).
- (2) Also, as seen from Fig. (4.2), the concentration gradient at the interface between matrix and clusters is not sharp.
- (3) The profile of  $R(\tilde{\beta})$  vs.  $\beta$  curve obtained by the experiment coincides with the theoretical curve of Fig. (4.4).
- (4) The ratio of  $\beta_c$  vs.  $\beta_m$  will be nearly  $\sqrt{2}$ .
- (5) The plots of  $R(\tilde{\beta})/\beta^2$  vs.  $\beta^2$  keep linearity (see Eq. (4.16)).
- (6) The clusters formed inside the spinodal are homogeneously distributed in the matrix.

To see whether the above conditions are satisfied when the aging is carried out at low temperatures, the measurements of X-ray small angle scattering for the specimens aged at temperatures between 30°C and 100°C were carried out. As an example the scattering curves of the specimens aged isothermally at 40°C are shown in Fig. (4.6). From these curves the calculation of the integrated intensities and the analysis

of Porod's law were performed to clarify the degree of decomposition and the concentration gradient at the interface between clusters and matrix respectively.

(a) Integrated Intensity

Using Eq. (1.22) the integrated intensity  $Q_0$  is calculated for the specimens aged at 40, 60, 80 and 100°C. The results are shown in Fig. (4.7), where the values of  $Q_0$  increase for the initial few minutes up to time  $t_q$  (shown by arrows) and after  $t_q$  they show little change. At temperatures above 100°C,  $Q_0$  cannot be calculated because the intensities scattered by phase separation are too weak compared with the back ground. As seen from Eq. (1.20), the fact that after  $t_q$  the values of  $Q_0$  for the specimens aged at each temperature remain constant means that the decomposition has been progressed to the points of metastable miscibility gap<sup>(24)</sup>. Before  $t_q$  the decomposition will not be completed, which is expected from the sequence of the spinodal decomposition as illustrated in Fig. (4.2 ). Then, the condition (1) is satisfied at the initial stages of aging within  $t_q$  at each temperature.

(b) Porod's Law

In Fig. (4.8a ~ g) the values of  $s^3J(s)$  are plotted against  $s^3$  for the specimens aged at 40°C. In the early stage of aging,  $s^3J(s)$  increase



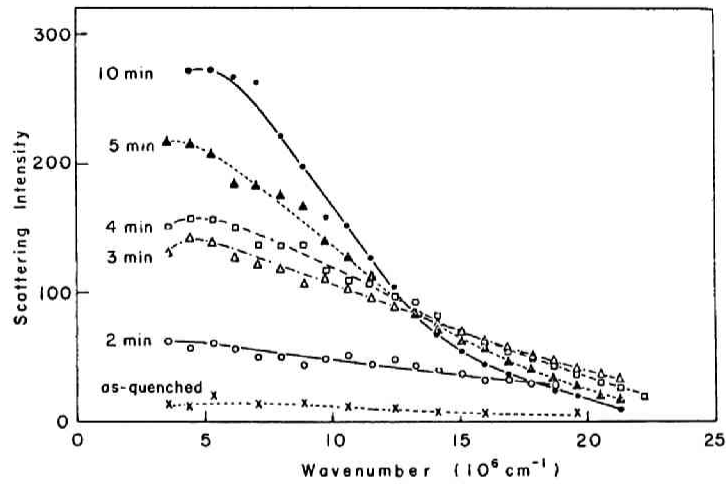


Fig. (4.6). X-ray intensities scattered from an Al-6.8 at.% Zn alloy quenched from  $300^{\circ}\text{C}$  in the as-quenched state, and aged for each time at  $40^{\circ}\text{C}$ .

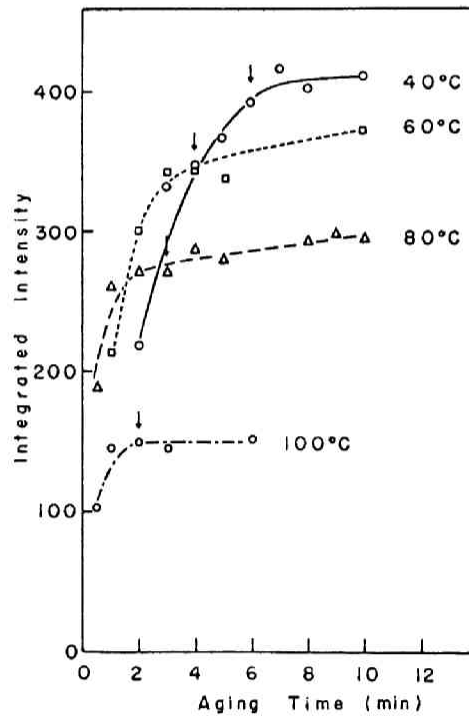


Fig.(4.7). Change of the integrated intensities of an Al-6.8at.% Zn alloy quenched from  $300^{\circ}\text{C}$  and aged at 40, 60, 80 and  $100^{\circ}\text{C}$ . The arrows show the time  $t_q$ .

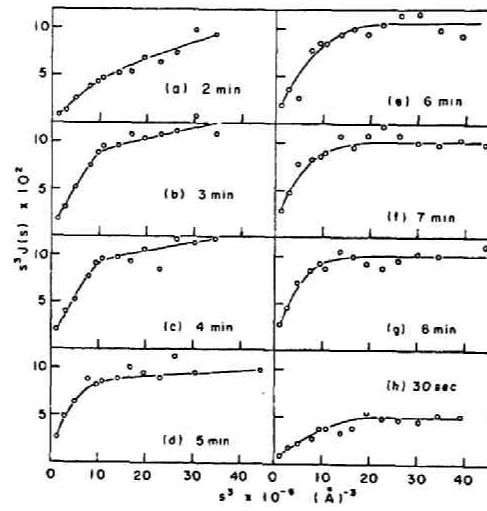


Fig.(4.8). Variation of  $s^3 J(s)$  as a function of  $s^3$  for an Al-6.8at.% Zn alloy quenched from  $300^\circ\text{C}$  and (a ~ g) aged at  $40^\circ\text{C}$  for each time and (h) aged at  $140^\circ\text{C}$  for 30 sec.

monotonously, but after 6 min ( $t_p$ ) they show a constant for large  $s$ , namely, that Porod's law is satisfied (Eq. (1.25)). These results mean that the particles with sharp interface between matrix are formed after  $t_p$  and that the interface is not sharp until the time  $t_p$ , which means the condition (2) is satisfactory within aging time of  $t_p$ . These times  $t_q$  and  $t_p$  are listed in Table (4.1) for each specimen aged at 40, 60, 80 and 100°C. It is to be noted that these obtained values of  $t_q$  and  $t_p$  almost coincide each other. This result indicates that until the time  $t_p$  (or  $t_q$ ) is reached the concentrations of solutes inside and outside the clusters and the concentration gradient at the interface do not have any fixed value but they increase with the aging time. This fact supports the occurrency of the spinodal decomposition but not the nucleation and growth mechanism.

At 140°C  $s^3J(s)$  is a constant even after the aging as short as 30 sec (Fig. (4.8h)). The mechanism of decomposition at this temperature is no longer spinodal, but nucleation and growth.

#### (c) Analysis of Amplification Factor $R(\beta)$

To obtain  $R(\beta)$  from the slope of the curves of  $\log J(s)$  versus  $t$  according to Eq. (4.24),  $J(s)$  is plotted against  $t$  at each wavenumber  $\beta$  for the specimens aged at 40°C as shown in Fig. (4.9). The use of

Table (4.1). The times  $t_q$  and  $t_p$  of an Al-6.8at.% Zn alloy quenched from 300°C and aged at each temperature.

| T (°C)      | 40 | 60 | 80 | 100 |
|-------------|----|----|----|-----|
| $t_q$ (min) | 6  | 4  | 3  | 2   |
| $t_p$ (min) | 6  | 5  | 3  | 2   |

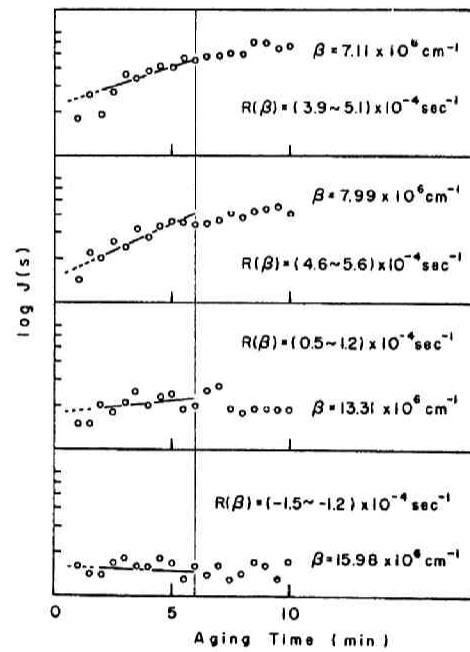


Fig.(4.9). Change of the scattering intensities measured at given wavenumbers for an Al-6.8at.% Zn alloy quenched from 300°C and aged at 40°C. The amplification factors are obtained for the aging times shorter than 6 min.

$J(s)$  instead of  $I(s)$  has been justified by Rundman and Hilliard<sup>(14)</sup>.

The slope should be taken for the aging times shorter than  $t_q$  or  $t_p$ , because the spinodal decomposition occurs only before this time. The plots are linear within experimental accuracy except initial few plots. The obtained  $R(\beta)$  are plotted against  $\beta$  as shown in Fig. (4.10). The shape of curve  $R(\beta)$  are found to coincide with the theoretically calculated one<sup>(25)</sup>, which shows that the condition (3) is satisfied.

It is seen in this figure that  $\beta_m$  and  $\beta_c$  shift to smaller wavenumber and that  $R(\beta)$  decrease as the aging temperature is increased. The  $\beta_m$ ,  $\beta_c$  and ratio  $(\beta_c/\beta_m)$  are given in Table (4.2) for the specimens aged at 30, 40, 50 and 60°C. At temperatures above 60°C the numbers of plots for times up to  $t_q$  or  $t_p$  are too scarce to determine the slope of curves. The theoretical ratio  $(\beta_c/\beta_m)$  should be 1.41 predicted by Eq. (4.19), but the observed ones are a little larger. That is, the condition (4) is approximately satisfied.

Equation (4.16) is rewritten as follows,

$$R(\beta)/\beta^2 = -(\tilde{D}/f'')(f'' + 2\eta^2 Y + 2K\beta^2). \quad (4.16')$$

According to this equation the plots of  $R(\beta)/\beta^2$  vs.  $\beta^2$  should keep linearity and this line has a slope of  $-(2K\tilde{D}/f'')$  and an intercept at  $\beta^2 = 0$  of  $-\tilde{D}(1 + 2\eta^2 Y/f'')$ . These plots for the specimens aged at 40°C

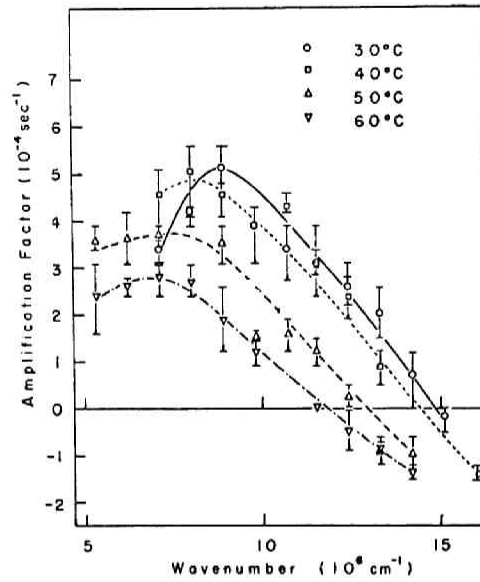


Fig.(4.10). Amplification factor vs. wavenumber of an Al-6.8at.% Zn alloy quenched from 300°C and aged at each temperature.

Table (4.2). The maximum wavenumber  $\beta_m$ , critical wavenumber  $\beta_c$  and ratio ( $\beta_c/\beta_m$ ) obtained from the curves of Fig.(4.10).

| T (°C) | $\beta_m (10^6 \text{ cm}^{-1})$ | $\beta_c (10^6 \text{ cm}^{-1})$ | $\beta_c/\beta_m$ |
|--------|----------------------------------|----------------------------------|-------------------|
| 30     | 8.5-9.0                          | 14.2-15.1                        | 1.58-1.78         |
| 40     | 8.0-8.5                          | 13.6-14.0                        | 1.60-1.75         |
| 50     | 7.0-8.0                          | 12.5-13.0                        | 1.56-1.85         |
| 60     | 7.0-7.6                          | 11.8-12.0                        | 1.55-1.71         |

are shown in Fig. (4.11) and from this figure it is found that plots show an excellent linearity within experimental errors (condition (5)) and the following equations are given :

$$-\tilde{K}D/f'' = -6.622 \times 10^{-32} \text{ cm}^4/\text{sec} \quad (4.25)$$

$$-\tilde{D}[1 + (2\eta^2 Y/f'')] = 12.32 \times 10^{-18} \text{ cm}^2/\text{sec} \quad (4.26)$$

When the values of  $f''$ ,  $\eta$  and  $Y$  are obtained in this alloy system at  $40^\circ\text{C}$ , the values of  $K$  and  $\tilde{D}$  are easily calculated from above equations.

However, using the thermodynamic values obtained by Hultgren et al<sup>(26)</sup>, the sign of  $f''$  at  $40^\circ\text{C}$  is positive, which means that the temperature of  $40^\circ\text{C}$  is already above the spinodal. This is inconsistent with the present results, then the calculation of  $\tilde{D}$  and  $K$  has not been carried out at the present.

(d) Determination of the Spinodal Temperature  $T_s$

The temperature dependence of  $\beta_m^2$  or  $\beta_c^2$  is given by<sup>(3)</sup>,

$$-\frac{T - T_s}{T_c} = \phi^2 c_o(1 - c_o) \beta_m^2 \quad (4.27)$$

$$-\frac{T - T_s}{T_c} = \phi^2 c_o(1 - c_o) \frac{\beta_c^2}{2} \quad (4.28)$$

where  $T_c$  is the critical unmixing temperature at composition  $c_o$  and  $\phi$

is an interaction distance. When the experimentally determined value

of  $\beta_m^2$  and  $\beta_c^2$  equal to zero, the corresponding aging temperature  $T$  should

be equal to the spinodal temperature  $T_s$ . In Fig. (4.12) the dependence of  $\beta_m^2$  and  $\beta_c^2$  on  $T$  is shown. From this figure  $T_s$  are estimated at  $\beta_m^2 = \beta_c^2 = 0$  according to above equations and found to be about  $120 \sim 130^\circ\text{C}$ . This temperature is not consistent with the one calculated by Rundman and Hilliard<sup>(14)</sup>.

#### 4-4-2. Decomposition in the Vicinity of the Spinodal

To verify the validity of the spinodal temperature estimated from Fig. (4.12), the investigation of the amplification factor  $R(\beta)$  was carried out in the vicinity of the spinodal. From Eq. (4.16) it is concluded that whether a particular Fourier component of fluctuations grows or decays depends on the sign of  $R(\beta)$ , thus, for growth :

$$f'' + 2\eta^2 K + 2K\beta^2 < 0 \quad (4.29)$$

This condition can be satisfied only inside the coherent spinodal and only for those components having wavenumbers less than a critical value,  $\beta_c$ , where  $R(\beta_c) = 0$ . The validity of this condition has been demonstrated within the spinodal in the previous section, and the shift of the maximum and the critical wavenumbers to smaller wavenumber with increasing aging temperatures was also recognized. On the other hand, this condition is not satisfied outside of the coherent spinodal and the sign of  $R(\beta)$  is expected to be negative even for fluctuations with small wavenumber.



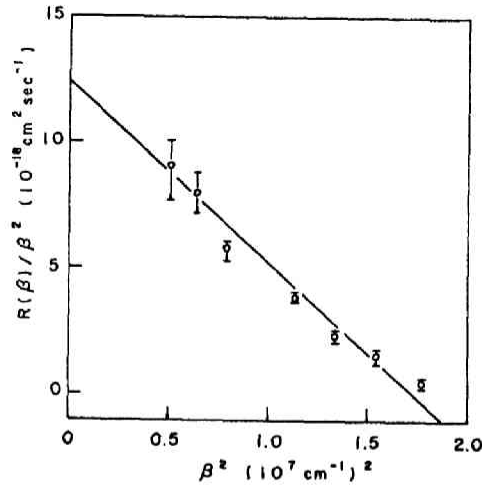


Fig.(4.11) Plots of  $R(\beta)/\beta^2$  vs.  $\beta^2$  for an Al-6.8at.% Zn alloy quenched from 300°C and aged at 40°C.

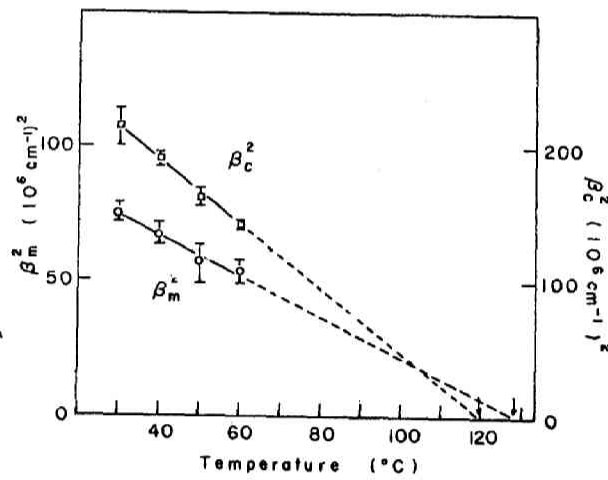


Fig.(4.12). Temperature dependence of the maximum and the critical wavenumbers of an Al-6.8at.% Zn alloy quenched from 300°C and aged at temperatures within the spinodal. The temperatures shown by arrows coincide with the spinodal temperature.

Experimentally,  $R(\beta)$  is obtained from the slope of  $\log I(\beta, t)$  vs.  $t$  curve at a given scattering angle.

In Fig. (4.13) the changes of scattering intensities measured at the angle of  $2\theta = 0.25^\circ$  for the specimens isothermally aged at  $120^\circ$ ,  $130^\circ$ , or  $140^\circ\text{C}$  are shown. This angle corresponds to the wavenumber of  $\beta = 1.78 \times 10^6 \text{ cm}^{-1}$  ( $\beta_0$ ) and is the experimentally allowed smallest scattering angle. The scattering intensities of the specimen aged at  $120^\circ\text{C}$  increase with aging time, while the  $130^\circ\text{C}$  aging shows no obvious change for the initial few minutes. The intensity shows an early decrease at  $140^\circ\text{C}$ . The values of  $R(\beta)$  can be obtained by the time dependence of the scattering intensity, according to Eq. (4.24). As this equation is valid only before decomposition is completed, the analysis should be carried out within the critical time  $t_0$  (at this time the decomposition is completed). This  $t_0$  can be determined by the changes of the integrated intensities which are a function of the local fluctuation of the electron densities. However, the integrated intensities of these specimens can not be calculated because the measured intensities are weak. Thus, only the sign of  $R(\beta_0)$  is roughly estimated from the initial few plots :  $R(\beta_0) > 0$  at  $120^\circ\text{C}$ ,  $R(\beta_0) \simeq 0$  at  $130^\circ\text{C}$  and  $R(\beta_0) < 0$  at  $140^\circ\text{C}$ .

These results suggest that for  $120^\circ\text{C}$ , since the condition of Eq.

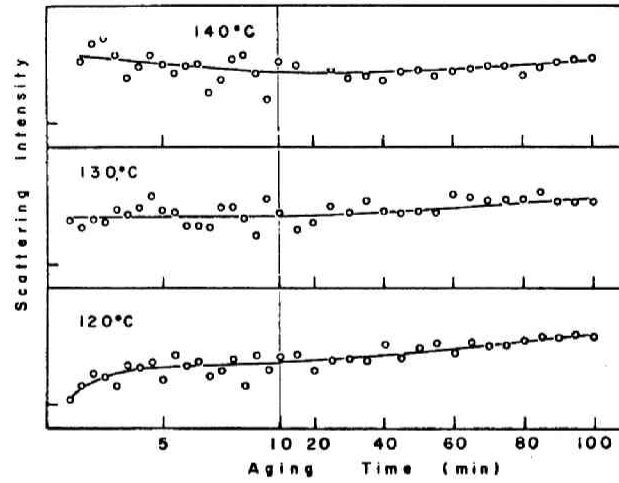


Fig.(4.13). Change of the scattering intensities measured at a constant wavenumber for an Al-6.8at.% Zn alloy quenched from 300°C and aged isothermally at 120,130 or 140°C respectively.

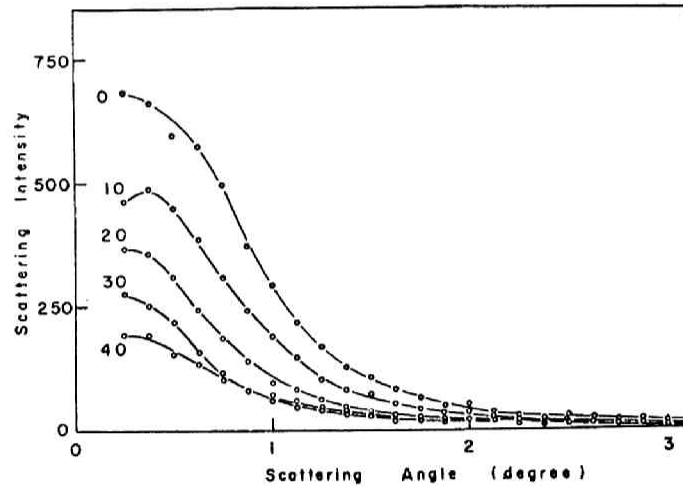


Fig.(4.14). X-ray intensities scattered from an Al-6.8at.% Zn alloy quenched from 300°C, pre-aged at 40°C for one hour and reverted at 160°C for each time (0, 10, 20, 30, 40 sec).

(4.29) is still valid, the Fourier component of fluctuations with wavenumber  $\beta_0$  seems to grow, for  $130^\circ\text{C}$  aging  $\beta_0$  may be equal to  $\beta_c$ , and for  $140^\circ\text{C}$  aging, since the condition is not satisfied, these fluctuations seem to decay. Hence, the temperature of  $120^\circ\text{C}$  is inside the coherent spinodal,  $130^\circ\text{C}$  is in the vicinity of the spinodal temperature, and  $140^\circ\text{C}$  is outside the spinodal.

Therefore, it is concluded that the spinodal temperature which was estimated to be  $120^\circ\text{C} - 130^\circ\text{C}$  from the temperature dependencies of the maximum and the critical wavenumbers in the temperature range between  $30^\circ\text{C}$  and  $60^\circ\text{C}$  agrees with the present results.

#### 4-4-3. Decomposition outside the Spinodal

In the theory of the spinodal it is predicted that above the spinodal  $\alpha(k)$  is negative at each wavenumber, which was illustrated in Fig. (4.4b). However, no one have obtained the negative value of  $\alpha(k)$  above the spinodal. If one measures the scattering intensities of the specimens aged above the spinodal which contain the composition fluctuations with various wavenumbers before aging, it is expected that the intensities decrease monotonously with aging time. Unfortunately as we do not have the equipment to make the composition fluctuation in a specimen artificially such as a rotating shutter, by utilizing the reversion

experiment the amplification factor above the spinodal was obtained below.

An aluminum-zinc alloy containing 6.8at.% Zn was homogenized at 300°C for one hour, dropped rapidly into the iced water and then aged at 40°C for one hour. These specimens are considered to contain the modulated fluctuation of composition and they are reverted at 160°C. This temperature is higher than the coherent spinodal judging from the result of Fig. (4.12). The curve of scattering intensities during reversion are shown in Fig. (4.14). From these curves the amplification factor is obtained at each wavenumber. Plots of  $\log J$  vs.  $t$  are given in Fig. (4.15) for each wavenumber and from the slope of these curves  $R(\beta)$  are estimated. The results are shown in Fig. (4.16), where it is noted that in the region of small values of  $\beta$ , this curve coincides with the one of Fig. (4.4b), however, in the region of large  $\beta$  there seem to exist two minima.

#### 4-5. Summary

Cahn-Hilliard theory of the spinodal was reviewed briefly and the present investigation was carried out according to this theory in an Al-6.8at.% Zn alloy by means of the X-ray small angle scattering method.

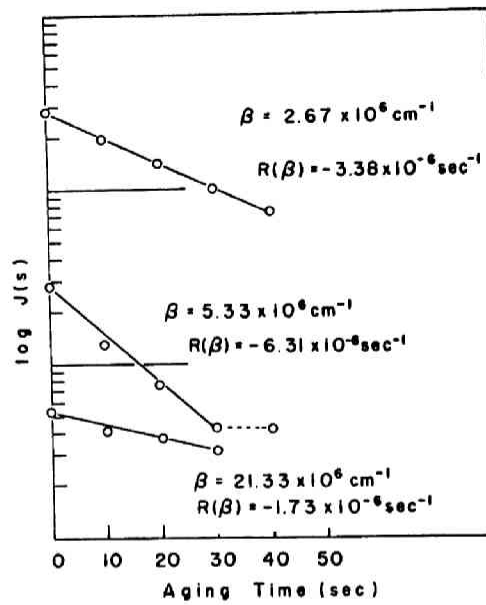


Fig.(4.15). Change of the scattering intensities at each wavenumber. The intensities were taken from Fig.(4.14). From the slopes of these curves the amplification factors are obtained.

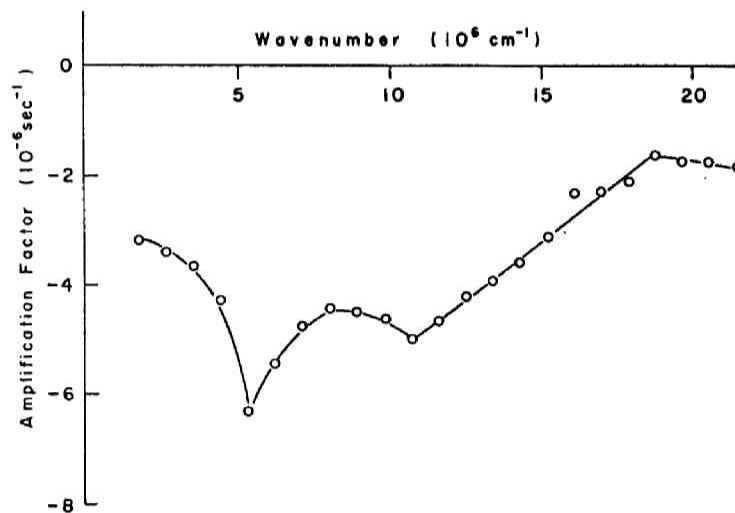


Fig.(4.16). Amplification factors vs. wavenumber of an Al-6.8at.% Zn alloy quenched from  $300^{\circ}\text{C}$ , pre-aged at  $40^{\circ}\text{C}$  for one hour and reverted at  $160^{\circ}\text{C}$ .

The examination of the integrated intensity and the application of Porod's law yielded the results that the quenched specimens decomposed by the spinodal mechanism during the course of the initial decomposition, when the specimens were aged at low temperatures. The shape of the experimentally obtained amplification factor inside the spinodal was seen to coincide with the theoretically calculated one and the spinodal temperature was determined from the dependence of the maximum and the critical wavenumbers on temperatures to be approximately  $120^{\circ} \sim 130^{\circ}\text{C}$ .

Moreover, the examination of the amplification factor above the spinodal was carried out by utilizing the reversion experiment. It was indicated that above the spinodal the shape of this factor was also coincided the theoretical one in the region of small wavenumbers.

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## CHAPTER 5

### KINETICS OF THE GROWTH OF G.P. ZONES

#### 5-1. Introduction

In chapter 3 it was indicated that at the initial stage of aging within the critical time the decomposition of the solid solution was not completed. During subsequent aging it was concluded that the solute concentrations inside and/or outside G.P. zones remained constant and that there existed the definite interface between zones and matrix. However, zones have been found to grow in radius at this stage to reduce the interfacial energy, that is, "the growth process of G.P. zones" occurs<sup>(1)</sup>. At this process it is well known that the quenched-in vacancies play a very important role in the kinetics of growth as well as the formation process of G.P. zones<sup>(2-4)</sup>, which was confirmed by the investigation of the effects of quenching temperatures<sup>(5)</sup>, neutron irradiation<sup>(6)</sup> or plastic deformation<sup>(7)</sup> on the growth process. Besides, quenched-in vacancies are concluded to be trapped near or at zones and do not, to any significant degree, annihilate during aging<sup>(8)</sup>.

The model of a diffusion process, so-called "vacancy pump model", involving solute atom-vacancy complexes was proposed by Girifalco and Herman<sup>(9)</sup>, which explains G.P. zones growth by taking into account two

important experimental facts : (a) the number of quenched-in vacancies always several orders of magnitude less than the number of solute atoms finally clustered in the zones: (b) G.P. zones growth continues for periods of time much longer than the vacancy mean life time in a pure metal.

To see the effects of the amounts of the quenched-in vacancies on the growth process of G.P. zones, the measurements for the alloys, which were quenched from various homogenization temperatures or reverted above solvus temperature for zones and then aged, were carried out by means of X-ray small angle scattering and electrical resistivity. Also, to examine the validity of the assumptions for vacancy pump model (these assumptions will be reviewed later), radius or number of G.P. zones were obtained from X-ray profiles.

Furthermore, to calculate the diffusion coefficient of zinc complex, Lifshitz-Wagner theory was applied to zone growth. Lifshitz and Slyozov<sup>(10)</sup> and Wagner<sup>(11)</sup> established the theory for the growth of particles which was based on the diffusion equations. The validity of this theory was confirmed experimentally by Ardell<sup>(12)</sup> in a binary Ni-Al alloy. At stages when the solid solution decomposed completely to the expected points of metastable miscibility gap, this theory was applied to the

zone growth and the diffusion coefficient of solute atoms was evaluated from the slope of a plot of  $R^3$  ( $R$  : average zone radius) and  $t$  (time). Also, from the temperature dependence of diffusion coefficients, the migration energy of zinc atoms were also obtained.

## 5-2. Review of Lifshitz-Wagner Theory

When the solute concentration in the solid solution has almost reached its equilibrium value, the Lifshitz-Wagner theory<sup>(10, 11)</sup> is applicable to spherical G.P. zones dispersed in matrix.

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

$$R^3 - R_0^3 = k(t - t_0) \quad (5.1)$$

where  $R$  and  $R_0$  are the average zone radius at time  $t$  and at the onset of coarsening ( $t_0$ ) respectively. The rate constant  $k$  is given by,

$$k = \frac{2\sigma D C_e V_m^2}{\rho_c^2 RT} \quad (5.2)$$

where  $D$  is the diffusion coefficient of the solute,  $V_m$  is the molar volume of the zone,  $C_e$  is the concentration of solute in equilibrium with a particle of infinite size,  $\rho_c$  is a numerical constant related to the distribution of zone sizes (theoretically  $\rho_c = 3/2$ ),  $RT$  has its usual meaning, and  $\sigma$  is the interfacial free energy of the zone-matrix

interface.

$\sigma$  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  $\Delta F^{\text{str}}$  and the chemical interfacial energy  $\Delta F^{\text{chem}}$ .

In the case of the coherent zone-matrix boundary  $\Delta F^{\text{str}} = 0$ .

Then,

$$\Delta F^{\text{chem}} = \Delta H^{\text{chem}} - T\Delta S^{\text{chem}} \quad (5.3)$$

To calculate the enthalpic component  $\Delta H^{\text{chem}}$  of the chemical interfacial energy, the relationship of Servi and Turnbull<sup>(13)</sup> can be applied to the zone-matrix boundary when the small misfit across the boundary is ignored :

$$\Delta H^{\text{chem}} = N_s Z_s (C_1 - C_2)^2 \Delta H_m \quad (5.4)$$

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  $\Delta H_m$  is the mixing enthalpy.

The entropic component  $\Delta S^{\text{chem}}$  of the chemical interfacial energy is defined by,

$$\Delta S^{\text{chem}} = S_{mz} - \frac{1}{2} (S_{mm} + S_{zz}) \quad (5.5)$$

where  $S_{mm}$ ,  $S_{zz}$  and  $S_{mz}$  are the respective positional entropy at fully

coherent matrix-matrix, zone-zone and matrix-zone boundaries.  $\Delta S^{\text{chem}} = 0$  because the juxtaposition of two random solid solution produces an interphase boundary at which the randomness of the bond arrangements is exactly the average of that at crystallographically identical boundaries within the component phases.

Hence,

$$\Delta H^{\text{chem}} = \sigma \quad (5.6)$$

Then, using the calculated value of  $\sigma$ , from the slope of the plots  $R^3$  vs.  $t$  curve the diffusion coefficient  $D$  of the solute atom is graphically obtained according to Eq. (5.2).

On the other hand, the relation of  $D$  and  $T$  is given by<sup>(14)</sup>,

$$D = D_0 \exp \left( - \frac{E_m}{RT} \right) \quad (5.7)$$

where  $D_0$  is the constant,  $E_m$  is the migration energy of solute atom in the matrix. Also, from the plots of  $\log D$  vs.  $1/T$ ,  $E_m$  and  $D_0$  can be graphically obtained.

### 5-3. Experimental Results and Discussions

#### 5-3-1. Growth Process of G.P. Zones

##### (a) Growth Process immediately after Quenching

The growth process of G.P. zones of the Al-Zn alloys aged immediately

after water quenching were followed by the X-ray small angle scattering method and the electrical resistivity measurements. The experimental procedures were the same as the investigations of the previous chapters.

Figure (5.1) shows the change of G.P. zone radius for a binary Al-6.8at.% Zn alloy quenched either from  $300^{\circ}\text{C}$  or  $450^{\circ}\text{C}$  and aged at room temperature (about  $22^{\circ}\text{C}$ ). These zone radii were obtained from the scattering intensity curve of each specimen by using Guinier approximation (Eq. (1.19)). The scattering intensities of the specimen of immediately after quenching from  $300^{\circ}\text{C}$  were not observed, but in the specimen of immediately after quenching from  $450^{\circ}\text{C}$ , the intensities due to the existence of zinc-clusters formed during quenching were observed. From this figure it is observed that G.P. zones of the specimens quenched from  $300^{\circ}\text{C}$  grow gradually with aging time till 100 min and during subsequent aging zone radius stays constant at a value of  $44\text{\AA}$ . However, zones in the specimens quenched from  $450^{\circ}\text{C}$  reach a constant value of  $24\text{\AA}$  in the earlier stage of aging, but it is found that zones grow very slowly during a long aging process. The results of electrical resistance measurements coincide with the present results as shown in Fig. (5.2). The value of the resistance remains constant at the same times indicating a constant zone size.

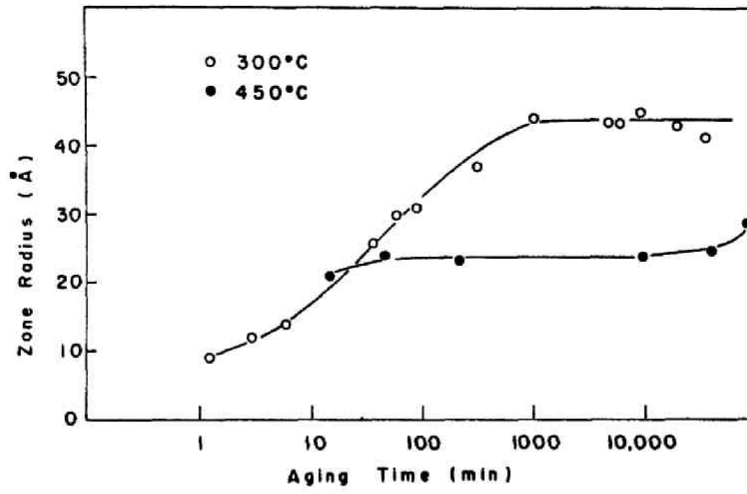


Fig.(5.1). Change of zone radius during aging at room temperature in an Al-6.8at.% Zn alloy quenched from 300° or 450°C.

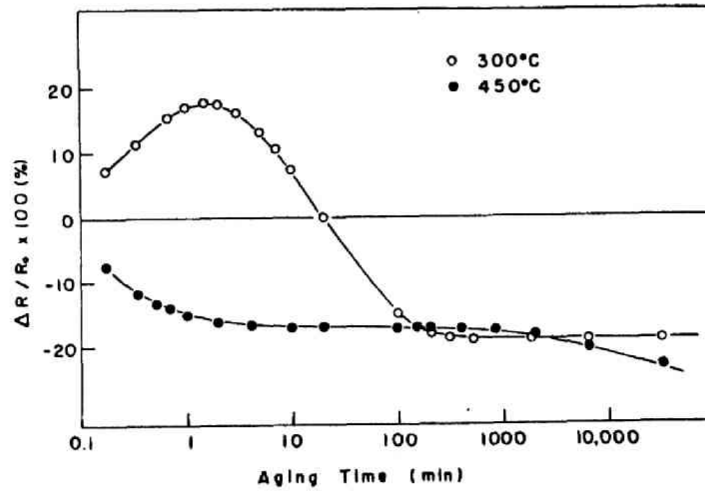


Fig.(5.2). Change of fractional electrical resistance during aging at room temperature in an Al-6.8at.% Zn alloy quenched from 300° or 450°C.



These experimental results are explained in terms of the amounts of the available vacancies for diffusion of zinc atoms. At the early time of aging the quenched-in vacancies can act as carriers of zinc atoms, but during aging they migrate to sinks and are annihilated there, so that the aging process slows down. Though in the specimens quenched from higher temperature contain higher concentration of quenched-in vacancies immediately after quenching, they annihilate to dislocation loops quickly compared with those quenched from lower temperature, then the concentration of vacancies available for zinc diffusion is fewer for the specimens quenched from higher temperature. Thus, zone radius in the specimens quenched from higher temperature reaches constant earlier than those of the lower temperature.

Also, the growth process of zone radius for the alloys containing various zinc concentration in the range of 4.4 ~ 12.4at.% Zn quenched from 300°C were shown in Fig. (5.3), where zones are observed to grow at the early stage of aging and reach a constant value later. It is found that alloys of higher zinc concentrations reach the final value earlier. This is also confirmed by the results of the electrical resistivity measurements of Fig. (5.4), where the resistivity maximum is observed in the each specimen. The times to reach the maxima are

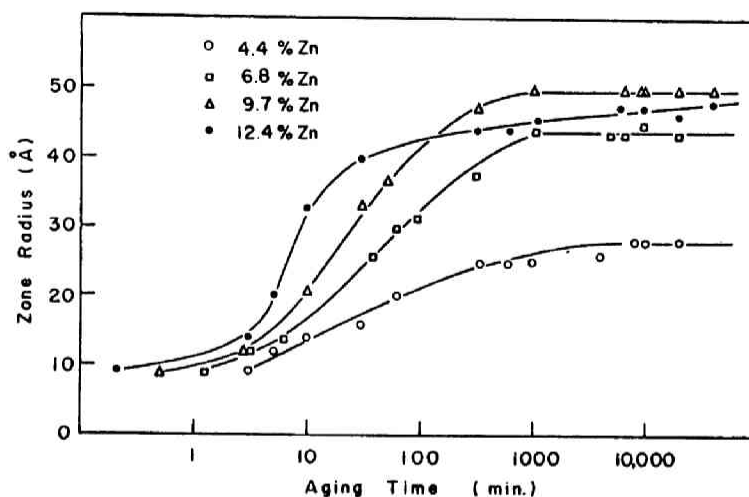


Fig.(5.3). Change of zone radius during aging at room temperature for binary Al-Zn alloys containing various zinc contents quenched from 300°C.

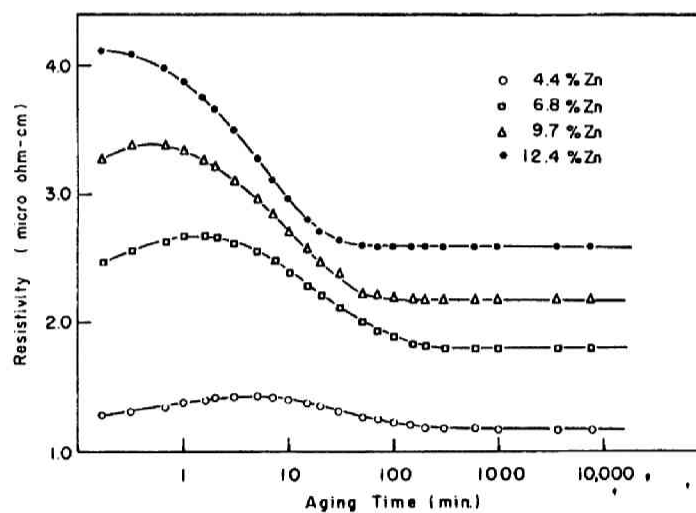


Fig.(5.4). Change of electrical resistivity during aging at room temperature for binary Al-Zn alloys containing various zinc contents quenched from 300°C.

shown to be shorter in the alloys with higher zinc concentration, which indicates that the formation process is accelerated by an increase in the zinc concentration.

For the first step to investigate the kinetics of zone growth, the examinations of the volume fraction of zones and zone numbers calculated by Eq. (1.23) were carried out. The results are shown in Fig. (5.5). As expected, the volume fraction does not change during the course of the growth process, the zone radius grows continuously till a certain aging time and the zone number, on the contrary, decreases. This confirms the suggestion that larger zones grow at the expense of the smaller ones when the decomposition has been completed, that is, Greenwood's model<sup>(1)</sup> of growth process is indicated to be applicable for the zone growth. The detailed analysis will be given in the section (5-3-2).

Here, it is noted that the assumptions which were made on developing the vacancy pump model are not valid in the growth process of G.P. zones. Girifalco and Herman<sup>(9)</sup> have proposed their model for the early formation stages, when there are supposed to be very few zones, separated by a mean distance much greater than their radius. Based on this assumption, they have considered this distance as being constant during the aging process, a simplification which enabled them to further the

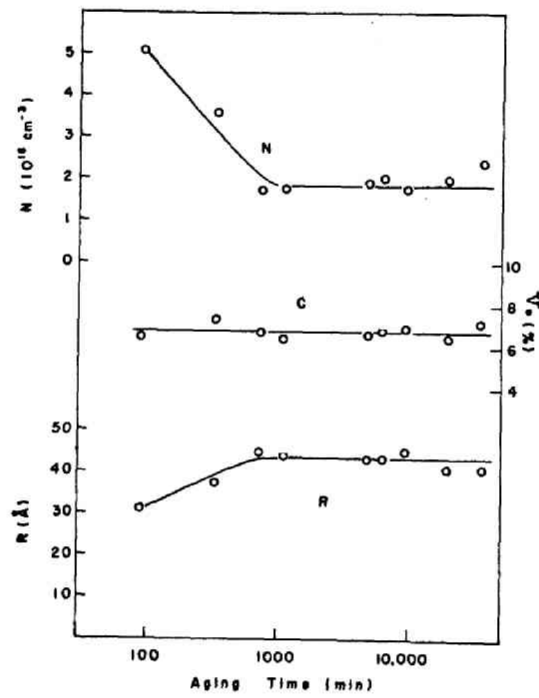


Fig.(5.5). Change of zone radius,  $R$ , volume fraction,  $V_v$ , and zone number,  $N$ , of an Al-6.8at.% Zn alloy quenched from  $300^\circ\text{C}$  and aged at room temperature.

mathematical treatment of the model. However, as seen from Fig. (5.5), the distance between zones increases as the aging proceeds.

(b) Growth after Reversion

The change of zone radius during re-aging at  $80^{\circ}\text{C}$  for an Al-6.8 at.% Zn alloy quenched from  $300^{\circ}$  or  $450^{\circ}\text{C}$ , pre-aged at room temperature for 1000 min or 10,000 min and then reverted for 15 min at  $175^{\circ}\text{C}$  was shown in Fig. (5.6). As the temperature of  $175^{\circ}\text{C}$  is above the solvus temperature of G.P. zones, zones formed at room temperature will completely dissolved within 15 min at this reversion temperature. Zones grow monotonously for a long time and do not reach a constant value. Also, the change of electrical resistivity is shown in Fig. (5.7). Each specimen shows no discrepancy in the growth process, which means that G.P. zones formed at room temperature are completely dissolved and that the vacancy concentration in each specimen is the same. Compared with the previous results of Figs. (5.1) or (5.2), the life time of vacancies available for zinc diffusion is longer for the specimens containing lower vacancy concentration.

(c) Contribution of Zones to Electrical Resistivity

The total contribution  $\bar{\Delta\rho}$  to resistivity of isolated atoms and of zones is considered by Panseri and Federighi<sup>(3)</sup> as follows:

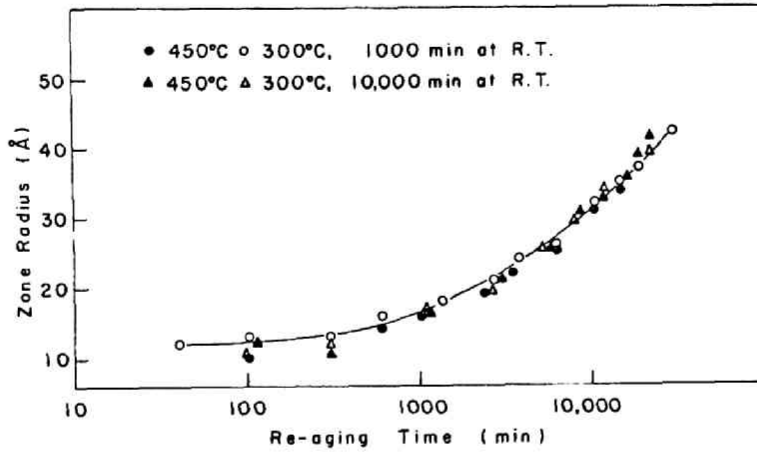


Fig.(5.6). Change of zone radius during re-aging at 80°C in an Al-6.8at.% Zn alloy quenched from 300°C or 450°C, pre-aged for 1000 or 10,000 min at room temperature and then reverted for 15 min at 175°C.

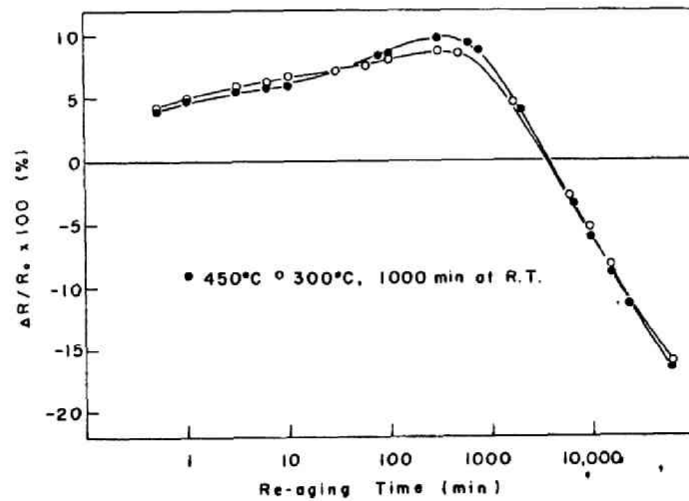


Fig.(5.7). Change of electrical resistance during re-aging at 80°C in an Al-6.8at.% Zn alloy quenched from 300°C or 450°C, pre-aged for 1000 min at room temperature, and then reverted for 15 min at 175°C.

$$\bar{\Delta\rho} = n_s \Delta\rho_s + z \left[ \Delta\rho_z(R) - \frac{16\pi V_o}{3} (R/a)^3 \Delta\rho_s \right] \quad (5.8)$$

where  $\Delta\rho_z(R)$  is the contribution of one zone of radius  $R$  per unit volume,  $\Delta\rho_s$  is the contribution of an isolated solute atom,  $n_s$  is the total number of solute,  $Z$  is the number of zones per unit volume (all having radius  $R$ ),  $a$  is the lattice parameter,  $V_o$  is the fraction of solute inside the zones (supposed to be constant). Since  $n_s \Delta\rho_s$  is constant, the experimental variation of resistivity is simply given by Eq. (5.9):

$$\Delta\rho = Z \left[ \Delta\rho_z(R) - \frac{16\pi V_o}{3} (R/a)^3 \Delta\rho_s \right] \equiv Z \phi(R) \quad (5.9)$$

The function  $\phi(R)$  is the contribution of a zone radius  $R$  to resistivity, corrected for the depletion of the matrix during the re-aging and direct aging process as shown in Fig. (5.8). The critical radius associated with the peak is about 10-15 Å, and it is unaffected by prior treatments.

### 5-3-2. Growth Law 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 a view-point of stability, G.P. zones are classified to the metastable precipitates. However, Merz and Gerold<sup>(14)</sup> revealed that the structure of the zones in the aluminum rich aluminum-zinc alloys which were formed at room temperature did not change during

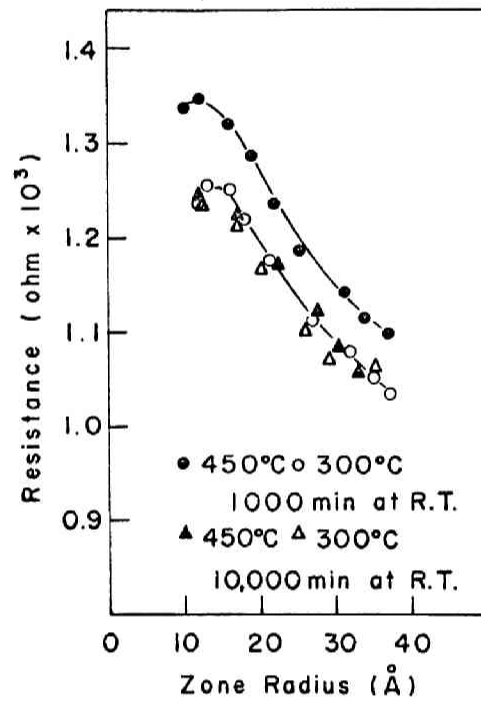


Fig.(5.8). Contribution of zone radius to electrical resistance. The profiles of curves indicate the function  $\phi(R)$  for an Al-6.8at.% Zn alloy quenched from 300° or 450°C, pre-aged for 1000 or 10,000 min at room temperature, reverted for 15 min at 175°C and re-aged at 80°C.



aging. Besides, the constancy of the integrated intensity  $Q_0$  as shown in Fig. (3.4) of chapter 3 or in the previous results<sup>(15)</sup> confirms that the solute concentrations of G.P. zones and matrix do not change after the critical aging time. Then G.P. zones may be considered to be the "stable" precipitates in a view-point of stability, so the Ostwald ripening, or Greenwood model, can be applicable to the growth of G.P. zones. Plots of  $R^3$  vs.  $t$  for specimens aged at 0, 17 or 40°C are given in Fig. (5.9), where data <sup>were</sup> found to show the excellent linearity. Also, the integrated intensities of each specimen are shown in Fig. (5.10), in which it is noted that they are constant at later stage of aging, that is, the solute concentrations both inside and outside zones do not change at this stage. Then, from the slopes of each line in Fig. (5.9) the diffusion coefficient can be obtained by using Eq. (5.1). The necessary values and the calculated diffusion coefficients at each temperature are given in Table (5.1). The  $\log D$  vs.  $1/T$  are plotted in Fig. (5.11), where the plots show the linearity within experimental accuracy. Thus, it is obvious that  $D$  varies with temperature in accordance with Arrhenius relation given by,

$$D = D_0 \exp \left( - \frac{E_m}{RT} \right) \quad (5.7)$$

where  $E_m$  is the activation energy for complex diffusion. Graphically

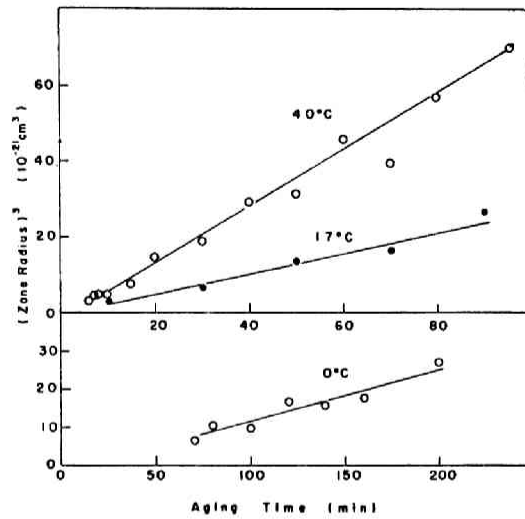


Fig.(5.9). Plots of  $R^3$  vs.  $t$  for an Al-6.8at.% Zn alloy quenched from 300°C and aged at 0, 17 or 40°C respectively.

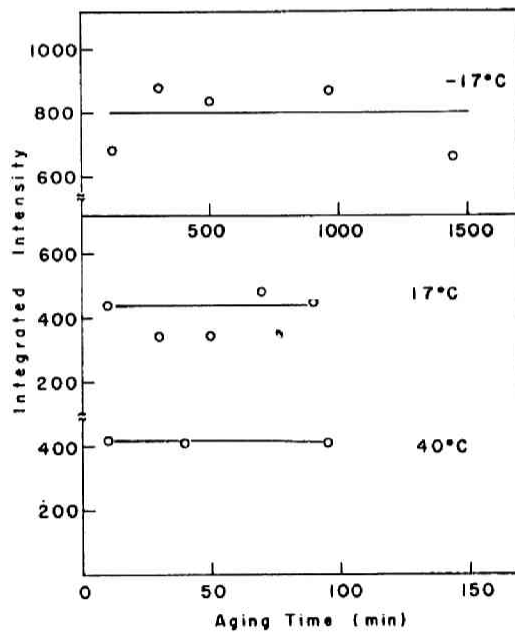


Fig.(5.10). Integrated intensities of an Al-6.8at.% Zn alloy quenched from 300°C and aged at -17, 17 or 40°C respectively.

Table (5.1). Values of  $k$ ,  $C_1$ ,  $C_2$ ,  $V_m$ ,  $\sigma$  and  $D$  for an Al-6.8at.% Zn alloy quenched from 300°C and aged at -17, 0, 17 or 40°C.

|                                            | Temperature (°C) |       |       |       | References |
|--------------------------------------------|------------------|-------|-------|-------|------------|
|                                            | - 17             | 0     | 17    | 40    |            |
| $k$ ( $10^{-24}$ cm <sup>3</sup> /sec)     | 0.346            | 2.24  | 4.48  | 12.45 | Fig.(5.9)  |
| $C_1$                                      | 0.742            | 0.752 | 0.740 | 0.725 | Fig.(2.10) |
| $C_2$                                      | 0.012            | 0.013 | 0.016 | 0.019 |            |
| $C_e$ ( $10^{-3}$ mol/cm <sup>3</sup> )    | 1.251            | 1.331 | 1.572 | 1.896 | $C_2$      |
| $V_m$ (cm <sup>3</sup> /mol)               | 9.363            | 9.359 | 9.369 | 9.382 | $C_1$      |
| $\sigma$ ( $10^{-8}$ cal/cm <sup>2</sup> ) | 127              | 130   | 125   | 118   | Eq.(5.4)   |
| $D$ ( $10^{-14}$ cm <sup>2</sup> /sec)     | 0.142            | 0.903 | 1.683 | 4.401 | Eq.(5.2)   |

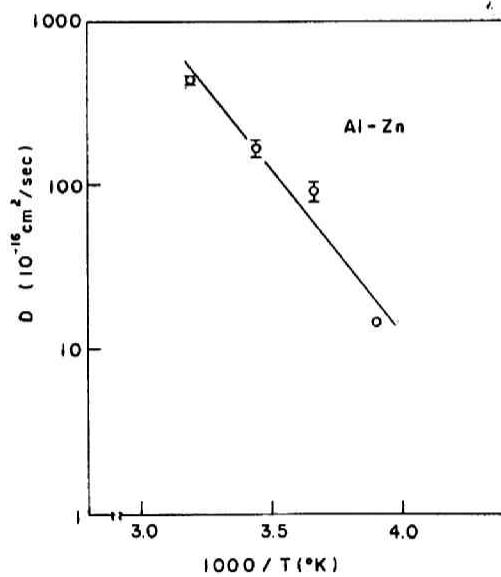


Fig.(5.11). A plot of  $\log D$  vs.  $1/T$  for an Al-6.8at.% Zn alloy quenched from 300°C and aged at -17, 0, 17 or 40°C.

$E_m$  is estimated to be  $0.38 \pm 0.04$  eV.

To compare the present values of  $D$  and  $E_m$  with those calculated by other authors, they are listed in Tables (5.2) and (5.3) respectively which were obtained by various experimental methods for Al-Zn alloys. Though the values of  $D$  coincide with others,  $E_m$  is a little smaller. 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 when the electrical resistivity measurements were carried out to determine the value of  $E_m$ , the decomposition seems not to be completed.

#### 5-4. Summary

The growth process of G.P. zones in binary Al-Zn alloys was followed by means of the X-ray small angle scattering method and the electrical resistivity measurements.

The difference of the growth processes of the each specimen quenched from various homogenization temperatures were remarkable, which was interpreted in terms of the difference of the amounts of the quenched-in vacancies immediately after quenching. That is, the growth process was confirmed to be controlled by the point defects of vacancy type.

Table (5.2). Diffusion coefficients of zinc complexes for binary Al-Zn alloys.

| Zn(at.%)  | D (cm <sup>2</sup> /sec)                                    | T <sub>A</sub> (°C) | References   |
|-----------|-------------------------------------------------------------|---------------------|--------------|
| 4.4       | 10 <sup>-10</sup> ~ 10 <sup>-12</sup>                       | -50 ~ 20            | (9)          |
| 4.4       | 10 <sup>-15</sup><br>10 <sup>-14</sup><br>10 <sup>-14</sup> | -50<br>-20<br>20    | (16)         |
| 4.4       | 10 <sup>-14</sup>                                           | 27                  | (17)         |
| 6.8       | 10 <sup>-13</sup> ~ 10 <sup>-14</sup>                       | 25                  | (18)         |
| 4.7 ~ 8.6 | 10 <sup>-13</sup> ~ 10 <sup>-15</sup>                       | -20 ~ 40            | (19)         |
| 6.8       | 10 <sup>-14</sup>                                           | -17 ~ 40            | present work |

Table (5.3). Migration energies of zinc complexes for binary Al-Zn alloys.

| Zn(at.%)  | E <sub>m</sub> (eV)    | T <sub>A</sub> (°C)   | T <sub>Q</sub> (°C) | References   |
|-----------|------------------------|-----------------------|---------------------|--------------|
| 12.5      | 0.58                   | -30 ~ 20              | 300                 | (20)         |
| 9.7       | 0.50                   | -50 ~ 50              | 250                 | (21)         |
| 3.6       | 0.39±0.04              | -35 ~ -15             | 300                 | (4)          |
| 4.4       | 0.38±0.02<br>0.43±0.02 | -70 ~ -30<br>-30 ~ 50 | 300<br>450          | (3)          |
| 6.8       | 0.43±0.01              | 20 ~ 50               |                     | (22)         |
| 9.7       | 0.45±0.04              | 20 ~ 50               | 300                 |              |
| 12.4      | 0.39±0.07              | 20 ~ 50               |                     |              |
| 4.7 ~ 8.6 | 0.43                   | -20 ~ 40              | 250<br>550          | (19)         |
| 6.8       | 0.38±0.04              | -17 ~ 40              | 300                 | present work |

By examining changes of zone radius and zone number during the aging, it was found that G.P. zones grow in accordant with the growth model of so-called "Ostwald ripening", that is, the larger zones grow at the expense of small zones, while the solute concentrations both in zones and in matrix remain constant. Therefore, the average distance between zones decreases as aging proceeds, which is noted to be contradictory with the assumption of Girifalco and Herman made in developing the vacancy pump model. They assumed that the average distance between zones was constant during aging to simplify the mathematical treatments.

Moreover, by applying the Lifshitz-Wagner theory to the zone growth, the diffusion coefficients of zinc atoms at low temperature agings were calculated to be around  $10^{-14} \text{ cm}^2/\text{sec}$ . The order of the value <sup>of</sup> this coefficient was found to agree with the previously reported values by other authors. Also, by the temperature dependence of the diffusion coefficient, the migration energy of the zinc atoms was obtained to be  $0.38 \pm 0.04 \text{ eV}$ .

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## CHAPTER 6

### KINETICS OF THE DISSOLUTION OF G.P. ZONES

#### 6-1. Introduction

Previous investigations have revealed that G.P. zones in Al-Zn alloys exist metastably at room temperature and that these zones dissolve completely at temperatures above the solvus. In a binary aluminum-6.8 at.% zinc alloy the solvus temperature was determined to be 155°C in chapter 2 and also the model for G.P. zones during dissolution was indicated to be the reverse of that of during growth (Chapter 3).

In the present chapter the investigations of the dissolution of G.P. zones in a binary Al-6.8at.% Zn alloy at the temperature above the solvus were performed by means of the electrical resistivity measurements and the X-ray small angle scattering method (a) to examine the stability of G.P. zones, (b) to calculate the diffusion coefficient of the solute in the matrix and (c) to know which controls the dissolution, the solute diffusion through the matrix or the transfer of atoms across the zone-matrix interface.

Kimura<sup>(1)</sup> has proposed that G.P. zones contain vacancies inside and that during aging these vacancies are emitted from zones to annihilate into sinks. Thus, it is expected that zones of a specimen aged for

shorter time at room temperature prior to reversion will dissolve earlier than those pre-aged for longer time when zones are re-aged at temperatures above the solvus. Experimentally by the electrical resistivity measurement, Katz, Rao and Herman<sup>(2)</sup> showed that the time to reach the fully reverted state is proportional to the aging time at room temperature prior to reversion. In this chapter the effects of pre-aging time, quenching temperatures and prior zone size on the stability of zones are examined.

Several authors<sup>(3 ~ 6)</sup> have considered the dissolution process to be the reverse of the growth process and shown the time dependence of zone radius ( $R$ ) as  $R^2 = k D t$  where  $k$  is the rate constant,  $D$  is the diffusion coefficient of the solute in the matrix and  $t$  is the reversion time. This relation was examined experimentally in a binary Al-Cu alloy by Thomas and Whelan<sup>(7)</sup>. Recently Whelan<sup>(8)</sup> has proposed the more exact relation of the time dependence of zone radius considering both the steady state part and the transient part of the diffusion field around a spherical zone. Using this relationship, the measurement of the zone radius at each reversion time determined the diffusion coefficient.

The rate of dissolution as well as growth is limited by the solute diffusion through the matrix and/or by the transfer of atoms across the

zone-matrix interface. Recently a single parameter  $\sigma$  which reflects the rate controlling process was proposed by Nolfi et al.<sup>(9)</sup>  $\sigma$  takes the value between 0 and 1 according to the rate controlling process:  $\sigma = 0$  for the diffusion controlled migration (DCM),  $\sigma = 1$  for the interface controlled migration (ICM) and  $0 < \sigma < 1$  for the mixed control. Therefore, the determination of this parameter  $\sigma$  yields the information on the rate controlling process.

## 6-2. Theoretical Consideration

### (a) Diffusion Coefficient D of Solute Atom in the Matrix

The time dependence of the radius of dissolving spherical zones was given for the diffusion controlled dissolution as follows<sup>(8)</sup>,

$$\frac{dR}{dt} = -\frac{kD}{2R} - \frac{k}{2} \sqrt{\frac{D}{\pi t}} \quad (6.1)$$

$$k = 2(C_s - C_E)/(C_l - C_s) \quad (6.2)$$

where R is the average zone radius at reversion time t,  $C_s$  and  $C_E$  are solute concentrations at the interface and at a large distance from the zone respectively. In this equation the motion of the interface was not allowed for and the diffusion coefficient of the solute atoms was assumed to be independent of time and composition. By this equation

the value of D can be obtained graphically from the slope of a plot of zone radius and reversion time.

(b) Parameter  $\sigma$

The relation between the parameter  $\sigma$  and the solute concentration

in the matrix is given<sup>(9)</sup>,

$$\frac{dC_2}{dt} = A \exp \left( - \frac{D\alpha_o^2 t}{R_s^2} \right) \quad (6.3)$$

where A is the constant,  $R_s$  is the radius of the equivalent spherical

cell in which a zone is contained and  $\alpha_o$  is the function of the parameter

$\sigma$  obtained by the following equation,

$$\tan \left[ \alpha_n (1 - \beta) - n\pi \right] = \frac{\alpha_n (1 - \sigma \beta)}{1 + \sigma \beta \alpha_n^2} \quad (n = 0, 1, 2, 3)$$

$$\beta = \frac{R_o}{R_s} = \sqrt[3]{\sigma}$$

where  $R_o$  is the initial zone radius. To apply these equations to zone

dissolution the following conditions are required: (1) The reversion

time is longer than the time  $t^*$  defined by  $(10R_s^2/D\alpha_1^2)$ , (2) the matrix

is divided into identical, symmetrical cells and then dissolution is

considered only in a single cell, (3) during dissolution the zone radius

is nearly constant in comparison with the initial radius  $R_o$  and (4) the

value of  $(C_1 - C_E)$  is much larger than that of  $(C_s - C_E)$ . If these

conditions are satisfied, according to above Eq. (6.3) from the slope of the curve of  $\ln(dC_2/dt)$  vs.  $t$  the parameter  $\sigma$  can be calculated as a function of the diffusion coefficient. Here, the value of  $C_2$  is estimated by Eq. (1.20).

### 6-3. Experimental Procedures

The measurements of electrical resistivity and X-ray small angle scattering intensity were carried out at liquid nitrogen temperature with the foils of 0.2 mm thick of an aluminum-6.8at.% zinc alloy. For the study of stability of G.P. zones, specimens were quenched either from 450°C or 300°C into iced brine and aged for various times at room temperature. The changes of zone radius or electrical resistivity during aging at room temperature were shown in previous chapter (Chap.5). Then, these specimens were reverted at the temperature of 175°C and the measurements of electrical resistivity were carried out during reversion.

For the studies of calculations of  $D$  and  $\sigma$ , the measurements of X-ray small angle scattering, using Ni-filtered  $CuK_\alpha$  radiation, were carried out. The specimens were initially annealed at 450°C for one hour and homogenized at 300°C for one hour, then dropped rapidly into water bath of 0°C beneath the furnace, held at this temperature for 15

sec and kept in the liquid nitrogen before aging. These specimens were pre-aged isothermally at  $40^{\circ}\text{C}$  for one hour and then reverted at  $160^{\circ}\text{C}$ . The temperature of  $160^{\circ}\text{C}$  was confirmed to be above the solvus temperature of G.P. zones in this alloy (Chap. 2). The aging and reversion were performed in an air furnace keeping the temperature within  $\pm 1^{\circ}\text{C}$  of the desired temperature. The heat up time of the specimens was less than 10 sec.

The intensities were counted at liquid nitrogen temperature at  $1/8^{\circ}$  intervals in the scattering angle. The calculation of the integrated intensity was carried out by the method developed by Gerold. The average zone radius was calculated by using Guinier approximation.

#### 6-4. Experimental Results and Discussions

##### 6-4-1. Stability of G.P. zones

The investigation on the stability of G.P. zones was carried out by the electrical resistivity measurements during reversion at  $175^{\circ}\text{C}$  with specimens of the various heat-treatments prior to reversion. Particular attentions were paid to the influences of the pre-aging times, quenching temperatures or the prior zone radius on the stability of G.P. zones. Previous investigation by means of electrical resistivity

has shown that when the alloy, in which zones formed at low temperature agings contains, is re-aged at temperatures above the solvus of G.P. zones, the resistivity of the alloy coincides approximately with the one of the solid solution calculated by using the Northeim's law<sup>(10)</sup> and that during subsequent reversion they remain constant. Then, the time to reach the constant value (the time to reach the resistivity of the solid solution) is used as a parameter of stability of zones, that is, the longer the time to reach the constant value is, the more stabilized zones at room temperature aging are.

The isothermal resistance curve during reversion at  $175^{\circ}\text{C}$  in specimens quenched from  $300^{\circ}\text{C}$ , and pre-aged at room temperature for 30 min ( $R = 30 \text{ } \Omega$ ), 100 min ( $44 \text{ } \Omega$ ), 1000 min ( $44 \text{ } \Omega$ ) and 10,000 min ( $44 \text{ } \Omega$ ) is illustrated in Fig. (6.1). Here the fractional change of resistance is plotted as a function of the holding time at  $175^{\circ}\text{C}$ .  $R_0$  is the end of value of resistance, as determined from the final value of resistance after reversion. The alloy aged for 30 min at room temperature shows a maximum associated with the critical size of the dissolving zones, but no maxima are observed in the specimens with large initial zone sizes, because of a wide size distribution in such a case. Though the zone radius in the three specimens, which were pre-aged at room temperature

for 100 min, 1000 min and 10,000 min, is the same, the time required to reach the as-reverted value is different. It increases with increasing pre-aging time as shown by points B, C and D. This observation agrees with the results of Katz et al<sup>(2)</sup>.

To see the effect of quenching temperatures on the stability, the changes of electrical resistivity during reversion is shown in Fig. (6.2) for specimens quenched from 450°C and aged at room temperature for 1000 min or 10,000 min. It is noted that these specimens reach a constant value in shorter reversion time than those quenched from 300°C and that a resistance maximum is observed in each specimen.

The time for completion of reversion is dependent on the pre-procedures, that is, on the pre-aging time at room temperature, on the quenching temperature and on the prior zone size as illustrated in Fig. (6.3). The effect of the pre-aging time is illustrated for the binary alloys, which were quenched from the same temperature (300°C), had the same initial zone radius ( $44 \text{ \AA}$ ), and were pre-aged for various times. It is found that the time for completion of reversion increases with increasing the pre-aging time. This may be due to a decrease of the vacancy concentration inside and outside the zones during aging at room temperature. It is also found that the higher the quenching temperature,



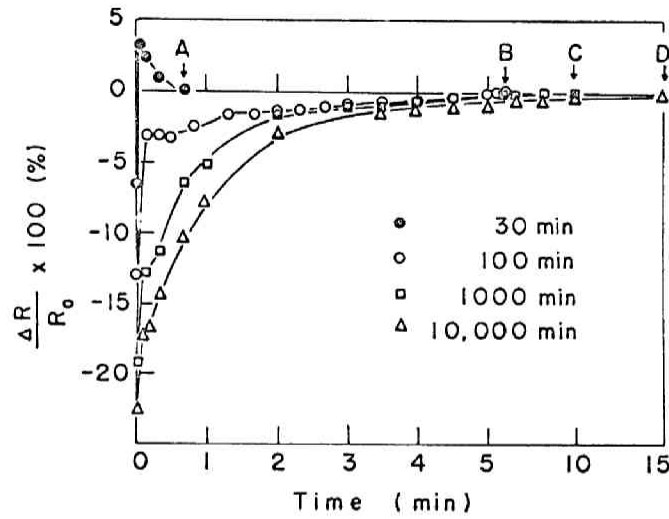


Fig.(6.1). Fractional change of electrical resistance during reversion at  $175^{\circ}\text{C}$  for Al-6.8at.% Zn alloys quenched from  $300^{\circ}\text{C}$  and pre-aged for 30, 100, 1000 and 10,000 min at room temperature. The points A, B, C and D show the time for completion of reversion in each specimen.

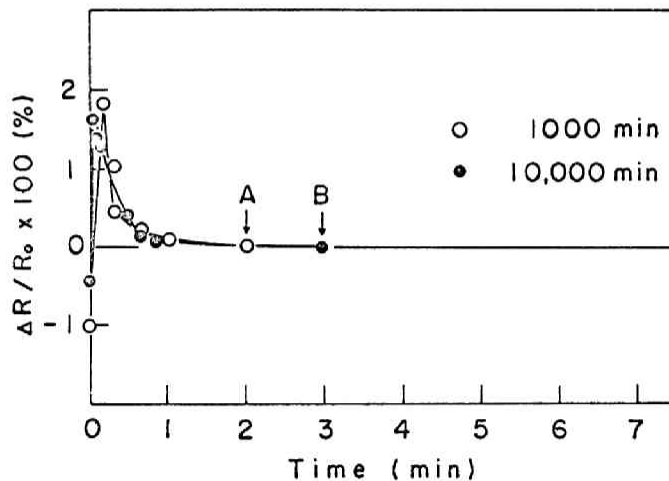


Fig.(6.2). Fractional change of electrical resistance during reversion at  $175^{\circ}\text{C}$  for Al-6.8at.% Zn alloys quenched from  $450^{\circ}\text{C}$  and pre-aged for 1000 min and 10,000 min at room temperature. The points A and B show the time for completion of reversion in each specimen.

the shorter is the time to completion of the reversion. This is also attributed to the amount of quenched-in vacancies existing in the matrix. It is difficult to discuss the effect of the prior zone size, as it depends on the quenching temperature and pre-aging time. But comparing the binary alloys quenched from  $450^{\circ}\text{C}$  ( $24 \text{ \AA}$ ) and  $300^{\circ}\text{C}$  ( $44 \text{ \AA}$ ) respectively, the initially small zones tend to dissolve more easily than the larger ones.

#### 6-4-2. Zone Radius and Diffusion Coefficient

The X-ray small angle scattering curves of the specimens which were quenched from  $300^{\circ}\text{C}$ , pre-aged at  $40^{\circ}\text{C}$  for 60 min and then reverted at  $160^{\circ}\text{C}$ , measured at liquid nitrogen temperature, are shown in Fig. (2.4) of Chap. 2. As is evident from this figure, the scattering intensities decrease monotonously with reversion times.

The change of zone radius with reversion time is shown in Fig. (6.4) and from this figure the diffusion coefficient can be obtained graphically by Eq. (6.1). This equation is applicable only to the zones with the sharp interface between the matrix, which requires that the analysis should be done by these plots within the reversion times of 30 sec considering the results of chapter 3. Previous experiments confirmed that the supersaturated solid solution has decomposed to the

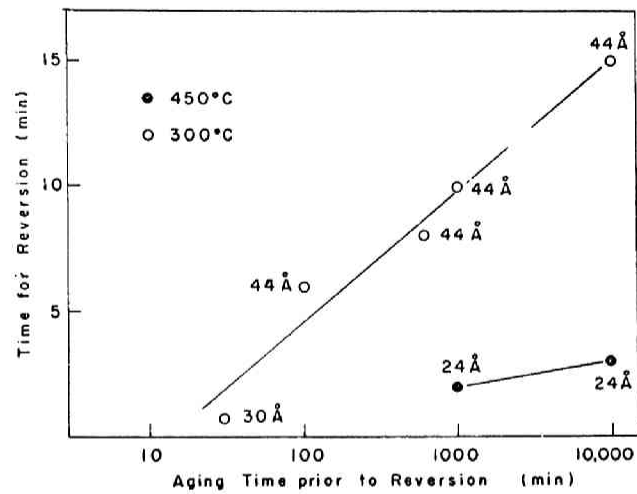


Fig.(6.3). Time for completion of reversion vs. the aging time at room temperature. The sizes indicated in this figure show the zone radii prior to reversion.

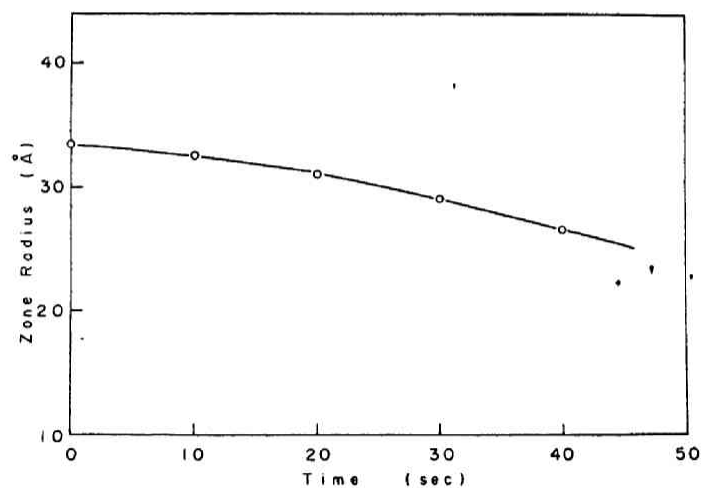


Fig.(6.4). Change of zone radius of an Al-6.8at.% Zn alloy quenched from 300°C, pre-aged at 40°C for one hour and then reverted at 160°C.

points of the metastable miscibility gap within 60 min aging at 40°C.

So,  $k$  is calculated by putting  $C_1 = 0.719$  and  $C_E = 0.0175$  which were determined by Gerold<sup>(11)</sup> and  $C_s = 0.068$  ( $C_o$ ) into Eq. (6.2), to be 0.155.

Substituting these values into Eq. (6.1) the diffusion coefficient of the solute in the matrix was calculated to be approximately  $(0.5 \pm 0.1) \times 10^{-14} \text{ cm}^2/\text{sec}$ .

This diffusion coefficient was calculated by using the condition that the solute concentration at the distance  $R_s$  from the center of a given zone remained constant. This condition is satisfied when the mean diffusion distance is nearly equal to the equivalent sphere radius, that is,  $2\sqrt{Dt} \sim R_s$ . Using  $D = 10^{-14} \text{ cm}^2/\text{sec}$  and  $t = 30 \text{ sec}$ , the value of  $2\sqrt{Dt}$  is calculated to be approximately 100 Å. As  $R_s$  was calculated to be 81 Å, this condition is considered reasonable in the present case.

If the values of  $C_2$  which varied with reversion time are used as the values of  $C_E$  in the calculation of  $k$ , the average diffusion coefficient  $D$  within 30 sec of reversion time is calculated to be about  $(1.0 \pm 0.5) \times 10^{-14} \text{ cm}^2/\text{sec}$ .

#### 6-4-3. Integrated Intensity and Parameter $\sigma$

The change of the integrated intensity  $Q_o$  with reversion time is shown in Fig. (6.5). In the early stage of dissolution when the zones

have the sharp interface between the matrix, the requirements of  $C_1$  ( $= 0.719$ )  $\gg C_0$  or  $C_2$  will be satisfied (Chap. 3). Then, the value of  $C_2$  was obtained at each reversion time from Eq. (1.20) on the assumption that  $C_1$  is constant at this stage. The value of  $C_1$  is used the one determined by Gerold<sup>(11)</sup> and the results are shown in the same figure. The plots of  $\ln(dC_2/dt)$  vs.  $t$  obtained from Fig. (6.5) is shown in Fig. (6.6) and the parameter  $\sigma$  was calculated as a function of diffusion coefficient  $D$ , according to Eq. (6.3) as illustrated in Fig. (6.7).

In the derivation of Eq. (6.3), several conditions were required. The discussions on these conditions will be given below. (1) When  $t > t^*$ , Eq. (6.3) is valid. If  $\sigma = 0$ , putting  $D = 10^{-14} \text{ cm}^2/\text{sec}$ ,  $R_s = 81 \text{ \AA}$  and  $\beta = 0.41$  the time  $t^*$  was calculated to be about 10 sec. If  $\sigma = 1$ , putting  $D = 10^{-12} \text{ cm}^2/\text{sec}$  the time  $t^*$  was 0.2 sec which was much less than 10 sec ( $\sigma = 0$ ). Then Eq. (6.3) is applicable to the present experiment to obtain the value of  $\sigma$  when the reversion time is longer than 10 sec. (2) The zone number  $N$  per unit volume was calculated at each reversion time by Eq. (1.23) using the experimental values of  $R$  in Fig. (6.4) and  $Q_0$  in Fig. (6.5). The results are  $N = 4.6 \times 10^{17}/\text{cm}^3$  at  $t = 0$  sec,  $N = 3.2 \times 10^{17}/\text{cm}^3$  at  $t = 10$  sec,  $N = 2.7 \times 10^{17}/\text{cm}^3$  at  $t = 20$  sec,  $N = 2.8 \times 10^{17}/\text{cm}^3$  at  $t = 30$  sec and  $N = 3.3 \times 10^{17}/\text{cm}^3$  at  $t = 40$  sec.

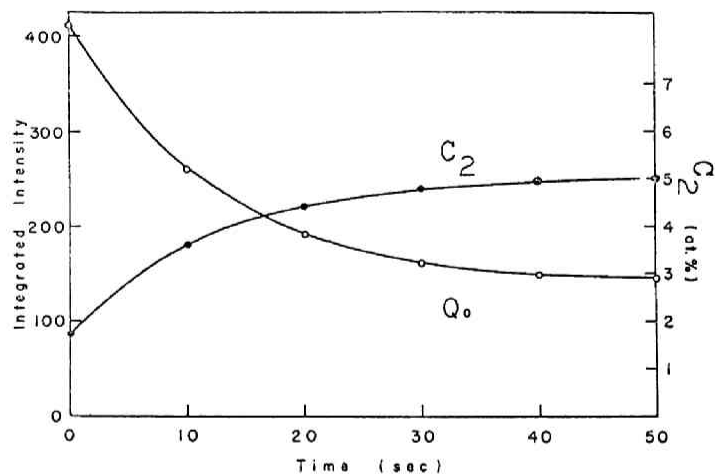


Fig.(6.5). Change of the integrated intensities ( $Q_0$ ) and the average solute concentration in the matrix ( $C_2$ ) of an Al-6.8at.% Zn alloy quenched from 300°C, pre-aged at 40°C for one hour and then reverted at 160°C.

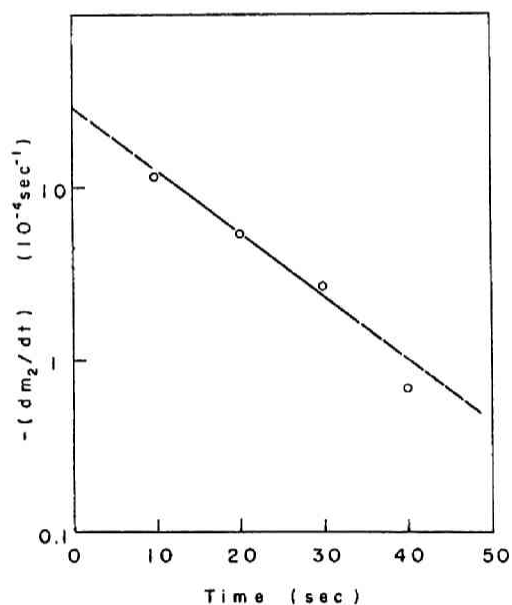


Fig.(6.6). Plots of logarithm of the derivative of the average solute concentration in the matrix vs. reversion time at 160°C for an Al-6.8at.% Zn alloy quenched from 300°C and pre-aged at 40°C for one hour.

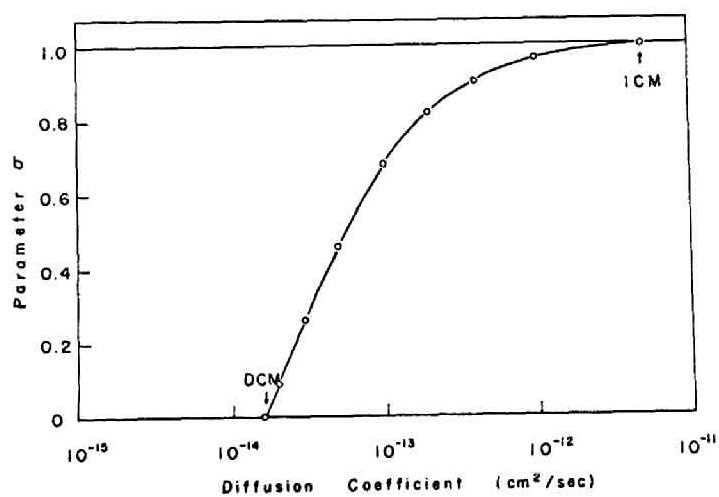


Fig.(6.7). Variation of a parameter  $\sigma$  as a function of the diffusion coefficient  $D$ .

Thus  $N$  is almost constant after about 10 sec, which means that the matrix can be divided into identical cells, namely, "isolated particle approximation" can be allowed. (3) The fraction of the decrease of zone radius reverted at  $160^{\circ}\text{C}$  for 30 sec to the initial radius was about 13%. Hence, the condition of constant precipitate size is approximately satisfied. (4) In the initial stage of dissolution when the zones have almost sharp interface between the matrix, as  $C_1$  ( $= 0.719$ ) is much greater than  $C_s$  and  $C_E$ , the condition of  $(C_1 - C_E) \gg (C_s - C_E)$  is satisfied. Considering from these examinations of several conditions, the theory of Nolfi et al.<sup>(9)</sup> can be applicable to the dissolution process in this alloy.

As seen from Fig. (6.7), the upper limit of diffusion coefficient corresponding  $\sigma = 0$  when the solute diffusion through the matrix controls the interface migration, is about  $1.6 \times 10^{-14} \text{ cm}^2/\text{sec}$ . The experimentally obtained value of  $D$  is smaller than this value, which indicates that the rate of dissolution is truly limited by diffusion controlled migration (DCM). Thus, the assumption of diffusion controlled migration on the determination of the diffusion coefficient is reasonable.

When  $D = 10^{-14} \text{ cm}^2/\text{sec}$ , using the frequency factor  $D_0^* = 0.28 \text{ cm}^2/\text{sec}$



obtained by Hilliard et al.<sup>(12)</sup> of this alloy, the activation energy for dissolution of zones is calculated to be about 1.16eV, which almost coincides with that for the self-diffusion of zinc atom (1.20eV).

In calculating the diffusion coefficient  $D$  and parameter  $\sigma$ , the dependences of  $D$  on time and component and the driving force for diffusion such as the coherent strain were not taken into consideration. Therefore, the value of diffusion coefficient  $D$  obtained in the present experiment is considered to be rough approximation.

#### 6-5. Summary

An investigation of dissolution of G.P. zones in a binary Al-6.8 at.% Zn alloy was carried out on the basis of the zone model during dissolution proposed in chapter 3. By the electrical resistivity measurements, the influences of pre-aging times at room temperature prior to reversion, quenching temperatures or prior zone sizes on the stability of G.P. zones were studied and they were found to be remarkable. Moreover, from the changes of scattering intensities measured by the X-ray small angle scattering, the diffusion coefficient of zinc atoms in the matrix was determined to be approximately  $10^{-14} \text{ cm}^2/\text{sec}$ . Also, the rate limiting process during dissolution was concluded to be diffusion

controlled migration by examining the value of parameter  $\sigma$ .

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## CHAPTER 7

### EFFECTS OF THE ADDITION OF THE THIRD ELEMENTS ON G.P. ZONES IN BINARY ALUMINUM-ZINC ALLOYS

#### 7-1. Introduction

It has been well known that the aging process of G.P. zones in Al-Zn alloys is influenced by the addition of small quantity of the third elements and that the additions of Ag,<sup>(1,2)</sup> Si<sup>(3,4)</sup>, Mg<sup>(5 - 8)</sup>, Be<sup>(9)</sup>, Sn<sup>(10,11)</sup> or Fe<sup>(4)</sup> were remarkable. In the present chapter the particular attention was paid on the effects of third elements, Ag, Si or Mg, on the temperature range of the existence of G.P. zones and on the formation and growth of zones. Also, the interesting results were obtained through the reversion experiment in the Ag containing Al-Zn alloys.

Three elements, Ag, Si and Mg, were chosen as the third elements for the following reasons:

Ag . . . . In the binary Al-Ag alloy the spherical disordered  $\eta'$  - zones were observed immediately after quenching<sup>(12)</sup>. Therefore, in the Al-Zn-Ag alloys, it is suggested that Ag atoms might <sup>induce</sup> cluster formation during quenching. Also, since the migration energy of the Zn atoms was found to be raised by the addition of Ag atoms<sup>(1)</sup>, Ag atoms may have a great

effect of the zinc diffusion, especially during low temperatures agings.

Si . . . . The effects of the addition of Si atoms were found to be marked, especially at low temperature aging. In the binary Zn-Si system, no mutual solid solubilities between Si and Zn<sup>(13)</sup> and no intermetallic compounds<sup>(14)</sup> are reported to exist. Shashkov and Buynov<sup>(15)</sup> investigated the behavior of Si atoms in Al-Zn alloys and showed that silicon was not in the G.P. zones. The interaction between Si atoms and vacancies is strong enough to increase the quenched-in vacancy concentration<sup>(16)</sup>.

Mg . . . . Mg atoms are reported to trap quenched-in vacancies and after much longer aging times, these trapped vacancies will become free and act as diffusion carriers<sup>(15)</sup>. Therefore at intermediate aging times, the diffusion of Zn atoms in Al-Zn-Mg alloys will be slower than in the binary Al-Zn alloys, whereas at longer times Zn diffusion will become faster.

## 7-2. Experimental Procedures

The experiments were carried out by means of electrical resistivity measurements, X-ray small angle scattering and transmission electron microscopy. The methods of heat-treatments or measurements were already given in previous chapters, thus, they are not given here. The alloy components used in the present experiments are given in Table (7.1).

Table (7.1). Analyses of alloys in at.%. The main impurities of the binary alloys are Fe < 0.002wt.%, Si < 0.002wt% and Cu < 0.001wt.%.

| Alloy        | Zn    | Ag   | Si   | Mg   |
|--------------|-------|------|------|------|
| Al-4.4 % Zn  | 4.39  |      |      |      |
| -0.5 % Ag    | 4.53  | 0.53 |      |      |
| -0.5 % Si    | 4.34  |      | 0.49 |      |
| Al-6.8 % Zn  | 6.82  |      |      |      |
| -0.1 % Ag    | 6.76  | 0.09 |      |      |
| -0.5 % Ag    | 7.01  | 0.54 |      |      |
| -0.1 % Si    | 6.88  |      | 0.12 |      |
| -0.5 % Si    | 6.85  |      | 0.47 |      |
| -0.1 % Mg    | 6.74  |      |      | 0.15 |
| Al-9.7 % Zn  | 9.67  |      |      |      |
| -0.5 % Ag    | 9.78  | 0.53 |      |      |
| -0.5 % Si    | 9.79  |      | 0.53 |      |
| Al-12.4 % Zn | 12.44 |      |      |      |
| -0.5 % Ag    | 12.84 | 0.62 |      |      |
| -0.1 % Si    | 12.38 |      | 0.11 |      |
| -0.5 % Si    | 12.48 |      | 0.48 |      |

### 7-3. Experimental Results and Discussions

#### 7-3-1. Effects of Third Elements on the Temperature Range of G.P. Zones

##### (a) On the Formation Temperature for G.P. Zones

In the previous chapter (Chap. 2) it was found that formation temperatures of G.P. zones of binary Al-Zn alloys were around  $-30 \sim -90^{\circ}\text{C}$  and that these temperatures depended on the quenching temperatures (see Fig. (2.3)). This was explained in terms of the difference of amounts of quenched-in vacancies. To determine  $T_f$ , the changes of the scattering intensity for the quenched specimens were measured at a constant angle of  $2\theta = 0.5^{\circ}$  during heating from liquid nitrogen temperature to room temperature at a constant heating rate of  $2^{\circ}\text{C}/\text{min}$ . The results of Al-12.4at.% Zn alloys with or without 0.5at.% Ag or Si which were quenched from  $450^{\circ}\text{C}$  are shown in Fig. (7.1), where above the temperature indicated by arrows the increase of intensities due to clustering of zinc atoms are observed. These temperatures are considered to be formation temperature of zones and they are listed in Table (7.2) for each alloy. From this table it is recognized that the addition of small amounts of third elements, Ag, Si or Mg, has the remarkable effects on the formation of zones: additions of both silver and silicon lower the temperature for the formation of zones, whereas the existence of magnesium raises it.

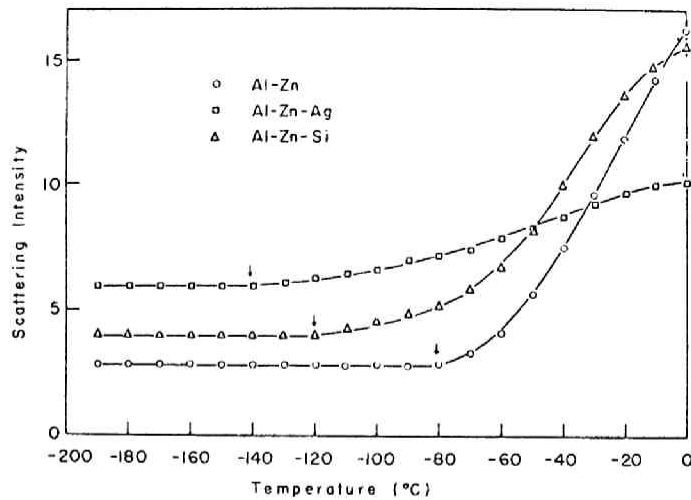


Fig.(7.1). Change of the scattering intensities measured at the fixed angle ( $2\theta = 2/3^\circ$ ) for the Al-12.4at.% Zn alloys with or without 0.5at.% Ag or Si. The specimens were quenched from  $450^\circ\text{C}$  and heated at the constant rate of  $2^\circ\text{C}/\text{min}$ . The arrows show the temperatures at which the increase of the scattering intensities is observed.

Table (7.2). Temperatures at which the increase of the scattering intensity is observed in the specimens with or without third elements quenched from  $450^\circ\text{C}$ .

| Alloy        | Temperature ( $^\circ\text{C}$ ) |
|--------------|----------------------------------|
| Al-4.4 % Zn  | - 61                             |
| -0.5 % Ag    | - 76                             |
| -0.5 % Si    | -92                              |
| Al-6.8 % Zn  | - 80                             |
| -0.5 % Ag    | - 106                            |
| - 0.5 %Si    | - 84                             |
| -0.1 % Mg    | - 58                             |
| Al-9.7 % Zn  | - 90                             |
| -0.5 % Ag    | - 120                            |
| -0.5 % Si    | - 94                             |
| Al-12.4 % Zn | - 80                             |
| -0.5 % Ag    | - 140                            |
| -0.5 % Si    | - 120                            |



(b) On the Solvus Temperature for G.P. Zones

The solvus temperature ( $T_c$ ) for G.P. zones was indicated to be determined experimentally within errors of  $\pm 5^\circ\text{C}$  by examining the integrated intensities which were calculated from the scattering intensities of the specimens reverted at each temperature. In a binary Al-6.8at.% Zn alloy  $T_c$  was determined to be  $155^\circ\text{C}$ . This temperature was also shown to coincide with the results of electrical resistivity measurements and transmission electron microscopy. Then, it is concluded that the measurements of X-ray scattering are sufficient to determine the solvus temperature.

In this section by utilizing the reversion experiment, the solvus temperatures for Al-6.8at.% Zn alloys containing 0.1at.% Ag, 0.1at.% Si or 0.15at.% Mg are determined. All specimens were quenched from  $300^\circ\text{C}$  and pre-aged at room temperature for 100 min and then reverted at each high temperature for 100 min. The scattering curves for various alloys reverted at each temperature are shown in Fig. (7.2a - c). In each figure it is found that the intensities decrease monotonously with increasing reversion temperatures. The integrated intensities for each alloy reverted at each temperature are shown in Fig. (7.3). As stated before, the solute concentration of the matrix increases with increasing temperature and

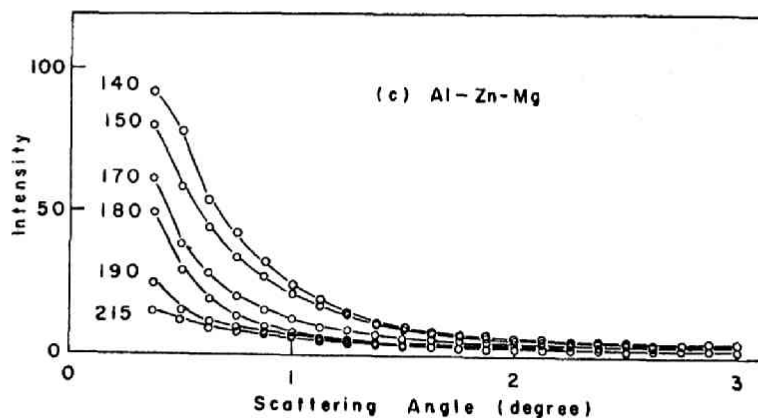
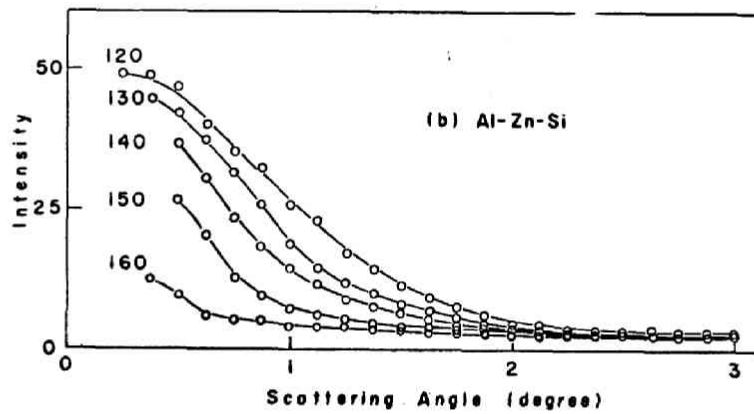
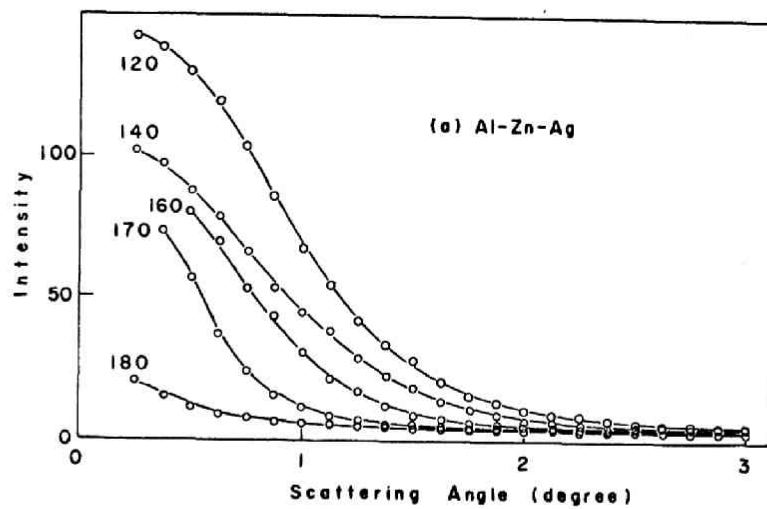


Fig.(7.2). Scattering intensities for the Al-6.8at.% Zn alloys containing 0.1at.% Ag, Si or Mg respectively. Each specimen was quenched from 300°C, pre-aged at room temperature for 100 min and then reverted at each temperature indicated in figures for 100 min.

in the vicinity of the solvus temperature it approaches to the average solute concentration of the alloy. From Eq. (1.20) it is expected that the integrated intensity is nearly zero above the solvus temperature, but in reality  $Q_0$  does not equal zero due to the other scatterings. Then, the temperatures shown by arrows are considered to be the solvus temperature of each alloy. These temperatures are listed in Table (7.3), where it is noted that the addition of Ag or Mg raised  $T_c$ , but Si has not remarkable effect on  $T_c$  : in other words, addition of Ag or Mg stabilizes G.P. zones, but Si does not.

#### 7-3-2. Effects of Third Elements on the Formation and Growth Processes

##### (a) On the Formation and Growth Processes at $-85^{\circ}\text{C}$

The effects of the addition of small amounts of Ag, Si or Mg on the formation and growth processes of G.P. zones are examined by the isothermal experiments at  $-85^{\circ}\text{C}$ . In Fig. (7.4), the changes of scattering intensities measured at a constant angle of  $2\theta = 0.5^{\circ}$  for Al-6.8at.% Zn alloys with or without 0.5at.% Ag which are quenched from  $450^{\circ}\text{C}$  and isothermally aged at  $-85^{\circ}\text{C}$  are shown. In this figure it is remarkable that the intensities for Ag containing alloy are strong compared with a binary alloy. Considering from Eq. (1.5), this may be due to the occurrence of the decomposition during quenching. That is,

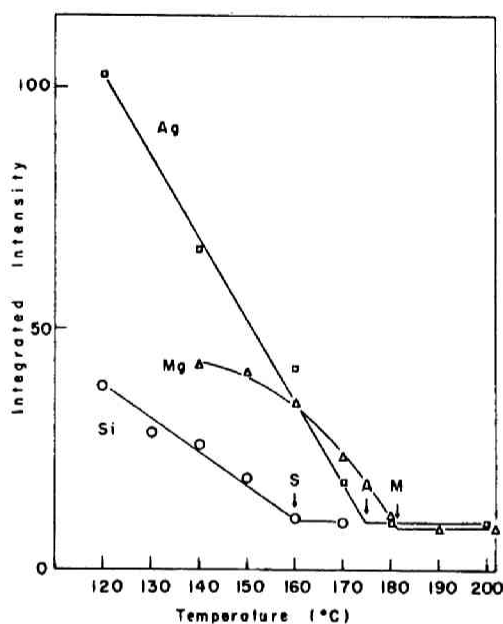


Fig.(7.3). Change of the integrated intensities for the Al-6.8at.% Zn alloys containing 0.1at.% Ag, Si or Mg respectively. Each specimen was quenched from 300°C, pre-aged at room temperature for 100 min and then reverted at each temperature for 100 min. The points A, S and M show the solvus temperatures of each alloy.

Table (7.3). The solvus temperatures for Al-6.8at.% Zn alloys with or without 0.1at.% Ag, Si or Mg respectively.

| Alloy       | Solvus Temperature |
|-------------|--------------------|
| Al-6.8 % Zn | 155°C              |
| -0.1 % Ag   | 175°C              |
| -0.1 % Si   | 160°C              |
| -0.1 % Mg   | 180°C              |

the addition of Ag atoms accelerates the decomposition during quenching. However, the rate of the increase in intensities during aging are almost the same in both two alloys, which means that Ag atoms have not remarkable effects on the growth rate of zones. It is reported<sup>(1)</sup> that the addition of small quantity of silver increase the migration energy of zinc atoms in Al-Zn alloys.

The effects of the addition of the Si atoms on the zone growth at a low temperature are investigated by the isothermal aging at  $-85^{\circ}\text{C}$  as shown in Fig. (7.5). In the binary alloys it is found that the scattering intensities in the specimens quenched from each temperature are stronger in order of the temperatures  $300^{\circ}$ ,  $500^{\circ}$  and  $450^{\circ}\text{C}$ . In contrast to the effects found in the binary alloy, in Al-Zn-Si alloys, the change of the scattering intensities is influenced neither by the quenching temperatures nor by the amounts of Si atoms. This is explained as follows : the binding energy between silicon atoms and vacancies is appreciably larger than that between zinc atoms and vacancies<sup>(16)</sup>, thus, the silicon atoms will tend to deplete the Al-Zn-Si alloys of vacancies available for growth of G.P. zones.

#### (b) Growth Process at Room Temperature

The effects of the third elements on the growth at room temperature

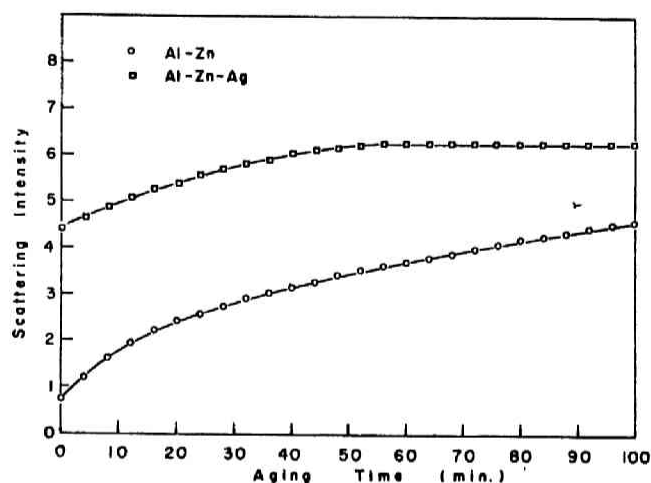


Fig.(7.4). Change of the scattering intensities measured at the fixed angle ( $2\theta = 2/3^\circ$ ) for the Al-6.8at.% Zn alloys with or without 0.5at.% Ag quenched from  $450^\circ\text{C}$  and aged isothermally at  $-85^\circ\text{C}$ .

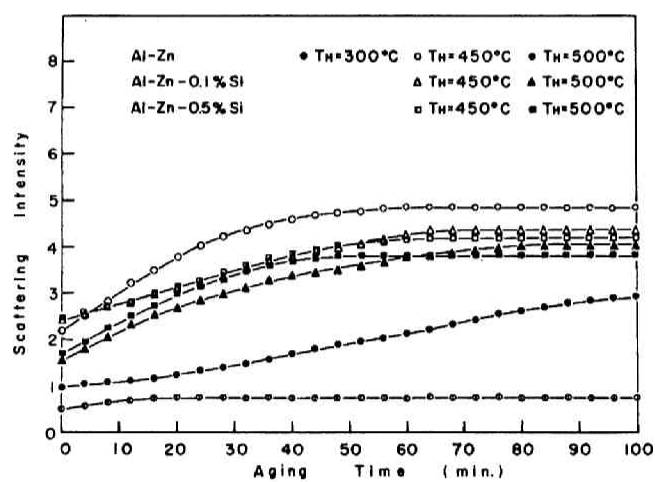


Fig.(7.5). Change of the scattering intensities measured at the fixed angle ( $2\theta = 2/3^\circ$ ) for the Al-12.4% Zn alloys with or without 0.1 or 0.5at.% Si quenched from  $300^\circ$ ,  $450^\circ$  or  $500^\circ\text{C}$  and aged isothermally at  $-85^\circ\text{C}$ .

are shown in Fig. (7.6). Although Ag and Si atoms accelerated the process at low temperatures, these atoms do not show much effect at room temperature except that Si addition gives slightly smaller zone size compared with that of the binary or Al-Zn-Ag alloys. Mg atoms retarded the process at low temperatures. This behavior is also seen at room temperature as shown by the slow change of the zone size in Fig. (7.6). Note that the Al-Zn-Mg curve does not level off at long aging times. With prolonged aging, these zones may become larger than those of the other alloys. For Al-Zn-Mg alloys Perry<sup>(5)</sup> suggested that as the quenched-in vacancies are initially trapped by the Mg atoms because of the strong binding energy between vacancies and Mg atoms, the vacancy concentration available for zinc diffusion decreases, so the formation process is at first retarded. At the later stage of aging the marked zone growth is explained by vacancy release from the trapped state.

The effect of the amount of Si atoms was determined by measuring the change of the scattering intensity of Al-12.4at.% Zn alloys with or without Si atoms, quenched from 450°C and aged at room temperature as shown in Fig. (7.7). The intensity is found to be influenced by the addition of Si atoms. The zone radius after 100 min aging is smallest in the alloy containing 0.5at.% Si. And the zone numbers were calculated

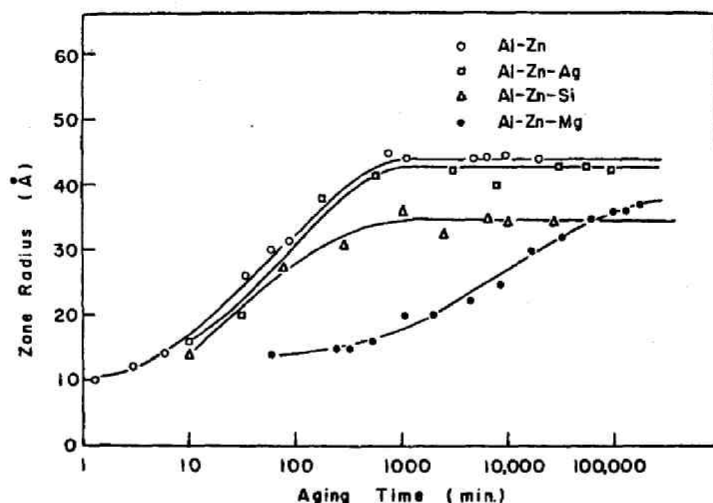


Fig.(7.6). Change of the zone radius for the Al-6.8at.% Zn alloys with or without 0.1at.% Ag, Si or Mg quenched from 300°C and aged at room temperature.

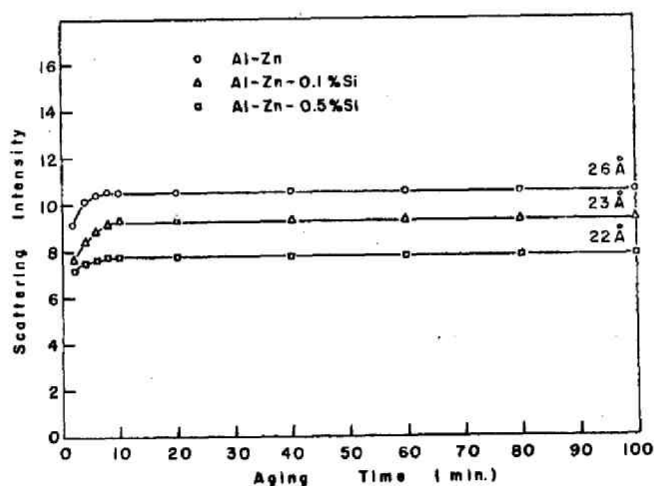


Fig.(7.7). Change of the scattering intensities measured at the fixed angle ( $2\theta = 2/3^\circ$ ) for the Al-12.4at.% Zn alloys with or without 0.1 or 0.5at.% Si quenched from 450°C and aged isothermally at room temperature. The average radii of zones after 100 min of aging are shown in Å.



to be 0.71, 0.94 and  $1.05 \times 10^{18}/\text{cm}^3$  for the binary, and the ternary alloys with 0.1at.% Si and 0.5at.% Si respectively.

Examinations of the change of the size, volume fraction and number of zones are performed. In the Al-Zn-Mg alloys the volume fractions are calculated from the integrated intensity putting the concentrations of solute atoms inside and outside G.P. zones 83at.% and 1.4at.%(7), and the results are shown in Fig. (7.8). Those for the binary and ternary alloys containing Ag or Si are given in Table (7.4). In Table (7.4) it is seen that at the early stage of aging, the zone radius increases and zone number decreases, while the total volume fraction stays approximately constant for all three alloys. This result supports the hypothesis that the larger zones grow at the expense of smaller ones. Note that the growth of larger zones and the dissolution of small ones in Al-Zn-Ag alloys, which was not observed at low temperature aging, is evident during room temperature aging.

(c) Determination of the Diffusion Coefficient and Migration Energy  
of Zinc Atoms

In chapter 5, by applying the Lifshitz-Wagner theory to the zone growth, the diffusion coefficient of zinc atoms in an Al-6.8at.% Zn alloy was graphically obtained. In that case G.P. zones were considered to be the "stable" precipitates from the fact that both the solute concentra-

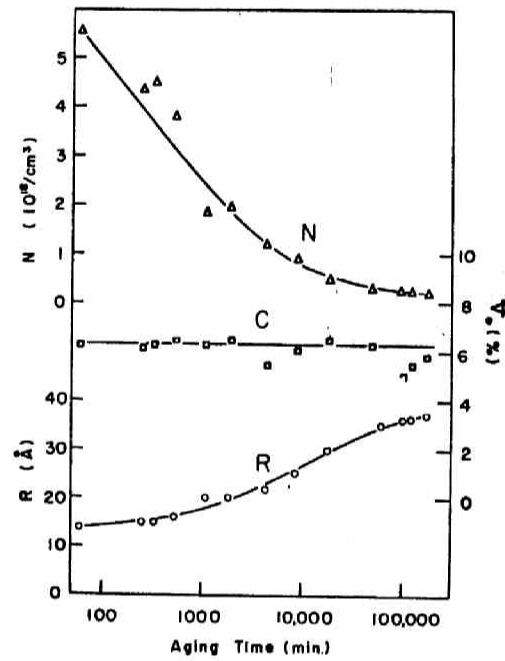


Fig.(7.8). Change of the zone radius ( $R$ ), volume fraction ( $V_o$ ) and zone number ( $N$ ) of an Al-6.8at.% Zn alloy containing 0.1at.% Mg quenched from  $300^\circ\text{C}$  and aged at room temperature.

Table (7.4). Change of zone radius (R), volume fraction ( $V_o$ ) and zone number (N) of Al-6.8at.% Zn alloys containing 0.1at.% Ag or Si quenched from 300°C and aged at room temperature.

| Al - Zn - Ag |          |              |                                | Al - Zn - Si |          |              |                                |
|--------------|----------|--------------|--------------------------------|--------------|----------|--------------|--------------------------------|
| t<br>(min)   | R<br>(Å) | $V_o$<br>(%) | N<br>( $10^{17}/\text{cm}^3$ ) | t<br>(min)   | R<br>(Å) | $V_o$<br>(%) | N<br>( $10^{17}/\text{cm}^3$ ) |
| 95           | 35       | 8.05         | 4.48                           | 300          | 30       | 7.25         | 6.41                           |
| 180          | 38       | 8.50         | 3.70                           | 1065         | 36       | 8.15         | 4.17                           |
| 550          | 42       | 8.20         | 2.64                           | 2585         | 32       | 7.60         | 5.54                           |
| 2970         | 42       | 7.65         | 2.46                           | 6775         | 35       | 7.55         | 4.20                           |
| 7320         | 40       | 7.35         | 2.74                           | 10165        | 34       | 7.72         | 4.69                           |
| 16420        | 42       | 7.55         | 2.43                           | 28405        | 34       | 8.05         | 4.89                           |

tions inside and outside zones did not change during aging. Also from the temperature dependence of diffusion coefficients, the migration energy of zinc atoms was graphically calculated according to Eq. (5.7).

In this section the diffusion coefficients and migration energies for Al-6.8at.% Zn alloys containing 0.1at.% Ag, 0.1at.% Si or 0.15at.% Mg will be obtained by the same method utilized in chapter 5. All specimens are quenched from 300°C and isothermally aged at temperature of -17, 0, 17 or 40°C. The measurements of scattering intensities for each alloy are carried out at liquid nitrogen temperature and the changes of intensities for alloys aged at each temperature are shown in Fig.(7.9a-c). From these figures the average zone radii ( $R$ ) are obtained and the plots of  $R^3$  vs.  $t$  for each specimen are shown in Fig. (7.10a~c). In this figure it is seen that the plots show an excellent linearity in the each alloy. According to Eq. (5.1), the diffusion coefficients can be calculated from the slopes of the each line. However, the value of the surface energy of the ternary alloy can not be calculated exactly, because there are no available thermodynamic data for these ternary alloys. Then, the value of the surface energy of a binary alloy calculated before is utilized. It is estimated that the order of the value of the surface energy of ternary alloys will be same with the

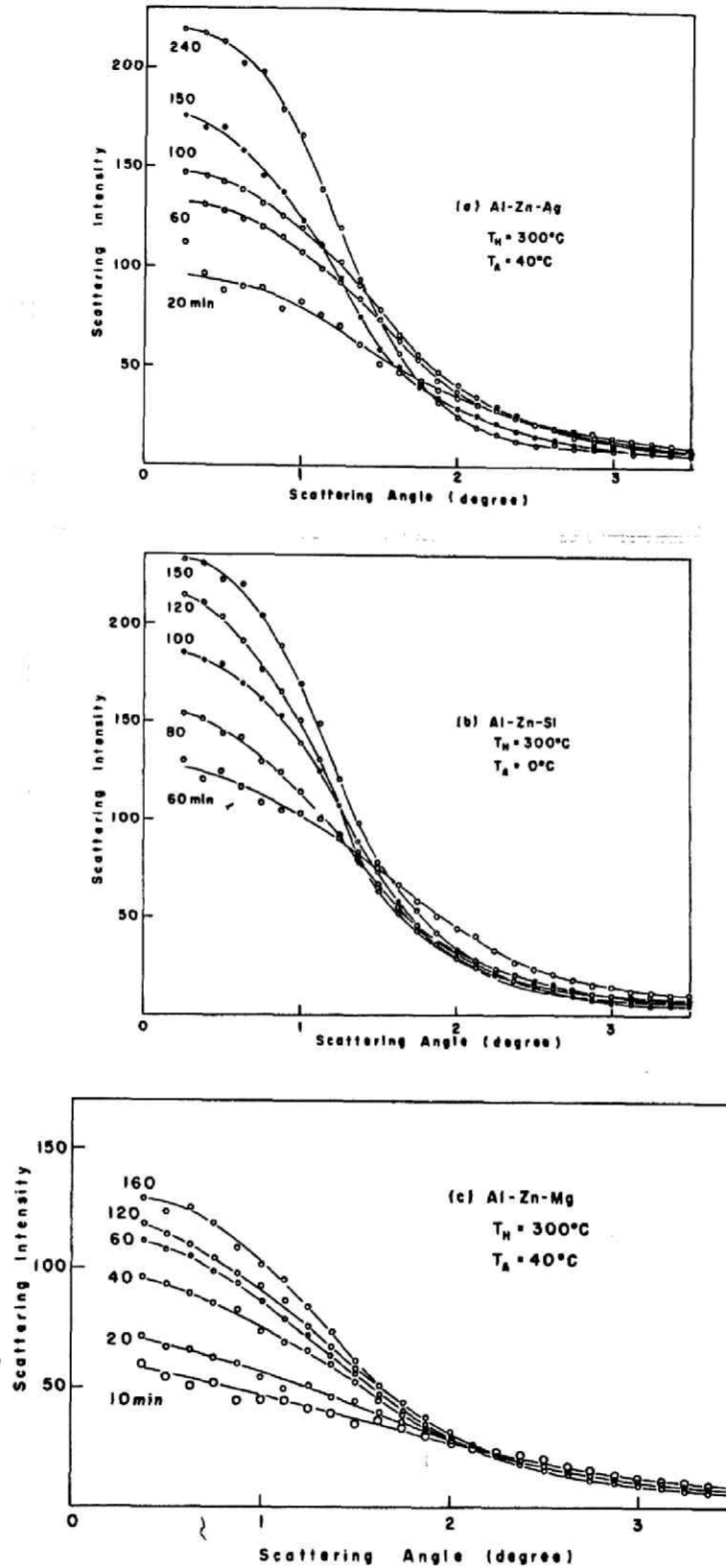


Fig.(7.9). Change of the scattering intensities of Al-6.8at.% Zn alloys containing 0.1at.% Ag, Si or Mg quenched from  $300^\circ\text{C}$  and isothermally aged at each temperature.

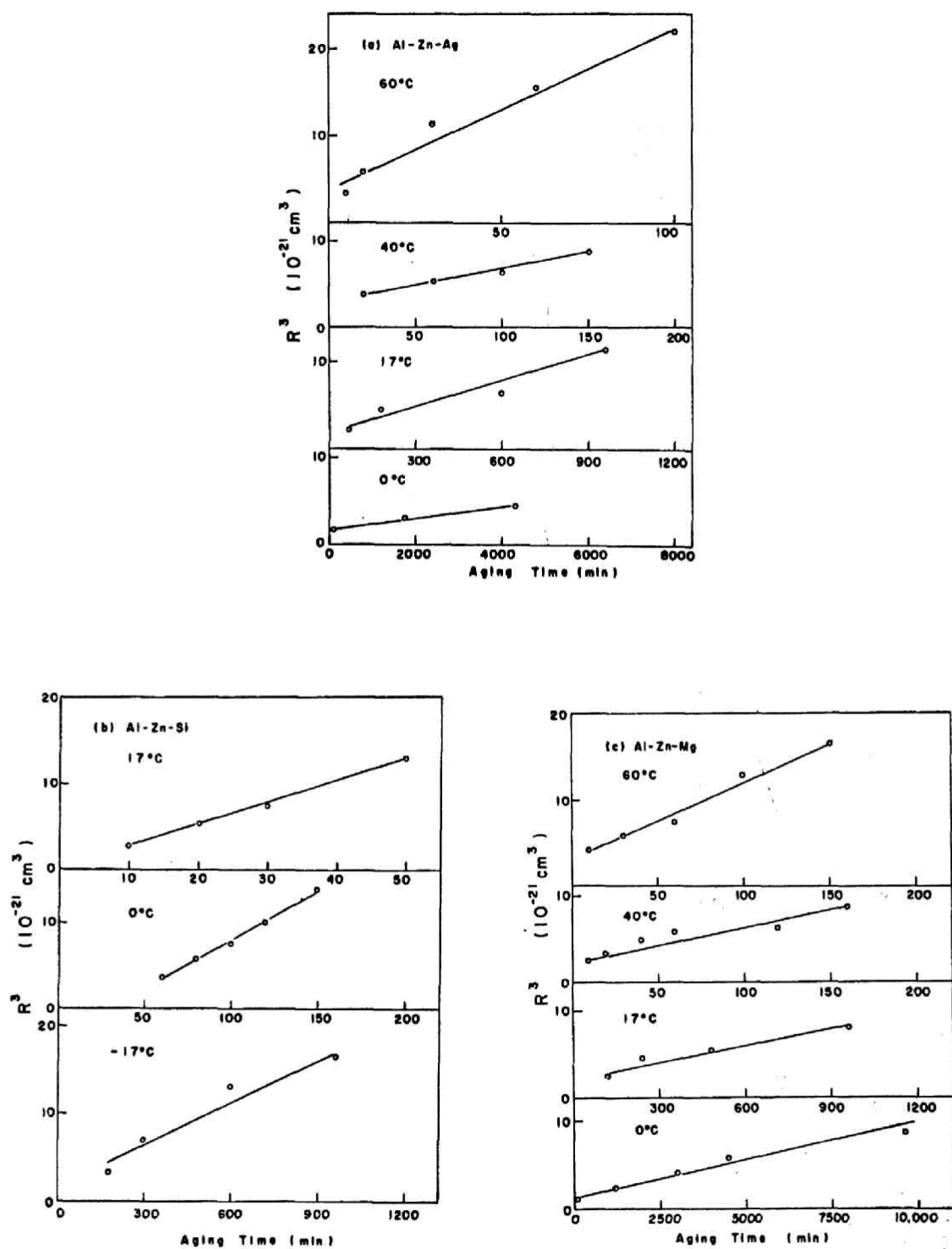


Fig.(7.10). Plots of  $R^3$  vs.  $t$  for Al-6.8at.% Zn alloys containing 0.1at.% Ag, Si or Mg quenched from  $300^\circ\text{C}$  and aged at each temperature shown in the figure.

one of a binary alloy, judging from the change of the solvus temperature by the addition of the small quantity of these third elements as shown in Fig. (7.3). Thus, there are not remarkable errors in calculation of  $D$ , if we use the value of  $\sigma$  in a binary alloy.

The plots of  $\ln D$  vs.  $1/T$  are given in Fig. (7.11) and from this curve the migration energies of ternary alloys are obtained graphically using Eq. (5.7). They are listed in Table (5.5).

### 7-3-3. Two Kinds of G.P. Zones for Ag Containing Al-Zn Alloys

Through the reversion experiment for ternary Ag containing Al-Zn alloys, the results which suggest that there exist two kinds of zones, the one is ternary zones based on Ag atoms and the other is those composed of Al and Zn atoms, are obtained. The results of a ternary Al-6.8at.% Zn - 0.1at.% Ag alloy and Al-12.4at.% Zn - 0.5at.% Ag alloy will be given below.

#### (a) Al-6.8at.% Zn - 0.1at.% Ag alloy

In Fig. (7.12) the changes of the electrical resistivity during reversion at  $175^{\circ}\text{C}$  are shown for an Al-6.8at.% Zn - 0.1at.% Ag alloy and also for binary Al-6.8at.% Zn and Al-0.1at.% Ag alloy for comparison.

The first figure shows a binary Al-Zn alloy quenched from  $450^{\circ}\text{C}$  and aged at room temperature for 1000 min, where only one resistance maxi-

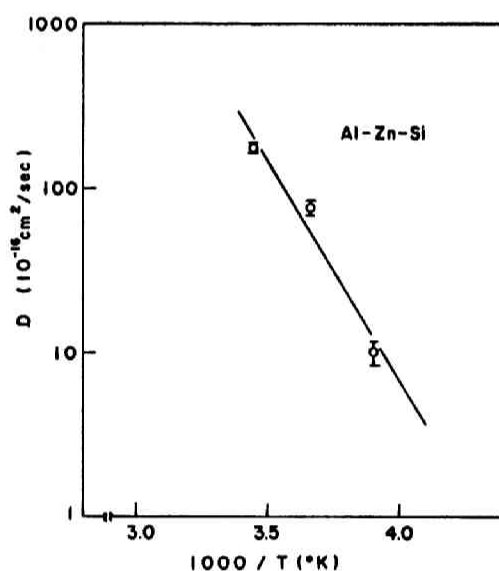
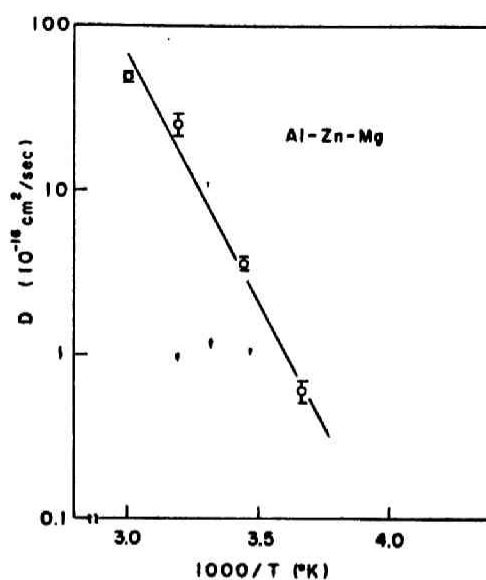
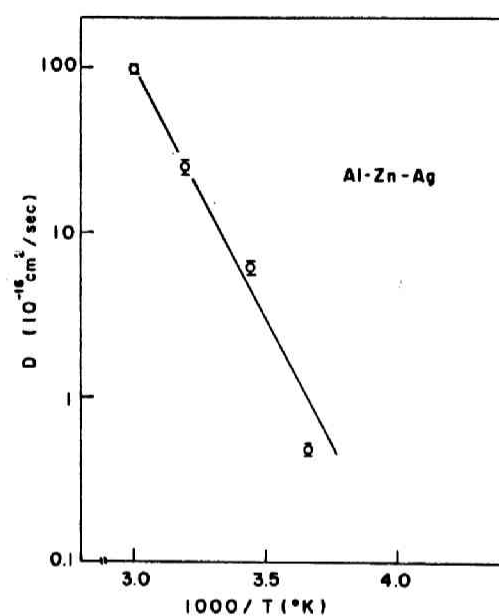


Fig.(7.11). Plots of  $\log D$  vs.  $1/T$  for Al-6.8at.% Zn alloys containing 0.1at.% Ag, Si or Mg quenched from 300°C and aged at each temperature.

Table (7.5). Migration energies of Al-6.8at.% Zn alloys containing 0.1at.% Ag, Si or Mg quenched from 300°C.

| Alloy    | Migration Energy (eV) |
|----------|-----------------------|
| Al-Zn-Ag | $0.62 \pm 0.04$       |
| Al-Zn-Si | $0.56 \pm 0.08$       |
| Al-Zn-Mg | $0.62 \pm 0.07$       |



mun is observed. However, in a ternary alloy two maxima, indicated by arrows are observed as shown in the second figure. These two maxima were always observed in Ag containing specimens, which were pre-aged for various times at room temperature. Considering the fact that the time, at which the first maximum is observed, coincides with that of the binary Al-Zn alloy, the first maximum may be due to the critical size of the dissolving zones composed of only Zn and Al atoms; the second maximum may appear, when either new zones based on Ag atoms are originated during reversion, or when zones including Ag atoms, which are then considered more stable than those in the binary alloy, dissolve to the critical size. The reason, why the second maximum is not due to zones composed of only Ag atoms, is that at the time of the appearance of the second maximum, no maximum is observed in a binary Al-0.1at.% Ag alloy as illustrated in the third figure.

Moreover, in the profiles of scattering intensities, the abnormality is observed. In Fig. (7.13) the profiles for a ternary alloy reverted at 175°C for each time are shown. For the specimen reverted for 7 min the intensities decrease monotonously with scattering angles, but after 10 min the abnormality of the profiles which may be due to newly originated zones based on Ag atoms (shown by arrows) is observed.

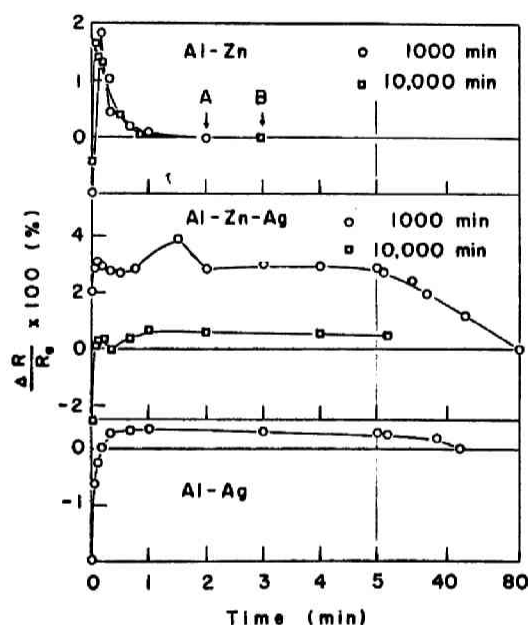


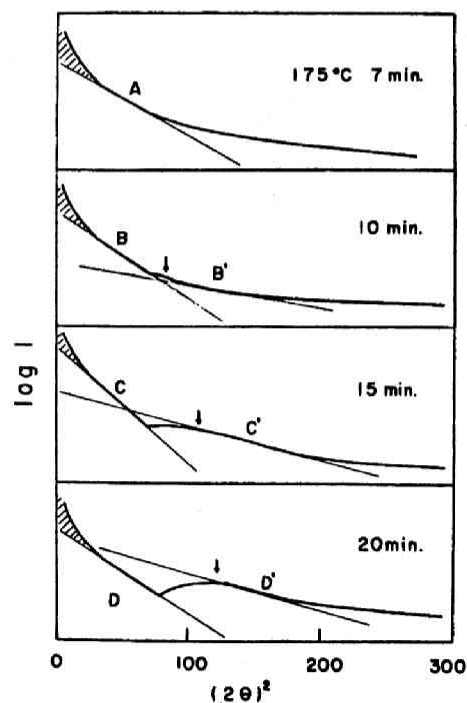
Fig.(7.12). Change of electrical resistance during reversion at 175°C .

Al-6.8at.% Zn : Quenched from 450°C and pre-aged for 1000 or 10,000 min at room temperature.

Al-6.8at.% Zn-0.1at.% Ag : Quenched from 450°C and pre-aged for 1000 min or 10,000 min at room temperature.

Al-0.40wt.% Ag : Quenched from 450°C and pre-aged for 1000 min at room temperature.

Fig.(7.13). Change of profiles of the X-ray small angle scattering in an Al-6.8at.% Zn-0.1at.% Ag alloy during reversion at 175°C. The arrows show the appearance of the newly originated zones based on Ag atoms.



That the intensity of this portion increases with reversion time suggests the growth of zones based on Ag atoms. This is also observed by the electron microscopy. The photographs of both the binary and ternary alloys which are reverted at  $175^{\circ}\text{C}$  for 100 min are shown in Fig. (7.14a, b) respectively. Though in a micrograph of a binary alloy no precipitates are observed, in a ternary alloy zones of  $150 \sim 200\text{\AA}$  in diameter can be seen. As the shape of these zones is spherical, they may be the ternary zones based on Ag atoms which are formed at  $175^{\circ}\text{C}$  by absorption of Zn atoms which are emitted from the dissolving zones composed of Al and Zn atoms.

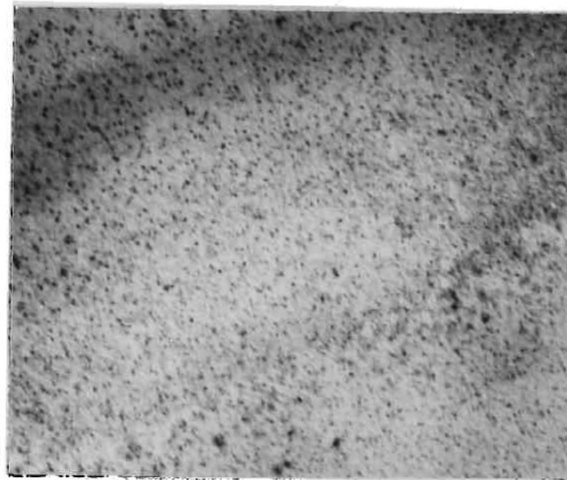
(b) Al-12.4at.% Zn-0.5at.% Ag alloy

Even in the change of the scattering intensity measured at a constant angle the abnormality is recognized in Ag containing Al-Zn alloy. This is also interpreted to be due to the existence of two kinds of G.P. zones by comparing with previous results.

In Fig. (7.15) the change of scattering intensity during reversion at  $206^{\circ}\text{C}$  is shown for an Al-12.4at.% Zn-0.5at.% Ag alloy which is quenched from  $450^{\circ}\text{C}$  and pre-aged at room temperature for 5 min prior to reversion. The measurement is carried out at a constant angle of  $2\theta = 0.5^{\circ}$  for the specimen placed in an air furnace kept at the desired temperature within  $\pm 1^{\circ}\text{C}$ . Though the increase of intensity within 2 min is



(a) Al-6.8at.% Zn



(b) Al-6.8at.% Zn-0.1at.% Ag

x 30,000

Fig.(7.14). Transmission electron micrographs of Al-6.8at.% Zn alloys with or without 0.1at.% Ag quenched from 300°C, pre-aged for 5400 min at room temperature and then reverted for 100 min at 175°C.

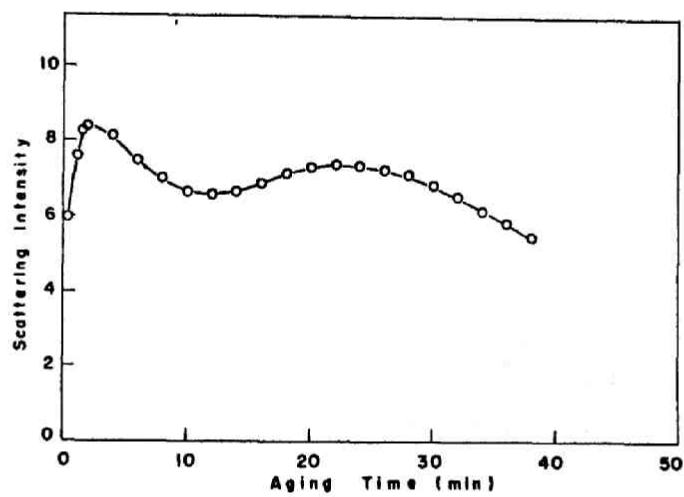


Fig.(7.15). Change of the scattering intensities measured at a constant angle of  $2\theta = 0.5^\circ$  for an Al-12.4at.%<sup>Zn</sup>-0.5 at.% Ag alloy quenched from  $450^\circ\text{C}$ , pre-aged at room temperature for 5 min and then reverted at  $206^\circ\text{C}$ .

observed, the experimental accuracy is poor, because these intensities are read from the chart. Thus, the interpretation on this increase is not given here. On subsequent reversion process the decrease of intensities is obvious until 12 min. Judging from the solvus curve for G.P. zones in Al-Zn alloys (Fig. (2.10)), the temperature of 206°C is above the solvus for a binary Al-12.4at.% Zn alloy. So, zones which are composed of the Zn and Al atoms, formed at room temperature, are dissolved at this high temperature. Therefore, this decrease of intensity until 12 min is attributable to the dissolution of zones composed of only Al and Zn atoms. After 12 min the increase is observed, which have never been observed in a binary alloy or other alloy systems. Combining with the previous results, this increase may be due to the formation of ternary zones based on Ag atoms. However, as the experimental results to confirm the formation of ternary zones are very few, another interpretations are also possible on this figure.

#### 7-4. Summary

The effects of the addition of the third elements, silver, silicon and magnesium, on G.P. zones of binary aluminum-zinc alloys were studied by means of X-ray small angle scattering, electrical resistivity

measurements and transmission electron microscopy.

It was found that the addition of the each element had the remarkable influences on the temperature range of the existence of G.P. zones in the binary Al-Zn alloys. The formation temperature for G.P. zones was lowered by the existence of silver or silicon atoms, and was raised by magnesium atoms. On the other hand, the solvus temperature for G.P. zones was raised by the existence of silver or magnesium atoms, but the existence of silicon atoms had not a remarkable influence on this temperature.

Furthermore, the growth process of G.P. zones was recognized to be remarkably influenced : it was accelerated by the addition of silver or silicon atoms and was suppressed by the addition of magnesium atoms, specially at the early stages of zone growth.

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## CHAPTER 8

### EFFECTS OF THE PLASTIC DEFORMATION ON G.P. ZONES

#### 8-1. Introduction

Turnbull, Rosenbaum and Treafis<sup>(1)</sup> have found that the formation and growth processes of G.P. zones in aluminum-zinc alloys are influenced by the quenching temperatures by means of the electrical resistivity measurements and from this experimental result it was indicated that the point defects of the vacancy type play an important role in the formation process. The facts that the formation and growth processes are influenced by the quenching temperatures (Chap. 5) and by the addition of the third elements (Chap. 7) support the above indication.

Recently the effect of plastic deformation on the growth process has received much attention and a number of studies of these effects have been reported. Ceresara and Federighi<sup>(2)</sup> also concluded that the rate of the growth process of the G.P. zones was controlled by point defects of the vacancy type at low temperature aging and found that this process was enhanced by deformation due to an increase in the number of vacancies. In addition, experiments in which the quench temperature is varied<sup>(3,4)</sup> and neutron irradiation experiments<sup>(5)</sup> produced further evidence of this

role of vacancies.

The present paper reports an investigation of the effect of plastic deformation at  $-196^{\circ}\text{C}$  on the aging process in an Al-6.8at.% Zn alloy.

The growth process of zones was followed by measuring changes in electrical resistivity and X-ray small angle scattering.

## 8-2. Experimental Procedures

Experiments were carried out with an aluminum-zinc alloy containing 6.8at.% Zn in the form of foils of 0.2 mm thick. The specimens were homogenized at  $300^{\circ}\text{C}$  for one hour, then dropped rapidly into a water bath of  $0^{\circ}\text{C}$  beneath the furnace, held at this temperature for 15 sec and cooled further to liquid nitrogen temperature. For the study of the effects of plastic deformation the specimens were strained each percentage by a tensile tester in a liquid nitrogen bath prior to aging. The shape of the specimens and the tensile tester are illustrated in Fig. (8.1). This strain produces negligible change in thickness.

## 8-3. Experimental Results and Discussions

### 8-3-1. Effects of the Plastic Deformation on the Temperature Range of the Existence of G.P. Zones

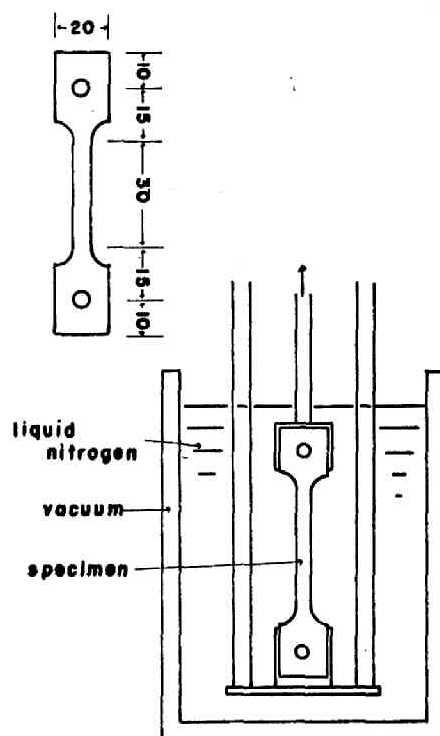


Fig.(8.1). Shape of the specimen and the instron apparatus.

(a) On the Formation Temperature for G.P. Zones

In the previous chapters the formation temperature was found to be influenced by the quenching temperatures or the addition of the small quantity of the third elements. They were explained in terms of the amounts of the vacancies available for diffusion of zinc atoms. As confirmed by several authors<sup>(2,5)</sup>, these vacancies are increased by the deformation and the formation temperature is expected to be influenced by the deformation

To determine this temperature, the change of scattering intensities of the deformed specimen is measured at a constant angle ( $2\theta = 0.25^\circ$ ) during heating at the rate of  $2^\circ\text{C}/\text{min}$ . The results are shown in Fig. (8.2) for the specimens quenched from  $300^\circ\text{C}$  and undeformed or strained 10% at liquid nitrogen temperature. It is noted that the intensity of the deformed specimen begins to increase at  $-140^\circ\text{C}$ , which is much lower than the one of the undeformed specimen. Thus, the formation temperature is shown to be lowered by the deformation. This may be due to the increase of the amounts of the available vacancies.

(b) On the Solvus Temperature for G.P. zones

The solvus temperature for G.P. zones was indicated to be influenced remarkably by the addition of the third elements, which was, as a matter

of course, attributable to the change of the free energy of a binary system by the addition of the third elements. In this section the effect of the plastic deformation on the solvus temperature for G.P. zones is investigated. For the determination of the solvus temperature ( $T_c$ ) of G.P. zones, the reversion experiment was indicated to be useful and in the previous chapters  $T_c$  for the binary and ternary alloys were determined from the change of the integrated intensities during reversion. Also, at present this method is utilized.

In Fig. (8.3) the scattering intensities for the alloys, quenched from 300°C, strained 2% at liquid nitrogen temperature, pre-aged at room temperature for 100 min and then reverted at each high temperature for 100 min, are shown. The intensities decrease monotonously with increasing the reversion temperatures and those of the specimens reverted at the temperatures above 150°C are the same with the one at 150°C. From this figure, the values of the integrated intensities are calculated and the results are shown in Fig. (8.4). At the temperatures above the solvus, the solute concentration of the matrix equals to the concentration of the alloy, thus the integrated intensity is nearly zero. Then, the temperature shown by an arrow is considered to be the solvus temperature for G.P. zones of the deformed specimen. This temperature is about 10°C

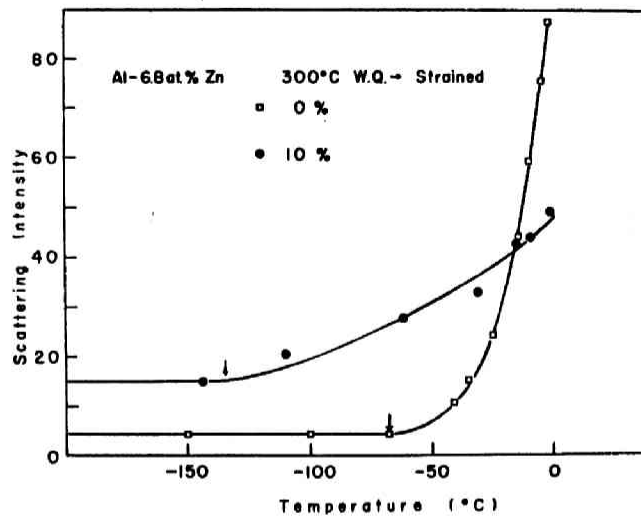


Fig.(8.2). Change of the scattering intensities measured at the fixed angle ( $2\theta = 0.25^\circ$ ) for Al-6.8at.% Zn alloys quenched from 300°C, strained 0 and 10% respectively at liquid nitrogen temperature and heated at the constant rate of 2°C/min. The arrows show the temperatures at which the increase of the scattering intensities are observed.

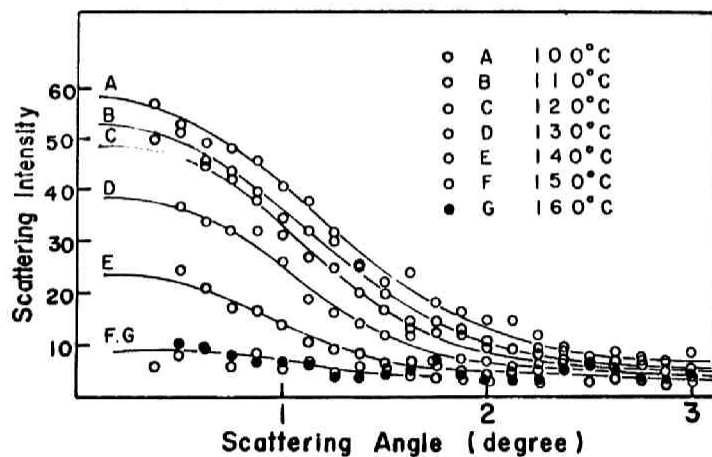


Fig.(8.3). Scattering intensities for Al-6.8at.% Zn alloys quenched from 300°C, strained 2%, pre-aged at room temperature for 100 min and then reverted at each temperature for 100 min.

lower than the one of the undeformed alloy ( $T_0 = 155^\circ\text{C}$ ).

As given in Eq. (4.11), Cahn<sup>(6)</sup> pointed out that the coherency strain energy should be taken into the consideration for the system containing coherent precipitates with the matrix. This was verified by the fact that the experimentally obtained solvus temperature for G.P. zones coincides with the result of the calculation which include the term of the elastic strain energy<sup>(7)</sup> (Fig. (2.10)). Then, the present result that the solvus temperature is influenced by the plastic deformation may be due to the addition of the extra strain energy to the free energy of the inhomogeneous system. The change of the solvus curve by the deformation will be also shown by the isothermal experiment at low temperature in the later section.

### 8-3-2. Effects of the Plastic Deformation on the Formation and

#### Growth Processes

To see the influence of the plastic deformation on the formation and growth processes of zones at the initial stage of aging, the measurements of the electrical resistivity were carried out. The fractional changes of the electrical resistance during the isothermal aging at  $-85^\circ\text{C}$  for the specimens, quenched from  $300^\circ\text{C}$  and strained 0, 1, 5 and 10% respectively at liquid nitrogen temperature, are shown in Fig. (8.5).



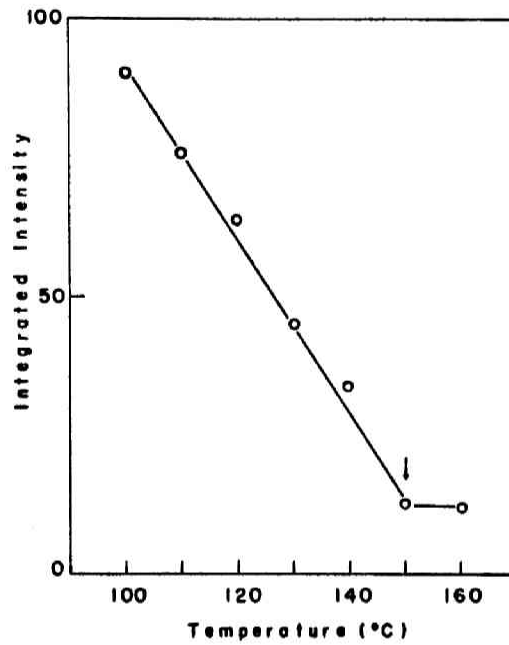


Fig.(8.4). Change of the integrated intensities for Al-6.8at.% Zn alloys quenched from 300°C, strained 2%, pre-aged at room temperature for 100 min and then reverted at each temperature for 100 min.

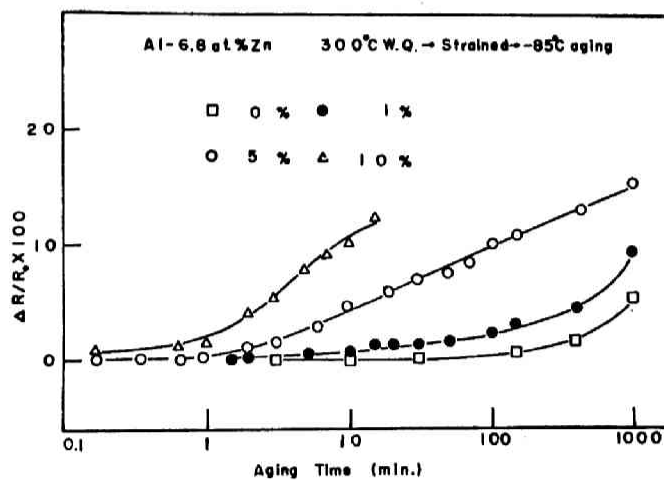


Fig.(8.5). Fractional change of the electrical resistance for Al-6.8at.% Zn alloys quenched from 300°C, strained 0, 1, 5, and 10% respectively and aged isothermally at -85°C.

It is obvious that the formation process is enhanced by the deformation as the degree of the deformation is increased. This result is also confirmed by the isothermal experiment at  $0^{\circ}\text{C}$  as shown in Fig. (8.6). The resistivity maximum is observed for each specimen and the critical time to reach the maximum is shorter with increasing the degree of the deformation. Also, the critical times for the specimens, undeformed or strained 10% immediately after quenching and aged at each temperature between  $-40$  and  $60^{\circ}\text{C}$ , are given in Table (8.1). In each specimen it is recognized that these critical times are shorter for the deformed specimen compared with the undeformed one.

Mott<sup>(8)</sup> suggested that the resistivity maximum is due to scattering of conduction electron by G.P. zones of critical dimensions and it has been shown that this critical dimension should be of the order of  $9\text{\AA}$  in radius<sup>(4)</sup>. Comparing the times required to reach the maximum values, it appears that the growth process is enhanced by the deformation of a quenched specimen prior to aging. As the growth process is controlled by the point defects of the vacancy type, this enhancement of zone growth suggests the presence of a large number of point defects.

However, at the later stage of aging it is found that the zone growth is retarded by the deformation, which is observed by the measure-

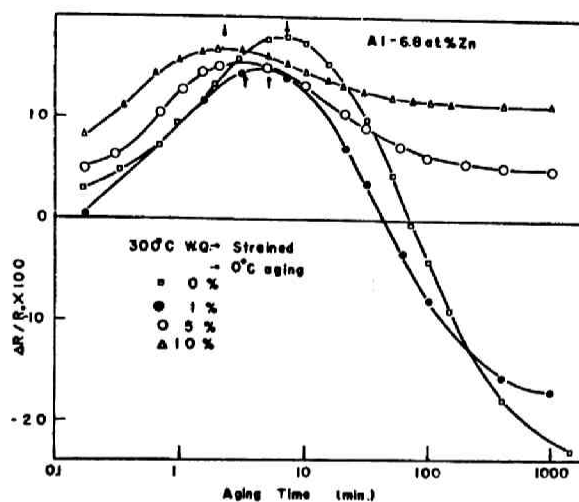


Fig.(8.6). Fractional change of the electrical resistance for Al-6.8at.% Zn alloys quenched from 300°C, strained 0, 1, 5 and 10% respectively and aged isothermally at 0°C. The arrows show the times to reach the electrical resistance maxima.

Table (8.1). Times to reach the electrical resistance maxima for Al-6.8at.% Zn alloys quenched from 300°C, strained 0 and 10% respectively and aged at each temperature.

| Temperature<br>(°C) | - 40 | - 20 | 0 | 20   | 40   | 60   |
|---------------------|------|------|---|------|------|------|
| undeformed          | 130  | 25   | 7 | 1.80 | 0.60 | 0.24 |
| 10% strained        | 30   | 7    | 2 | 0.46 | 0.17 | 0.17 |

ment of the X-ray small angle scattering. In Fig. (8.7) the change of scattering intensities during isothermal aging at room temperature for the specimens, quenched from 300°C and strained 0, 3, 5, 10 and 25% respectively, are shown. In this figure it is seen that the deformed specimens stay respective constant values earlier compared with the undeformed specimen. This is interpreted as follows. Though a number of point defects increases by the deformation, as aging proceeds, these vacancies will be annihilated at dislocations. Therefore, in the deformed specimen, at the later stage of aging, the zone growth is retarded by a reduction in the number of vacancies for diffusion because of the increased dislocation density. The dislocation density in the 2% deformed aluminum is about ten times higher than that in the undeformed specimen<sup>(9)</sup>. Therefore, the zone growth process is retarded by the rapid elimination of vacancies at dislocations

### 8-3-3. Effects of the Plastic Deformation on Zone Radius, Solute Concentrations in G.P. zones and in the Matrix and Zone Density

In this section the influences of the plastic deformation on zone radius, solute concentrations and zone density are examined by the X-ray small angle scattering method.

#### (a) Zone Radius

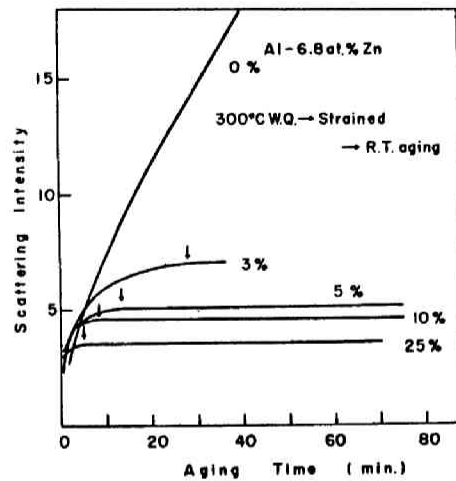


Fig.(8.7). Change of the scattering intensities measured at the fixed angle ( $2\theta = 0.25^\circ$ ) for Al-6.8at.% Zn alloys quenched from  $300^\circ\text{C}$ , strained 0, 3, 5, 10 and 25% respectively and aged isothermally at room temperature. The arrows show the transition times from fast to slow reaction.

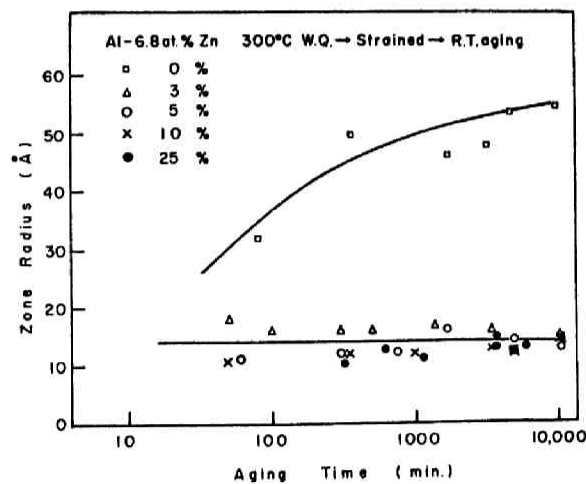


Fig.(8.8). Change of the zone radius for Al-6.8at.% Zn alloys quenched from  $300^\circ\text{C}$ , strained 0, 3, 5, 10 and 25% respectively and aged isothermally at room temperature.

In Figs.(8.8) and (8.9), the changes of the zone radii during the isothermal agings at room temperature or at 80°C for the specimens, underformed or deformed prior to aging, are shown. Though in the early stage of the formation process the process was found to be enhanced by the deformation, the deformed specimens show smaller zone radii and the zones of the deformed specimens grow very slowly during aging. It is noted that the dependence of zone radius on the degree of the deformation is not obvious.

The observation by means of the transmission electron microscopy also shows the small zone radius of the deformed specimen. The micrographs of the undeformed or deformed specimens aged at 80°C for 46,000 min are shown in Fig. (8.10). In the undeformed specimen the zones are distributed homogeneously in the matrix, but in the deformed specimen smaller zones in the matrix and also large precipitates on the dislocations which are induced by the deformation are observed. Considering from the dimension of the size these large precipitates are no more G.P. zones, but they are the partially coherent precipitates  $\alpha'_R$  or the incoherent precipitates  $\beta$ .

(b) Solute Concentrations in the G.P. zones and in the Matrix

Detailed investigation by means of the X-ray small angle scattering

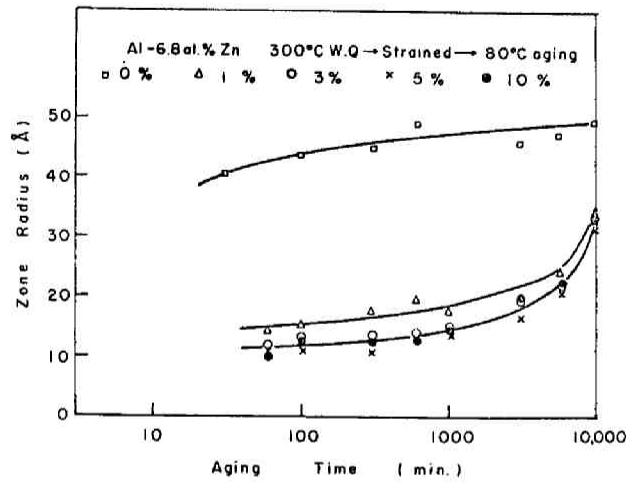
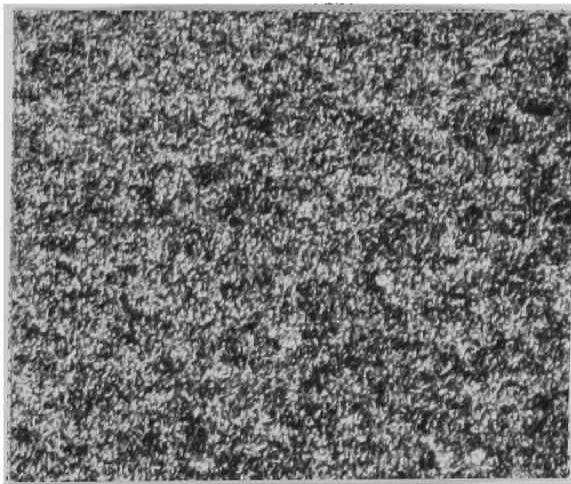
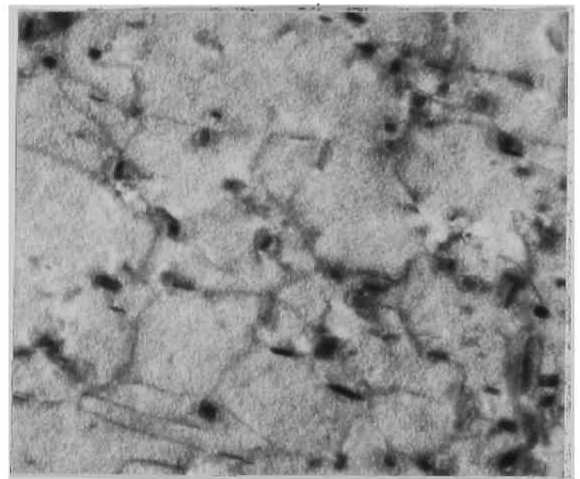


Fig.(8.9). Change of the zone radius for Al-6.8at.% Zn alloys quenched from 300°C, strained 0, 1, 3, 5 and 10% respectively and aged isothermally at 80°C.



(a) undeformed



(b) deformed

Fig.(8.10). Transmission electron micrographs of Al-6.8 at.% Zn alloys quenched from 300°C, strained 0 and 5% respectively and aged at 80°C for 46,000 min.

method gives further information on solute concentrations of G.P. zones and zone density. The X-ray intensities are counted at  $1/8^\circ$  intervals in scattering angle at liquid nitrogen temperature. The profiles of X-ray intensities versus scattering angle for the undeformed or deformed specimens are illustrated in Fig. (8.11). The difference between the two profiles is marked. At small scattering angles, the scattering intensity for the deformed specimen is much smaller than that of the undeformed specimen.

The average zone radius ( $\bar{r}$ ) and integrated intensity (arbitrary unit) of each specimen aged for various times are illustrated in Fig. (8.12). These average zone radii were obtained by using Guinier's approximation. The calculation of the integrated intensities was carried out by the method developed by Gerold. As shown in Fig. (8.12), the zone radii of both specimens increase with aging time and the deformed specimen shows smaller radius compared with the undeformed specimen. After 60 min aging, the integrated intensities are constant within experimental accuracy : however, the intensities of the deformed specimens are lower.

Note in this figure that the values of the integrated intensities of the deformed specimens are significantly smaller than those of the undeformed specimens. The average values are calculated to be 480 and



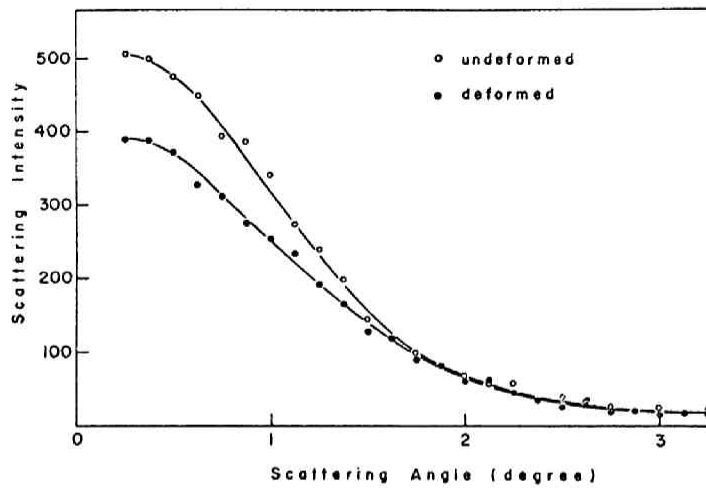


Fig.(8.11). Profiles of X-ray small angle scattering curves of Al-6.8at.% Zn alloys quenched from 300°C, undeformed or strained 2% prior to aging and aged for 160 min at 0°C.

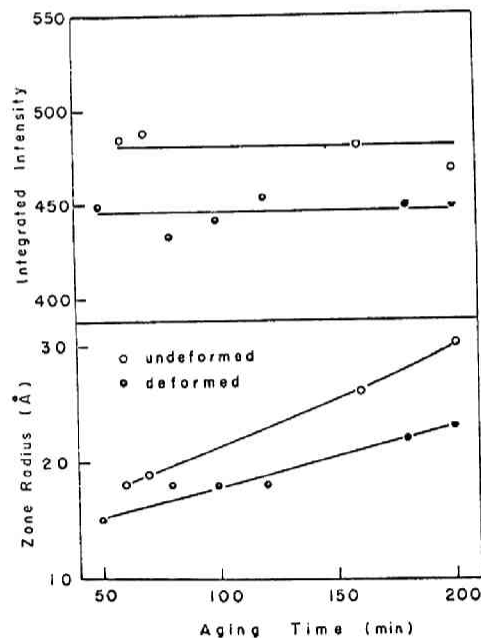


Fig.(8.12). Change of average zone radii and integrated intensities during aging at 0°C in Al-6.8at.% Zn alloys quenched from 300°C, undeformed or strained 2% prior to aging.

446 for the undeformed and deformed specimens respectively. Thus, the fraction of the decrease in the average integrated intensity of the undeformed specimen is about 0.07. By means of an analysis of these integrated intensities, the effect of the deformation on solute concentrations inside and outside G.P. zones will be discussed in this section, and the deformation effect on the zone density in the following section.

Theoretically, the scattered X-ray intensities are influenced by the shape of the particles<sup>(10)</sup>; however, since in the present experiments, the maximum average zone radius is only  $30\text{\AA}$ , the shape of zones may be considered to be spherical<sup>(11)</sup> and thus the influence of the shape of G.P. zones on values of  $Q_0$  may be neglected. The factors, therefore, which affect values of  $Q_0$  are  $p$ ,  $C_1$  and  $C_2$ .

In this analysis it is assumed that  $p$  is equal to unity for both specimens, i.e., the precipitate-free region produced by deformation are neglected. The justification of this assumption is given in the appendix. Therefore, the variable factors are  $C_1$  and  $C_2$ . During deformation the strain energy will change the solute concentrations  $C_1$  and  $C_2$  to  $C_1'$  and  $C_2'$  ( $C_1 > C_1'$ ,  $C_2 < C_2'$ ). The values of  $C_1'$  and  $C_2'$  are estimated by putting  $C_1 = 71.9 \text{ at.}\%$ ,  $C_2 = 1.7 \text{ at.}\%$ <sup>(12)</sup>,  $C_0 = 6.8 \text{ at.}\%$  and  $\Delta Q_0 = 0.07$  into Eq. (1.20). In this estimation it is assumed that

$C_1 - C'_1 \sim C'_2 - C_2 (= \Delta C)$ , and thus  $\Delta C$  is calculated to be 0.3 at. %.

Then the solute concentrations inside ( $C'_1$ ) and outside ( $C'_2$ ) G.P. zones of the 2% deformed specimen are estimated to be 71.6 at. % and 2.0 at. % respectively. (In the present experiment the extra intensity which is introduced by deformation (i.e., effect of the double Bragg scattering) is not corrected for. Thus, the estimated  $C'_1$  and  $C'_2$  are not exact values.

### (c) Zone Density

The possibility of changing the zone density in the specimen by deformation will be discussed from the following viewpoints : (i) Integrated intensity in Fig. (8.12) and (ii) electrical resistivity maxima.

#### (i) Integrated intensity in Fig. (8.12)

As given in chapter 1, the zone density  $N$  per unit volume is,

$$\frac{4}{3} \pi R^3 N = V_0 \quad (1.23)$$

where  $R$  is zone radius and  $V_0$  is volume fraction of zones and  $V_0$  is

related to solute concentrations by the following equation,

$$V_0 = \frac{C_0 - C_2}{C_1 - C_2} \quad (1.24)$$

Putting the solute concentrations  $C_1$  and  $C_2$  or  $C'_1$  and  $C'_2$  into Eq. (1.24)

and substituting the resultant  $V_0$  or  $V'_0$  into Eq. (1.23),  $N$  can be

calculated. In the case where the zone radii of the undeformed or

deformed specimens are the same (e.g. in Fig. (8.12), the zone radii of both specimens are found to be  $18 \text{ \AA}$  when the undeformed specimen is aged for 60 min or the deformed specimen is aged for 80 min), the zone number per unit volume is calculated to be  $3.1 \times 10^{18} \text{ cm}^{-3}$  and  $2.8 \times 10^{18} \text{ cm}^{-3}$  respectively. Apparently the number of zones (or zone density) of the deformed specimen is smaller than that of the undeformed specimen.

(ii) Electrical Resistivity Maxima (Fig. (8.13))

The results of the measurement of electrical resistivity also suggest the possibility of the change of the zone density. In Fig. (8.13) the changes of the electrical resistivity during the isothermal aging at  $0^\circ\text{C}$  for the specimens undeformed or strained 2% prior to aging are shown. The resistivity maximum is observed for each specimen. Furthermore, note that the value of the resistivity maximum of the deformed specimen is smaller than that of the undeformed specimen. The resistivity variation in the alloy during pre-precipitation is proportional to the product  $N\phi(R)$ ,  $N$  being the zone density and  $\phi(R)$  the contribution to resistivity of a zone of radius  $R$ <sup>(3)</sup>. At the critical points where the resistivity maxima were observed for both specimens, the radii of zones in each sample are the same and equal to the critical size of  $9 \text{ \AA}$ . Thus, the difference of resistivity maxima is due to  $N$ ,

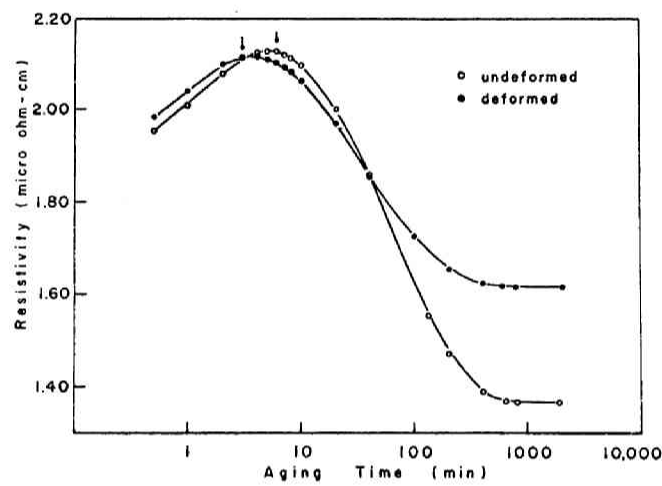


Fig.(8.13). Change of electrical resistivity during aging at  $0^{\circ}\text{C}$  in Al-6.8at.% Zn alloys quenched from  $300^{\circ}\text{C}$ , undeformed or strained 2% prior to aging. The arrows show the respective electrical resistivity maxima.

density of zones. As seen from Fig. (8.13), the resistivity maximum of the deformed specimen was smaller than that of the undeformed specimen, which means the number of zones is reduced by deformation.

#### 8-4. Summary

The effect of plastic deformation on the formation and growth processes of G.P. zones, the formation and solvus temperatures, solute concentrations inside and outside G.P. zones, and zone density have determined in a quenched Al-6.8at.% Zn alloy.

The measurement of electrical resistivity confirmed the enhancement of the growth process for the deformed specimen at the early stages of aging. Examination of X-ray small angle scattering curves suggested that deformation decreased the solute concentration inside the zones, increased the solute concentration in the matrix, and reduced the number of zones.

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## Appendix

The justification for neglecting the precipitate-free regions is given below. Here, we assume that the precipitate-free regions exist in the vicinity of dislocations induced by plastic deformation and that the presence of these regions cause the volume fraction of G.P. zones to decrease. This decrease in the volume fraction of zones is considered to be reflected in the value of  $p$ , that is,  $Q_0$  in Eq. (1.20). The volume fraction of precipitate-free regions  $\Delta V$  is given by the dislocation density  $d$  and the width of the regions  $r$  as follows,

$$\Delta V = \pi r^2 d \quad (\text{A-1})$$

Kiritani, Sato and Yoshida<sup>(9)</sup> found that the density of dislocations in pure aluminum was increased about  $3 \times 10^8 \text{ cm}^{-2}$  by deforming a quenched specimen 2%. Assuming that with 2% deformation, the dislocation density in a binary Al-Zn alloy equals that in pure aluminum,  $r$  is calculated to be  $9 \times 10^{-6} \text{ cm}$ . The precipitate-free regions of this width should be observed by the electron microscopy, but they were not observed. Therefore, the effect of the existence of precipitate-free regions on the integrated intensity is considered not so remarkable and it seems reasonable to assume that  $p$  is unity.



## CHAPTER 9

### GENERAL CONCLUSIONS

In the present investigation, the formation, growth and dissolution of G.P. zones of binary aluminum-zinc alloys containing 4.4 ~ 12.4 at.% Zn were studied by means of X-ray small-angle scattering, electrical resistivity measurements and transmission electron microscopy.

Also, the effects of the addition of small amounts of third elements, silver, silicon and magnesium, and the plastic deformation on the aging process were examined. As an example, the results of a binary Al-6.8 at.% Zn alloy can be summarized as follows:

#### (a) Formation of G.P. zones

The formation of zinc clusters (G.P. zones) in the quenched specimens was observed to occur at temperatures of  $-30 \sim -140^{\circ}\text{C}$ . This formation temperatures were found to be influenced by the quenching temperatures, addition of small amounts of third elements and plastic deformation. These results confirmed that the formation of zinc clusters was controlled by the point defects of vacancy type.

The models formerly proposed for the structure of zones at the initial stage of zone formation were pointed out to be contradictory with the present experimental results and an outline of a new model

for the structure of zones was given. That is, the solute concentration in the zones was smaller than the one determined by the metastable miscibility gap of this alloy system and the interface between zones and matrix was not definite. As the aging proceeded, the changes of solute concentrations inside and outside the zones and of the solute gradient at the interface were observed.

Furthermore, these zones were concluded to be formed by the spinodal mechanism from the facts that the sequence of the morphological change of zone formation was identical with the one proposed when the solid solution was assumed to decompose by the spinodal mechanism and that the shape of the experimentally obtained amplification factor was coincided with the theoretically calculated one. The upper limit of the temperature, within which the occurrence of the decomposition by the spinodal mechanism was possible, was determined to be approximately  $120 - 130^{\circ}\text{C}$ .

(b) Growth of G.P. zones

At the later stages of aging when the decomposition was completed, it was found that the solute concentrations inside and outside zones remained constant during aging and that there existed the definite interface between zones and matrix. The examinations of the changes

of zone radius and number indicated that G.P. zones grew in accordant with the growth model of so-called "Ostwald ripening", that is, the larger zones grew at the expense of smaller ones. Thus, by applying the Lifshitz-Wagner theory to the zone growth, the diffusion coefficients of zinc complexes at the temperatures of  $-17 \sim 40^{\circ}\text{C}$  were calculated to be about  $10^{-15} \sim 10^{-14} \text{ cm}^2/\text{sec}$ . Also, by the temperature dependence of the diffusion coefficient, the migration energy of zinc complexes was obtained to be  $0.38 \pm 0.04 \text{ eV}$ .

The existence of small amounts of third elements, specially Mg atoms, influenced the growth process of zones, that is, the addition of these atoms suppressed the process remarkably. Furthermore, the process of the alloy deformed prior to aging was found to be retarded compared with the undeformed one.

#### (c) Dissolution of G.P. zones

The solvus temperature for G.P. zones of this alloy was determined to be  $155^{\circ}\text{C}$  through the reversion experiment and this temperature was shown to coincide with the one calculated by using the thermodynamic equation given by Lašek. It was indicated that the addition of Ag and Mg or the plastic deformation prior to aging raised this temperature, but that the existence of Si had not the remarkable effect on it.

Also, the sequence of the morphological change of zones during dissolution was shown to be the reverse of that of formation and growth. The diffusion coefficient of zinc complexes at the initial stages of dissolution at 160°C was determined to be approximately  $10^{-14}$  cm<sup>2</sup>/sec by using the Whelan's equation. Moreover, the rate limiting process during dissolution was concluded to be the diffusion controlled migration.

A List of Publications

- (1) M. Murakami, O. Kawano and Y. Murakami  
"The Formation and Reversion of G.P. Zones in an Al-6.8at.% Zn Alloy and the Effects of Small Concentrations of Magnesium and Silver"  
Acta Met., 17, 29 (1969).
- (2) M. Murakami, O. Kawano and Y. Murakami  
"An Investigation of the Formation and Growth of G.P. Zones at Low Temperatures in Al-Zn Alloys and the Effects of the Third Elements Silver, Silicon, Magnesium"  
Trans. AIME, 245, 815 (1969).
- (3) M. Murakami, O. Kawano, Y. Murakami and M. Morinaga  
"On the Determination of the Spinodal Temperature in an Al-6.8 at.% Zn Alloy"  
Acta Met., 17, 1517 (1969).
- (4) M. Murakami, O. Kawano, T. Uyeda and Y. Murakami  
"The Effect of Plastic Deformation at  $-196^{\circ}\text{C}$  on Pre-Precipitation in a Quenched Al-6.8at.% Zn Alloy"  
Phil. Mag., 21, 1119 (1970).
- (5) M. Murakami, M. Morinaga, O. Kawano and Y. Murakami  
"The Structure and the Growth of Guinier-Preston Zones in an Al-6.8at.% Zn Alloy"  
Trans. JIM., 5, 318 (1970).
- (6) M. Murakami, O. Kawano and Y. Murakami  
"On the Determination of the Solvus Temperature for Guinier-Preston Zones in an Al-6.8at.% Zn Alloy"  
J. Inst. Metals (England) (in press)
- (7) M. Murakami and Y. Murakami  
"On the Kinetics of the Decomposition of the Super-saturated Solid Solution"  
Bulletin of JIM., vol 10, (1971) (to be published).

- (8) M. Morinaga, M. Murakami, O. Kawano and Y. Murakami  
"The Dissolution of Spherical G.P. Zones in a Binary Al-6.8at.  
% Zn Alloy"  
Phil. Mag., (to be published).



