KINETICS OF GROWTH OF GUINIER-PRESTON ZONES IN DILUTE Al-Zn ALLOYS

V.M.Stefanović,

Department of Material Science of the "Boris Kidrich" Institute of Nuclear Sciences-Vincha, 11001 Beolgrade, Yugoslavia

INTRODUCTION

Redistribution of the non-equilibrium concentration of quenched-in vacancies and solute atoms, including impurities, is the most important factor in the formation of Guinier-Preston (G.P.) zones. Vacancy enhanced precipitation in Al-Zn (1-3) and Al-Ag (3) alloys has been intensively studied, following the pioneering work of Panseri and Federighi (4). The changes of certain physical properties, which follow different reactions in quenched and aged alloys can easily be measured, but it is not so easy to ascribe them to some specific reactions. Considerable efforts have been made to discover the mechanism of the zone forming process as well as to interpret experimental results for the Al-Zn alloys. Based on the mechanism of cyclic transport of solute atoms by vacancies, Girifalco and Herman (5) have proposed a mathematical model (G.H. - model) for an early stage formation of an "ideal" G.P. zone, as it was defined by Guinier (6). An approximate integration of their differencial rate equation has been performed by Kahn and Girifalco (7) for physically important cases. Asimov (8), Ipohorski and Bonfiglioli (9) have further discussed various aspects of validity of the G.H. - model using experimental data.

In this work, a kinetic model of redistribution of defects during G.P. zone formation, based on the experimental results obtained earlier for an Al-3.9 at.%Zn alloy doped with 0.025at.%Cu (10) and a number of literature data, is presented. For this purpose a new approach was developed starting from the chemical rate theory sistematized by Koiwa (11). The process of zone formation is analized by analytical expressions for the zone growth law, and the zone radius and distance obtained by the comparison to the G.H. - model. The main advantage of such an approach is that it helps in identifying the mechanism of the process in a real system and promotes a physical understanding of the values of many kinetic parameters determined experimentally. Calculated values of the zone radius were also compared with the result of other authors.

FORMULATION OF THE PROBLEM

Consider two dilute aluminium alloys, a binary and a ternary, that exhibit formation of ideal G.P. zones from the mayor matrix constitutent (M_b) and M_b with the minor constituent (M_t), respectively ($M_b >> M_t$). The zone formation is analyzed from the very beginning: solution treatment, quenching and ageing. It is believed that in an alloy quenched and aged G.P. zones grow in a way illustrated in Fig.1, i.e., mostly by diffusion

of solute atom - vacancy pairs (M_b-V or M_t-V) from the sphere with the radius L centered at the zone. The concentration gradient of pairs on the surface of the sphere is $(\nabla C)_L = 0$. Simultaneously there is an annihilation of vacancies to sincs such as grain boundaries.

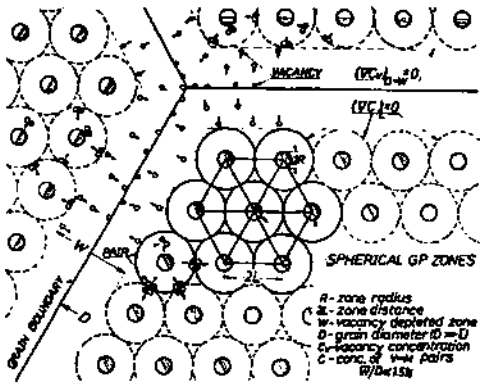


Fig.1.Schematic illustration of the redistribution of vacancies during formation of ideal G.P. zones in Al-Zn alloys.

To describe the model the following assumptions are made:1. The conditions for ideal pre-precipitation (12) are satisfied and the cyclic vacancy pump G.H.-model is aslo valid in this case; 2. High vacancy concentration in the process is maintained for a long period of time due to small concentration of sincs. This could not be valid for a narrow vacancy free region near grain boundaries. The major motivation for such an assumcion is supported by the electron - microscopy observations (10) in an Al-3.9at.%Zn alloy, i.e., after prolonged ageing the structure of the alloy includes, besides the zones, a number of dislocation loops created by condensation of vacancies, Fig.2. At the same time the precipitate or vacanci free zone width ($\bar{W}$) was much smaller than grain boundary ($\bar{D}$), i.e. $\bar{W}/\bar{D}<<0.01$; 3.The binding energy (B_b) of M_b and a vacancy is small, but high enough so that most of the vacancies exist as pairs. The added (impurity) element M_t has the binding energy (B_t) greather than B_b; 4. The initial concentration M_{ot} is by several orders of magnitude higher than the equilibrium concentration of vacancies (V_o^r). Therefore it is more likely that free vacancies form pairs than that they reach vacancy sincs.

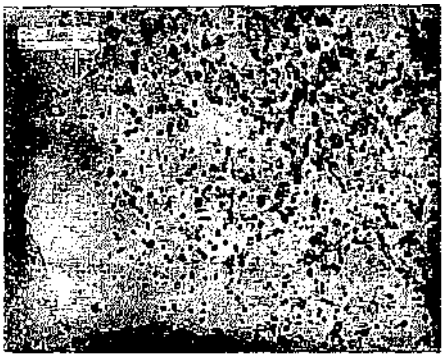


Fig.2. Microstructure of an Al-3.9 at.%Zn alloy near a grain boundary; quenched from 653°K and aged at 323°K for 2h + 373°K for 24h (10).

It is assumed that the following possible defect species could be presented in quenched aluminium alloys: A free vacancy and divacancy; isolated unbounded solute atoms M_b and M_t; pairs M_b-V and M_t-V; triplets from a solute atom and two vacancies, e.t.c.; and finally, sincs such as grain boundaires, e.t.c. Fig.3. shows a scheme of concentration change of the above main reaction components used in the course of the model formation. The triplet concentration is probably small and neglected here. The zone forming process may be descriebed by the following kinetic reaction scheme:

quenching

$$V + M_b \underset{k'_1}{\overset{k_1}{\rightleftharpoons}} C_b, \quad \ldots\ldots\ldots \quad /1/$$

$$V + M_t \underset{k'_2}{\overset{k_2}{\rightleftharpoons}} C_t, \quad \ldots\ldots\ldots \quad /2/$$

$$V + V \underset{k'_3}{\overset{k_3}{\rightleftharpoons}} C_{2v}, \quad \ldots\ldots\ldots \quad /3/$$

$$V \underset{k'_o}{\overset{k_o}{\rightleftharpoons}} f_o \left(\frac{\text{sincs}}{\text{source}}\right), \ldots \quad /4/$$

ageing

$$V + M_b \underset{k'_1}{\overset{k_1}{\rightleftharpoons}} C_b, \quad \ldots\ldots\ldots\ldots \quad /1/$$

$$V + M_t \underset{k'_2}{\overset{k_2}{\rightleftharpoons}} C_t, \quad \ldots\ldots\ldots\ldots \quad /2/$$

$$C_b \underset{k'_4}{\overset{k_4}{\rightleftharpoons}} Z \text{ (zone)}, \quad \ldots\ldots \quad /3/$$

$$C_t \underset{k'_5}{\overset{k_5}{\rightleftharpoons}} Z \text{ (zone)}, \quad \ldots\ldots \quad /4/$$

$$V \underset{k'_o}{\overset{k_o}{\rightleftharpoons}} f_o \left(\frac{\text{sincs}}{\text{source}}\right), \ldots \quad /5/.$$

Two sets of non-linear, coupled, differential rate equations corresponding to this scheme could be established, see also Koiwa (11) when a vacancy is accepted as a third reaction component:

quenching

$$dV/dt = -(k_1M_b + k_2M_t)V + k_1C_b + k'_2C_t - 2k_3V^2 + 2k_3C_{2v}, \ldots\ldots \quad /1/$$

$$dC_b/dt = k_1M_bV - k'_1C_b, \quad \ldots\ldots\ldots \quad /2/$$

$$dC_t/dt = k_2M_tV - k'_2C_t, \quad \ldots\ldots\ldots \quad /3/$$

$$dC_{2v}/dt = k_3V^2 - k'_3C_{2v}, \quad \ldots\ldots\ldots \quad /4/$$

ageing

$$dV/dt = -(k_1M_b + k_2M_t)V + k'_1C_b + k'_2C_t - k_oV, \ldots\ldots \quad /1/$$

$$dz/dt = k_4C_b + k_5C_t, \quad \ldots\ldots\ldots \quad /2/$$

$$dC_b/dt = k_1M_bV - k'_1C_b - k_4C_b, \ldots\ldots \quad /3/$$

$$dC_t/dt = k_2M_tV - k'_2C_t - k_5C_t, \ldots\ldots \quad /4/$$

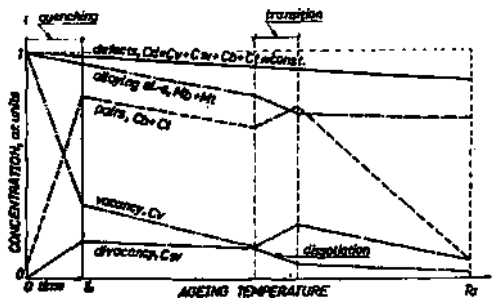


Fig.3. Schematic illustration of effect of ageing temperature on a concentration change of the main reaction components used in the model.

The symbols simultaneously represent atomic fractions of: V=free vacancies; C_{2v}=free divacancies; $C_b = M_b$-V pairs and $C_t = M_t$-V pairs; M_b or M_t = free solute atoms, and Z= solute atoms trapped at zones which take no furter part in the reaction.

Neglecting reaction /2/ for quenching, or reactions /2/ and /4/ for ageing, corresponding sets of rate equations can be obtained for a binary alloy. For ideal quenching, single vacancies are expected to be the predominant defects. The rate constants are (13, 14):

$k_o = f_o . \bar{\nu} \exp(-E_m/kT)$, $k'_o = V^r_o . \bar{\nu} \exp(-E_m/kT)$,

$k_1 = 84 . \bar{\nu} \exp(-E_m/kT)$, $k'_1 = 7 . \bar{\nu} \exp[-(E_m+B_b)/kT]$,

$k_2 = k_1$, $k'_2 = 7 . \bar{\nu} \exp[-(E_m+B_t)/kT]$,

$k_3 = k_1$, $k'_3 = 14 . \bar{\nu} \exp[-(E_m+B_{2v})/kT]$,

$k_4 = a^2 . \bar{\nu} . \bar{N}_{zb} \exp(-E^*_{mb}/kT)$, $k'_4 = C_{ob} . \bar{\nu} \exp(-E^*_{mb}/kT)$ i

$k_5 = a^2 . \bar{\nu} . \bar{N}_{zt} \exp(-E^*_{mt}/kT)$, $k'_5 = C_{ot} . \bar{\nu} \exp(-E^*_{mt}/kT)$.

where $f_o (= f'_o a^2)$ is the initial fraction of sincs; f'_o= vacancy sinc density; a= lattice parameter of pure aluminium; E_m and E^*_m is activation energy for vacancy migration in pure aluminium and in an alloy, respectively; $\bar{N}_z$=effective density of G.P. zones and B_{2v}= divacancy binding energy. Subscript "o" denotes initial concentrations.

ANALYTICAL APPROXIMATIONS AND SOLUTIONS

For obtaining analytical solutions certain approximations should be made which uncouple the differential equations to linear form. For quenching we have: 1) The total defect concentration (measurable value) $C_d = V + C_{2v} + C_b + C_t = V^r_o - C_{2v} \approx$ constant, 2) the total concentration of vacant sites, $V^r_o = V + 2C_{2v} + C_b + C_t$, 3) fractions $M_b = M_{ob} - C_b \approx M_{ob}$ and $M_t = M_{ot} - C_t \approx M_{ot}$ when $C_b << M_{ob}$ and $C_t << M_{ot}$, respectively, 4) local equilibrium conditions are established (11), i.e. $k_1/k'_1 = K_1 = 12 \exp B_b/kT$, $k_2/k'_2 = K_2 = 12 \exp B_t/kT$ and $k_3/k'_3 = K_3 = 6 \exp B_{2v}/kT$. Similarly, for ageing we have: 1) $M_b \approx M_{ob}$ and $M_t \approx M_{ot}$. This is supported by the work of Freise and al. (see ref. 15) that only a small volume about 10% of an Al-Ag alloy was precipitated in the form of G.P. zones. Finally, 2) we have assumed no back reaction $k'_4 \approx k'_5 = 0$ and $k_o = 0$. More accurate solutions could be realised by a computer.

The initial boundary conditions at the time t=0 are for quenching: $V_{tot} = V^r_o$, $C^o_{2v} \approx 0$, $C_{ob} \approx 0$ and $C_{ot} \approx 0$. From these conditions the solutions for C_{2v}, C_b, C_t, C_d and further, by summing, for $V = V^r_o - (2C_{2v} + C_b + C_t)$ could be obtained. The boundary conditions for ageing are: (t=o;t), $(V^r_o; V)$ and (Z=0;Z). Integration of rate equations for ageing yields the relations for V_b, V_t and then for Z:

For ternary alloy

(I) $Z_t = V^r_o \dfrac{k_4 . K' + k_5 . K''}{K_{et}} \left[1 - \exp(-K_{et} . t)\right]$, where the equivalent constants are:

$$K' = \frac{k_1 . M_{ob}}{k'_1 + k_4 - K_{et}}, \quad K'' = \frac{k_1 . M_{ot}}{k'_2 + k_5 - K_{et}} \quad \text{and} \quad K_{et} = \frac{k_o + k_4 . K_1 . M_{ob} + k_5 . K_2 . M_{ot}}{1 + K_1 . M_{ob} + K_2 . M_{ot}} .$$

For binary alloy

(I') $Z_b = V_o^r \frac{K_o \cdot k_4}{K_{eb}} \left[1-\exp(-K_{eb}\cdot t)\right]$, $K_o = \frac{k_1 \cdot M_{ob}}{k_1' + k_4 - K_{eb}}$ and $K_{eb} = \frac{k_o + k_4 \cdot K_1 \cdot M_{ob}}{1 + K_1 \cdot M_{ob}}$.

The equation (I) or (I') represents the zone growth law and may be compared to the similar one given by Girifalco and Herman (5,7):

(II) $(R/L)^3 = V_m \cdot C_o \left[1-\exp(-3D_c \cdot R \cdot t/L^3)\right]$, where is V_m= the increase in zone volume per atom entering the zone, and D_c= diffusion coefficient of a pair.

The equations (I) or (I') and (II) are indentical functions. Equaling the corresponding parameters in these equations we have for the zone radius $R = \left[Z/(f \cdot \bar{N}_z)\right]^{1/2}$ and the zone distance $\overline{2L} = 2R \cdot Z^{-1/3}$, where $f_b = K_{eb}/k_4$ or $f_t = K_{et}/k_5$.

COMPARISON WITH EXPERIMENT

Let us consider numerical values of Z, R and L for the Al-3.9at.%Zn and Al-3.9at.%Zn - 0.025at.%Cu alloys (10). The zone densities and all reaction rate constants must be known. The values of some kinetic parameters accepted for calculation are:

$E_f = 0.76$eV(1,4); $B_b = 0.06$eV(4,10); $E_m = 0.62$eV(1,14); $M_{ob} = 3.9 \cdot 10^{-2}$; $a^2 = 1.63 \cdot 10^{-15}$cm^2

$E_{fb}^* \approx 0.74$eV(10); $B_t = 0.19$eV(10); $E_{mb}^* = 0.43$eV(1,10); $M_{ot} = 2.6 \cdot 10^{-4}$; $S_f = 2.4$k(16.1)

$E_{ft}^* \approx 0.73$eV(10); $B_{2v} = 0.17$eV(1,14); $E_{mt}^* = 0.42$eV(1,10); $\bar{\nu} \approx 10^{13}$sec^{-1}.

The magnitude of thermal equilibrium vacancy concentration is determined from Lomer's equations (17) or from the relation $V_o^r = \exp(-E_f^* + S_f \cdot T_k)/kT_k$(16), where E_f^*= the vacancy formation energy in the alloy and S_f= the formation entropy of a vacany. So we have $V_{ob}^r = 2.84 \cdot 10^{-5}$ and $V_{ot}^r = 2.97 \cdot 10^{-5}$. Zone density in the alloys was determined from: 1. The resistivity-ageing time ratio (2,3,10), $A = t_{max}^t / t_{max}^b \approx V_b/V_t$, where t_{max} is a time to a resistivity maximum. This follows from the relation $A = (V_b/V_t) \times \left[1-12(M_{ob}+M_{ot})\right]/(1-12M_{ob})$, see ref. (2), since in the present case second term after the sign "x" is nearly one. The model also gives $A = (V_{ob}/V_{ot}) \exp\left[(K_{et}-K_{eb})t\right] = A_o \exp\left[(\bar{N}_{zt} \cdot f_t \cdot D_{ct} - \bar{N}_{zb} \cdot f_b \cdot D_{cb})t\right]$; 2. The empirical relation $\bar{N}_{zt}/\bar{N}_{zb} = \alpha - \beta T_a$(10), where T_a is in ^oK, $\alpha = 1.1867$ and $\beta = 0.7547 \cdot 10^{-3}$, since the resistivity maximum $\Delta\rho_{max} \propto \bar{N}_z$(4), and 3. the binding energy B_t (10) estimated from a set of A values, using Lomer's equations (2,3,17), see table.

T_a, ^oK	218	238	258	278	298
A	1.17	1.18	1.15	1.61	1.58
B_t, eV	0.125	0.13	0.132	0.175	0.18

The ratio of A_o strongly depends on quenching procedure (time), Fig.4. A_o was set equal to A_r(=7.10^5), where A_r^o is the ratio of free vacancy concentrations at 218^{o}K after a time t=t_r (≈6.84sec), measured time of quenching

was 6sec. The atomic fraction of Z is then estimated from equations (I) and (I') as a function of ageing time (Fig.5.) and isochronal ageing temperature (Fig.6.). The variation of constants K_o, K' and K'' is also plotted in Fig.6. From these curves is seen that the ageing occurs in two stages: the first, major reaction up to the maximum resistivity, below 253°K,

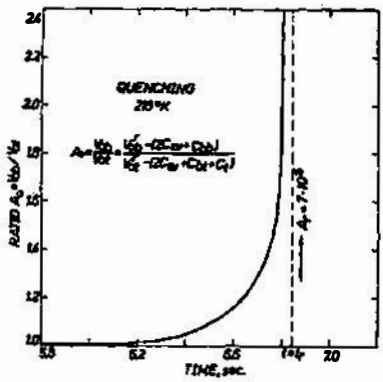


Fig.4. Effect of quenching time on the free vacancy concentration ratio A_o at 218°K(10)

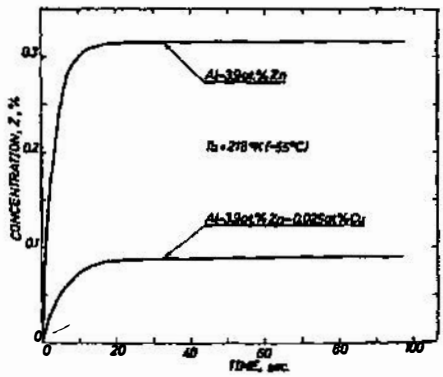
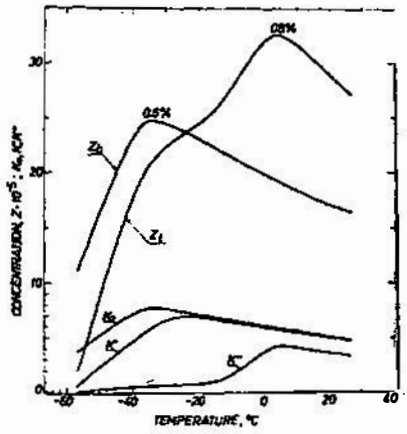


Fig.5.Effect of ageing time at 218°K on the change of precipitated atoms into G.P. zones.



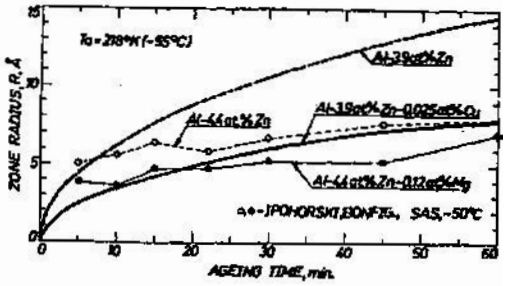


Fig.7. The dependence of the zone radius, R, on ageing time at 218°K.

Fig.6. The variation of Z and equivalent constants K_o, K' and K''on temperature.

is trapping of vacancies by copper atoms, which retards the ageing, and the second, beyond the maximum, above 253°K, detrapping of vacancies, begins due to dissociation of V-Cu pairs causing an increase of the ageing rate up to a maximum of Z, which corresponds to 0.8% of Zn precipitated into zones. The variation of R with ageing time and temperature is shown in Figs.7 and 8, respectively. In Fig.7., the X-ray small-angle scattering (SAS) results obtained by Ipohorski and Bonfiglioli (9) are shown for comparison. If a resistivity maximum is related to the critical zone radius (6,1), it follows from the curves in Fig.8 that R_{max} = 26Å, for both alloys. This radius corresponds to the volume zone density N_{zv}= $3.8.10^{17}$ z/cm^3 calculated by using Lasek's relation (18). This value falls into a range of densities of $10^{16} \div 10^{18}$ z/cm^3 reported by Nicholson (19) for aluminium alloys. Herman, Cohen and Fine (20) have estimated the zone radius of 18Å,

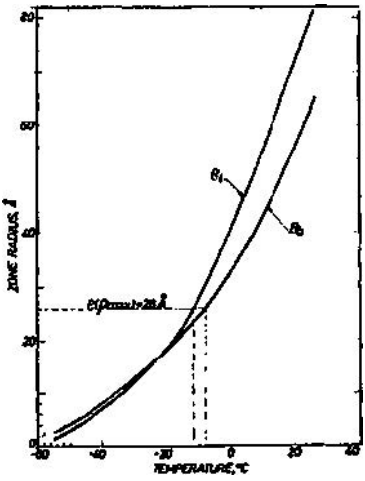


Fig.8. The variation of the zone radius with isochronal ageing temperature (2 min.at each temperature in steps of 20°K).

and, starting from SAS results, the same authors have found the radius of 9Å for an Al-5.3at%Zn alloy. Gerold and Schweizer (21) have reported the zone radius of 27Å for an Al-6.8at%Zn alloy aged at 293°K. Similar results were obtained by Guinier (6). The relation $\overline{2L}=2R.Z^{-1/3}$ shows that the zone distance depends on the zone radius 2L≈40R.

The proposed model is found to be valid for an early stage in the zone forming process. The SAS method is not accurate enough to discover G.P. zones less than 10Å. A better way would be to follow the zone growth by resistivity measurements and then to calculate the zone radius. The kinetic model presented here yields the possibility of calculation of the zone radius from resistivity data. In spite of the same uncertainties in the kinetic parameter determination, the values estimated from the model are in good agreement with those predicted by the other authors.

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