

On the Apparent Activation Energy for Clustering in Dilute Al-Zn Alloys

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Synopsis

The clustering phenomenon was observed when dilute Al-Zn alloys were annealed at temperatures higher than the solvus of the G.P.zones. In this report the apparent activation energy for clustering is estimated and compared with the experimental results. The estimated value of the apparent activation energy for clustering in several Al-Zn alloys comes to 0.51 eV, which is larger than the effective migration energy 0.43 eV of Zn atoms in Al-Zn alloys.

1. Introduction

Ohta et al.¹⁾ investigated clustering phenomena in dilute Al-Zn alloys by means of measurements of electrical resistivity. The specimen was quenched into the bath of ice water after the solution treatment for 1 hr at 300°C and annealed immediately at temperatures higher than the solvus of the G.P.zones. The electrical resistivity increases at first, reaches a certain value after t_E minutes, and remains constant. The logarithm of t_E for alloys containing 0.43, 0.84, 1.3 and 1.7 at% Zn was plotted against the reciprocal of T_A (Fig.1). The slopes of straight lines for these alloys are equal and the apparent activation energy estimated from

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the slope is 0.82 eV. This value is larger than the effective migration energy $0.43 \text{ eV}^{1), 2)}$ of Zn atoms in Al-Zn alloys.

In this report is studied the origin of the difference between the apparent activation energy and the effective migration energy of Zn atoms in Al-Zn alloys.

2. Model of Clusters

Fluctuations of density in a small portion of the solution are expressed in a Fourier form as³⁾

$$n - \bar{n} = \sum_{\mathbf{k}} n_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (1)$$

where n denotes the density, \bar{n} the mean density, \mathbf{k} a wave vector, and \mathbf{r} a position vector. Mean square value of the Fourier components can be represented as³⁾

$$\overline{|n_{\mathbf{k}}|^2} = kT / (V(a + bk^2)) \quad (2)$$

where a denotes $\partial^2 f / \partial n^2$, f the free energy per unit volume, V the total volume of the solution, b a positive constant, k Boltzman's constant, T the absolute temperature, and $k = |\mathbf{k}|$.

In the solid solution of the Al-Zn alloys above the solvus temperature of the G.P. zone, there will be an equilibrium distribution of the fluctuations about the average composition. Huston et al.⁴⁾ showed the mean square amplitude of the Fourier components of one-dimensional fluctuations in solid solution according to Eq.(2). It is given by

$$\overline{|A(\beta, T)|^2} = (kT / (V(f'' + 2\eta^2 Y + 2K\beta^2)))^{1/3} \quad (3)$$

where $A(\beta, T)$ is the amplitude of the Fourier components of one-dimensional fluctuations, $\beta = 2\pi/\lambda$, λ the wave length, $f'' = d^2 f / dc^2$, c the atomic fraction of Zn atoms, η the linear expansion per unit

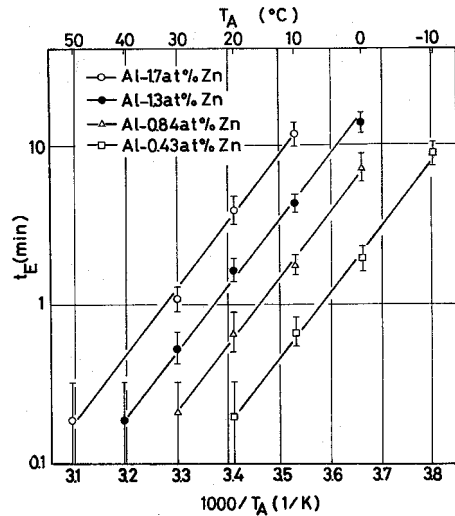


Fig.1 Logarithmic plot of t_E for several alloys quenched from 300°C against $1000/T_A$.

change in c , Y a function of elastic constants, and K the gradient-energy coefficient.

According to Ohta et al.¹⁾ the increase of the electrical resistivity is due to the formation of clusters. It is assumed here that the formation of clusters is the growth of the fluctuations and the increase of electrical resistivity is due to the growth of the fluctuations. We represent clusters with the sine curve which has the wave length independent of temperature and the amplitude proportional to the square of Eq.(3). Then, the metastable state of clusters will be represented as

$$\begin{aligned} c - \bar{c} &= \overline{A(\beta, T)^2}^{1/2} \sin(2\pi x/\lambda) \\ &= A(kT/(V(f''+2\eta^2 Y+2K\beta^2)))^{1/6} \sin(2\pi x/\lambda) \end{aligned} \quad (4)$$

where c is the atomic fraction of Zn atoms at any point in the specimen, \bar{c} the average atomic fraction of Zn atoms, A a positive constant, and x any point in the specimen.

Eq.(4) is appropriate at temperatures higher than the solvus of the G.P.zones. In the next place we estimate the values of f'' , $2\eta^2 Y$, $2K\beta^2$ and λ in Eq.(4).

3. f''

The second derivative of Helmholtz's free energy per mol of the Al-Zn solid solution with respect to c is given by⁵⁾

$$F'' = -2NzV+NkT/c(1-c) \quad (5)$$

where N is Avogadro's number, z the co-ordination number, and $V = V_{AZ} - (1/2)(V_{AA} + V_{ZZ})$; V_{AZ} , V_{AA} , V_{ZZ} are the binding energies of atomic pairs Al-Zn, Al-Al and Zn-Zn, respectively.

The heat of mixing per mol of the Al-Zn solid solution is given by

$$\begin{aligned} \Delta H_m &= P_{AZ}(V_{AZ} - (1/2)(V_{AA} + V_{ZZ})) \\ &= P_{AZ}V \end{aligned} \quad (6)$$

where P_{AZ} is the number of Al-Zn pairs per mol. P_{AZ} is given by⁶⁾

$$P_{AZ} = zNc(1-c)(1-\alpha_1) \quad (7)$$

where α_1 is short-range order parameter and is equal to $(1-p_1)/(1-c)$; p_1 is the probability of finding an Al atom about a Zn atom.

Substituting Eq.(7) into Eq.(6), we have

$$NzV = \Delta H_m / c(1-c)(1-\alpha_1). \quad (8)$$

Rudman et al.⁷⁾ have calculated the values of α_1 and ΔH_m by measuring the intensity of diffuse scattering of X-rays from several Al-Zn solid solutions. From those data we estimate the values of α_1 and ΔH_m

Table 1 Estimated values of α_1 , ΔH_m and NzV

c (at %Zn)	α_1	ΔH_m (cal /mol)	zN_0V (cal /mol)
0.43	3.70×10^{-3}	17.2	4032
0.84	7.22×10^{-3}	33.6	4063
1.3	1.12×10^{-2}	52.0	4098
1.7	1.46×10^{-2}	68.0	4129

Table 2 Estimated values of F''

c (at%Zn)	Temperature (K)							
	263	273	283	293	303	313	323	573
0.43	113605	118230	122856	127482	132109	136735	141361	257015
0.84	54388	56765	59142	61519	63896	66273	68650	128073
1.3	32389	33932	35475	37018	38561	40104	41647	80226
1.7	22904	24088	25273	26458	27643	28828	30013	59634

(cal /mol)

corresponding to the concentration of the alloys used in the investigation by Ohta et al.¹⁾ The results are shown in Table 1. Substituting these values into Eq.(8), we find the values of NzV . The results are also shown in Table 1.

The lattice parameters and the volume for each alloy at each temperature are obtained from the published data,^{8),9)} and are shown

Table 3 Estimated values of lattice parameters a and the volume per mol of several alloys

Al-0.43 at % Zn			Al-0.84 at % Zn		
T (°C)	a (Å)	Volume (cm ³ /mol)	T (°C)	a (Å)	Volume (cm ³ /mol)
-10	4.0461	9.968	-10	4.0459	9.9724
0	4.0470	9.9805	0	4.0468	9.9790
10	4.0480	9.9879	10	4.0478	9.9864
20	4.0489	9.9946	20	4.0487	9.9931
30	4.0498	10.0012	30	4.0497	10.0005
40	4.0507	10.0079	40	4.0506	10.0072
50	4.0516	10.0146	50	4.0516	10.0146
300	4.0726	10.1711	300	4.0728	10.1726
Al-1.3 at % Zn			Al-1.7 at % Zn		
T (°C)	a (Å)	Volume (cm ³ /mol)	T (°C)	a (Å)	Volume (cm ³ /mol)
-10	4.0456	9.9701	-10	4.0455	9.9694
0	4.0466	9.9775	0	4.0464	9.9761
10	4.0476	9.9849	10	4.0474	9.9835
20	4.0485	9.9916	20	4.0484	9.9909
30	4.0495	9.9990	30	4.0494	9.9983
40	4.0505	10.0064	40	4.0504	10.0057
50	4.0415	10.0138	50	4.0514	10.0131
300	4.0729	10.1734	300	4.0730	10.1741

in Table 3. The values of f'' can be obtained from F'' and the volume per mol. The results are shown in Table 4.

Table 4 Estimated values of f''

c (at%Zn)	Temperature (K)							
	263	273	283	293	303	313	323	573
0.43	4.77	4.96	5.15	5.34	5.53	5.72	5.91	10.58
0.84	2.28	2.38	2.48	2.58	2.67	2.77	2.87	5.27
1.3	1.36	1.42	1.49	1.55	1.61	1.68	1.74	3.30
1.7	0.96	1.01	1.06	1.11	1.16	1.21	1.25	2.45

$\times 10^{11} (\text{erg.cm}^{-3})$

4. $2\eta^2 Y$

The parameter η is defined by¹⁰⁾ $\eta = (1/a)(da/dc)$. The values of η estimated directly by taking the slope of the curve,⁸⁾ in which the lattice parameters are plotted versus composition, are shown in Table 5.

Estimation of the elastic coefficient parameters Y is uncertain because there are no experimental values available for the Al-Zn solid solutions. Therefore we approximate the values of Y as follows. Al-Zn solid solution may reasonably be isotropic and Y is equal to

Table 5 Estimated values of a , da/dc , η , Y and $2\eta^2 Y$

c (at %Zn)	a(25°C) (Å)	da/dc	η (at.fract. ⁻¹)	Y (dyne.cm ⁻²)	$2\eta^2 Y$ (erg.cm ⁻³)
0.43	4.0493	4.80×10^{-2}	1.18×10^{-2}	10.80×10^{11}	3.00×10^8
0.84	4.0491	5.86×10^{-2}	1.45×10^{-2}	10.83×10^{11}	4.56×10^8
1.3	4.0489	6.73×10^{-2}	1.66×10^{-2}	10.86×10^{11}	5.98×10^8
1.7	4.0486	7.27×10^{-2}	1.80×10^{-2}	10.88×10^{11}	7.06×10^8

$E/(1-\nu)^{10}$ where E is Young's modulus and ν Poisson's ratio. It will be reasonable to use the values of E and ν for the polycrystalline Al in estimating the value of Y for Al. Substituting the values of $E = 7.06 \times 10^{11}$ dyne·cm⁻² and $\nu = 0.345$ into $Y = E/(1-\nu)$, we have $Y = 10.78 \times 10^{11}$ dyne·cm⁻². On the other hand, Rundman et al.¹⁰⁾ have estimated the value of Y for Al-22 at% Zn alloy as $Y = 12.2 \times 10^{11}$ dyne·cm⁻². From these values Y for each alloy is found. The results are shown in Table 5. The values of $2\eta^2 Y$ are also shown in the Table. The order of $2\eta^2 Y$ is three powers of 10 smaller than that of f'' .

5. $2K\beta^2$

According to the statistical mechanical derivation of Chan and Hilliard,¹²⁾ K is given by $K = \omega\psi^2/2$, where ψ is an interaction distance and ω an interaction energy. Rundman et al.¹⁰⁾ estimated the value of K as $K = 8.5 \times 10^{-6}$ erg·cm.⁻¹

Since the value of the wave length of the fluctuations have not been measured experimentally, we assume it as follows. The number of Zn-Zn pairs per mol of in the random solid solution is given by $N_{ZZ} = N_Z c^2/2$. Since N_{ZZ} for Al-0.43 at% Zn alloy becomes 6.68×10^{19} and the volume per mol of this alloy at 300°C is 10.1711 cm³ (Table 3), the mean distance between Zn-Zn pairs becomes about 53.4 Å. We make this value upper limit for the length of fluctuations. The value of β for this wave length is about 1.18×10^7 cm.⁻¹

Substituting the values of K and β above into $2K\beta^2$, we have $2K\beta^2 = 2.35 \times 10^9$ erg·cm.⁻³, which is small compared with f'' .

6. Apparent Activation Energy

We neglect here $2\eta^2 Y$ and $2K\beta^2$ in Eq.(4), since they are small compared with f'' . Then, Eq.(4) is reduced to

$$c - \bar{c} = A(kT/Vf'')^{1/6} \sin(2\pi x/\lambda) \quad (9)$$

As mentioned previously, Eq.(9) represents the metastable state of clusters for Al-Zn alloys of composition c at temperature T . The solid solution at 300°C is thought to be almost random, and it is

thought that the fluctuations grow up from the random solid solution. When the specimen is annealed immediately after the quenching, the amplitude of the fluctuations will increase gradually and reach the metastable state at annealing temperature. This can be examined by substituting the values of f'' and T into Eq.(9). In Fig. 2 are shown schematically two metastable states of clusters at quenching and annealing temperatures.

Now, Zn atoms diffuse up the concentration gradient, and the solid solution is changed from Fig. 2(a) to Fig. 2(b). Then, the equation describing the clustering phenomenon will be given by changing the sign of the solution to the diffusion equation used in describing the homogenization of casting.¹³⁾ It is given by

$$c'(x,t) = c'(x,0)\exp(\pi^2 D_{Zn} t / \lambda^2) \quad (10)$$

where t is time, D_{Zn} the diffusion coefficient of Zn atoms,

$$\begin{aligned} c'(x,t) &= c(x,t) - \bar{c} \\ &= A(kT/Vf'')^{1/6} \sin(2\pi x/\lambda), \end{aligned} \quad (11)$$

$$\begin{aligned} c'(x,0) &= c(x,0) - \bar{c} \\ &= A(kT_Q/Vf''_Q)^{1/6} \sin(2\pi x/\lambda). \end{aligned} \quad (12)$$

$c'(x,t)$ in Eq.(11) is the state of clusters at time t of the annealing. $c(x,t)$ is the atomic fraction and \bar{c} the average composition. $c'(x,0)$ in Eq.(12) is the fluctuations about the average composition at quenching temperature. $c(x,0)$ is the atomic fraction. f''_Q is the value of f'' at quenching temperature. f'' in Eq.(11) is the second derivative of the free energy per unit volume at time t of the annealing with respect to c . T in Eq.(11) is the temperature of the

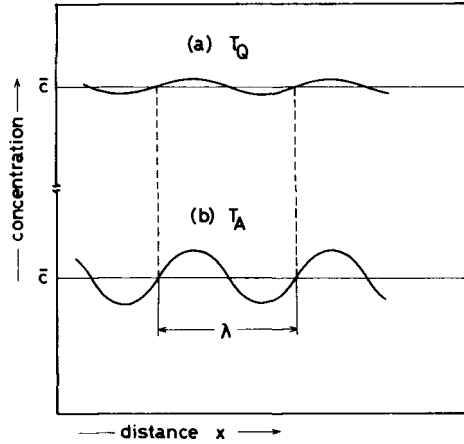


Fig.2 Schematical representation of clusters at quenching temperature T_Q and annealing temperature T_A . \bar{c} is the mean concentration and λ the wave length.

specimen. D_{Zn} can be written as follows¹⁴⁾ when annealed isothermally after quenching

$$D_{Zn} = \frac{1}{6}a^2 v_{Zn} f_{Zn} \exp((S_{Zn}^F + S_{Zn}^M)/k) \exp(-E_{Zn}^F/kT_Q) \exp(-E_{Zn}^M/kT_A) \quad (13)$$

where a = jump distance,

v_{Zn} = vibrational frequency of a Zn atom associated with a vacancy

f_{Zn} = correlation factor,

E_{Zn}^M = true activation energy for the movement of a Zn atom into an associated vacancy,

S_{Zn}^M = activation entropy for the movement of a Zn atom into an associated vacancy,

E_{Zn}^F = energy for the formation of a vacancy associated with a Zn atom,

S_{Zn}^F = entropy for the formation of a vacancy associated with a Zn atom.

Correlation factor can be written as¹⁵⁾

$$f_{Zn} = (w_{Al} + \frac{7}{2}K) / (w_{Al} + w_{Zn} + \frac{7}{2}K).$$

In this expression $w_{Al} = v_{Al} \exp(S_{Al}^M/k) \exp(-E_{Al}^M/kT_A)$ where v_{Al} is the vibrational frequency of an Al atom associated with a vacancy and a Zn atom, E_{Al}^M the activation energy for the movement of an Al atom into an associated vacancy, S_{Al}^M the activation entropy of that process.

$$w_{Zn} = v_{Zn} \exp(S_{Zn}^M/k) \exp(-E_{Zn}^M/kT_A).$$

$K = v_o \exp((S_{Al}^M + S_B)/k) \exp(-(E_{Al}^M + E_B)/kT_A)$, where v_o is the vibrational frequency of Al atoms which are nearest neighbor of a vacancy but are not those of a Zn atom, and S_B the binding entropy.

When we denote the effective activation energy of Zn atoms by E'_{Zn} , it is given by $-(d \ln D_{Zn} / d(1/T_A))^2$,¹⁴⁾ and becomes from Eq.(13)

$$E'_{Zn} = E_{Zn}^M - (d \ln f_{Zn} / d(1/T_A)).$$

Taking a logarithm of both side of Eq.(10), we have

$$\ln c'(x,t) = \ln c'(x,0) + \pi^2 D_{Zn} t / \lambda^2.$$

Taking again a logarithm, we obtain

$$\ln \ln(c'(x,t)/c'(x,0)) = \ln D_{Zn} + \ln t + 2 \ln(\pi/\lambda). \quad (14)$$

From Eqs.(11) and (12), we have

$$c'(x,t)/c'(x,0) = (Tf''_Q/T_Q f'')^{1/6} \quad (15)$$

Substituting Eqs.(13) and (15) into Eq.(14); and denoting collected terms independent of annealing temperature by C, we have

$$\ln t = E_{Zn}^M - \ln f_{Zn}'' + \ln \ln(Tf''_Q/T_Q f'') + C \quad (16)$$

In this equation the change of lattice parameter is neglected because the error that is introduced in the estimation of the apparent activation energy will be small.

When we make $T = T_A$ and $f'' = f''_A$ (Table 4), t in Eq.(16) corresponds to t_E because f''_A is the value for the alloy which is stable at each annealing temperature. The activation energy due to the first and second terms in the right hand side of Eq.(16) is 0.43 eV. When we plot the logarithm of t_E in Eq.(16) versus $1/T_A$, we can estimate the apparent activation energy for clustering. The results are shown by the broken lines in Fig.3. The constant C was so selected that t_E may coincide with the experimental result at the lowest annealing temperature.

The slopes of the broken lines are all equal and the estimated apparent activation energy comes to 0.51 eV.

7. Discussion

All broken lines in Fig.3 are parallel as those in Fig.1. This may suggest that there is a certain relation among the metastable states of clusters in the alloys of different composition. Eq.(9) shows that the metastable state of clusters varies with annealing temperature and composition. Ratios between the amplitude of clusters in alloys of different composition can be obtained from Eq.(9). They become almost constant independently of annealing

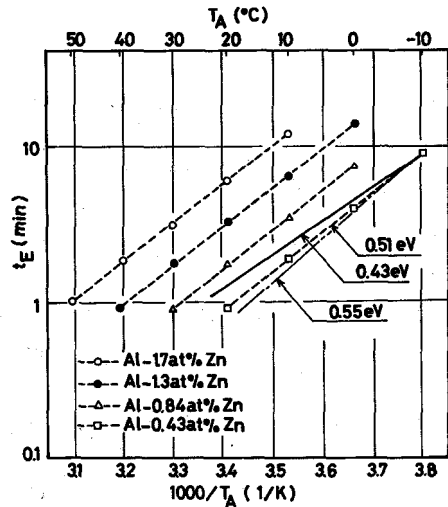


Fig.3 Logarithmic plot of t_E calculated from Eq.(16) or Eq.(19) for several alloys against $1000/T_A$.

temperature, and this may be related to the parallelism of the broken lines.

When we derive Eq.(9), we assumed that $2\eta^2\gamma$ and $2K\beta^2$ can be neglected since they are small compared with f'' . It may be adequate to neglect $2\eta^2\gamma$, but it is uncertain whether $2K\beta^2$ can be neglected or not. Though the estimated value of the wave length is 53.4 Å, it is not necessarily an adequate value because of the absence of the experimental value of the wave length. When we cannot neglect $2K\beta^2$, we must rewrite Eq.(15) as follows:

$$c'(x,t)/c'(x,0) = (T(f''_Q + 2K\beta^2)/T_Q(f'' + 2K\beta^2))^{1/6} \quad (17)$$

Now, it is confirmed experimentally that the electrical resistivity increases with annealing time. This is thought to be due to the growth of fluctuations. If the fluctuations grow up in case where $2K\beta^2$ is taken into account, we have from Eq.(17)

$$T(f''_Q + 2K\beta^2)/T_Q(f'' + 2K\beta^2) > 1 \quad (18)$$

Substituting the values of f'' and annealing temperature into Eq.(18), we can estimate the maximum value of $2K\beta^2$ or the minimum wave length of the fluctuations. For Al-0.43 at% Zn alloy at -10°C , we have $\lambda > 21$ Å. This wave length is equal approximately to 16 Å, which is the mean distance between Zn atoms in the random solid solution of this alloy at -10°C . Actual wave length of the fluctuations will be longer than the mean distance between Zn atoms.

Taking $2K\beta^2$ into consideration, we must also rewrite Eq.(16) as follows:

$$\ln t = E_{Zn}^M/kT_A - \ln f_{Zn} + \ln \ln(T(f''_Q + 2K\beta^2)/T_Q(f''_Q + 2K\beta^2)) + C \quad (19)$$

With Eq.(19) we estimate again the apparent activation energy for clustering in Al-0.43 at% Zn alloy, taking $\lambda = 25$ Å. This result is shown by the chain line in Fig.3. The estimated value of the apparent activation energy is in this case 0.55 eV, which is not so large. Since the wave length of the fluctuations will be longer practically than 25 Å, the error introduced by the negligence of $2K\beta^2$ may be small.

The difference between experimentally determined apparent activation energy for clustering and that estimated from Eq.(16) or Eq.(19) cannot still be explained fully. This discrepancies may be due to the assumptions on the wave length of the fluctuations and the one-dimensional model of clusters.

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