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## $\delta'$ GROWTH ON DISLOCATIONS IN Al -2.27 WT% Li

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### Abstract

The growth behavior of  $\delta'$  precipitates on dislocations in an Al -2.27 wt% Li alloy has been studied by TEM. The  $\delta'$  particle size was measured as a function of time and temperature in samples isothermally aged in the range between 210°C and 250°C. The experimental results show that the mean particle radius increases with time according to a power law dependence with an exponent ranging from 0.51 to 0.56. The activation energy for diffusion of Li atoms estimated from these results indicates that pipe diffusion is a contributing mechanism for precipitate growth. The effect of volume diffusion and pipe diffusion will be discussed and a model will be proposed to explain the experimental data.

### Introduction

The properties of a material are often influenced by the heterogeneous precipitation which can occur on dislocations and grain boundaries. Thus, there is a basic interest in understanding how such defect structures affect the precipitation process. Dilute Al-Li alloys undergo a phase transformation producing metastable precipitates of composition  $\text{Al}_3\text{Li}$ , i.e.  $\delta'$  phase. The precipitates are ordered with the  $\text{L1}_2$  structure, spherical and coherent with a very small elastic strain. The goal of this work is to correlate  $\delta'$  heterogeneous growth kinetics with previous models purported to explain such kinetics.

The theories accounting for the assistance provided to growing precipitate particles by defect structures have often dealt with the way these defects alter the flow of excess solute from the super-saturated matrix to the growing particles. Examples of such theories include the grain boundary "collector plate" of Aaron and Aaronson [1], the formulation by Cottrell and Bilby of the stress-assisted diffusion of solute to dislocations [2], and the analysis by Ham of cylindrical diffusion to dislocation line sinks [3]. Experimentally, the role of dislocations in assisting the growth of heterogeneous precipitate particles is best reflected in observations of the growth kinetics of fine scale particles which are still in intimate contact with catalyzing dislocation lines.

This paper describes the experimental observations on the  $\delta'$  initial growth behavior on dislocations in the aging temperature range 210°C to 250°C. An attempt is made to explain the role of dislocations on the growth kinetics of  $\delta'$  phase from a theoretical stand point based upon existing theories [2,3].

## Experimental Procedure

A single binary alloy of Al - 2.27 wt% Li was prepared by the Reynolds Metals metallurgical laboratory where high purity materials were induction melted and cast in an argon atmosphere. To obtain sufficient dislocation structure and sub-boundaries the alloy was cold rolled to 50% reduction in area prior to heat treatment. Samples of the thin sheet material encapsulated in an Ar environment were solution heat treated for 15 minutes at 550°C in a high temperature salt bath, followed by isothermally transforming the homogeneous alloy at temperatures from 210°C to 250°C for several aging time sequences listed in Table I. Samples were prepared for transmission electron microscopy (TEM) employing a twin-jet electropolisher and examined with a 120 keV TEM. Direct counting was used to determine the number of precipitates per unit length of dislocation. Where necessary,  $\delta'$  particle diameters were measured on centered dark-field micrographs imaged from  $\delta'$  superlattice reflections.

**Table I. Heat treatment conditions for Al - 2.27 wt% Li alloy**

Aging temperature (°C)	Aging time (min)
210	1, 2, 5, 10, 30, 60, 120, 180
230	5, 15, 30, 60, 90, 120, 180
240	15, 35, 45, 60, 90, 120, 155, 180
250	45, 60, 90, 120, 150, 180

## Background and Theory

Dislocations can affect long range diffusion in two ways. First, the stress field associated with the dislocation can exert an attractive force on misfitting solute atoms in the surrounding solid solution. Second, the dislocation itself serves as a high diffusivity path for the flow of solute. Both mechanisms will tend to enhance the growth kinetics of particles attached to the dislocation line. The earliest treatments of the effect of dislocations on precipitation were given by Cottrell-Bilby [2] and Ham [3]. In their papers, the dislocations are assumed to act as 'collector lines' for excess solute (in analogy to the grain boundary 'collector plate' of Aaron and Aaronson [1]). Any solute, beyond the equilibrium amount, which arrives at the core, is assumed to be immediately transported along the dislocation pipe and incorporated into the growing particles. The rate-limiting solute flow into this line sink from the supersaturated matrix therefore determines the heterogeneous precipitation kinetics.

Fick's first law for diffusion in the presence of the stress field of a dislocation can be written:

$$J = -D(\nabla C + \frac{C}{kT} \nabla W), \quad (1)$$

where J, D and C are the solute flux, diffusivity within the matrix and solute concentration, respectively, W is the attractive potential exerted on a misfitting solute atom at a distance r from the dislocation line, and kT has its usual meaning.

Taking into account the coupling between concentration gradients and the drift flux is a complication difficult to treat mathematically. As a simplification, Cottrell and Bilby [2] chose to limit their consideration to systems of initially uniform concentration of solute, aged for only short times. For this case,  $\nabla C = 0$  and  $C = C_0$  (the initial solute concentration). During the initial steps of aging, then

$$J = -DC_0 \frac{\nabla W}{kT} \quad (2)$$

and all of the solute flux is effectively due to drift in the dislocation potential field. It is predicted [2] from linear elasticity theory that the potential field for an edge dislocation is given by

$$W(r, \theta) = -A \frac{\sin(\theta)}{r} \quad (3.1)$$

and

$$A = (\mu \mathbf{b} / 3\pi) \frac{(1 + \nu)}{(1 - \nu)} \Delta v, \quad (3.2)$$

where  $\mu$  is the shear modulus of the matrix,  $\mathbf{b}$  is the Burger's vector of the dislocation line, and  $\Delta v$  is the volume difference between matrix and solute atoms. The potential defined by eqs.(3) is the case we are presently concerned with since  $\delta'$  has been shown to nucleate primarily on edge dislocations [4]. Using the approximation of eq.(2) combined with eq.(3), Cottrell and Bilby derived the amount of solute  $N(t)$  accumulated per unit length of dislocation by time  $t$  during an aging treatment as:

$$N(t) = \left(\frac{\pi}{2}\right)^{1/2} 3C_0 \left(\frac{AD}{kT}\right)^{2/3} t^{2/3} \quad (5)$$

An analytical solution to eq.(2) with the same potential was later obtained by Ham [3]. The following boundary conditions were applied:

$$r \rightarrow \infty \quad C = C_0 \quad (6.1)$$

$$r \rightarrow r_c \quad C = 0 \quad (6.2)$$

Ham first showed that at steady state the problem can be mathematically reduced to a pure diffusion problem without the external field, if the dislocation was replaced by a cylinder of radius  $R_c$ :

$$R_c \cong e^\gamma \frac{A}{4kT}, \quad (7)$$

where  $\gamma$  is the Euler constant ( 0.577) and  $R_c$  is the effective capture radius. Hence, the cylinder with radius  $R_c$  has the same probability of capturing the solute atoms as the dislocation with its associated stress field. The numerical integration of the corresponding formulation showed that

Ham's solution contains an initial transient corresponding to the  $t^{2/3}$  law in eq.(5) but tends to a higher growth rate at large times as:

$$N(t) \propto \left(\frac{Dt}{R_c}\right)^{0.8}, \quad (8)$$

where the dimensionless time  $\tau = \frac{Dt}{R_c}$  is in the range from 10 to  $10^4$ . In the present work, for a

lower limit,  $D= 9.01 \times 10^{-16}$  cm<sup>2</sup>/s and  $t= 5$  min at 210 °C gives  $\left(\frac{Dt}{R_c}\right)$  as 26.72; for an upper limit,

$D=8.96 \times 10^{-15}$  cm<sup>2</sup>/s and  $t=180$  min at 250 °C yields  $\left(\frac{Dt}{R_c}\right)$  as  $1.12 \times 10^4$ . Hence, the theoretical

considerations stated above hold for the heat treatment conditions used in our experiment. If the solute joins precipitate particles upon arriving at the dislocation core, then  $N(t) = n\rho V(t)$ , where  $V(T)$  is the mean precipitate volume at time  $t$ ,  $\rho$  is the number density of solute atoms in the particles, and  $n$  is the number of precipitates per unit length of dislocation line. Hence,

$$V(t) = \frac{N(t)}{n\rho} \quad (9)$$

For spherical particles,  $V(t) = \frac{\pi}{6} d^3$ , where  $d$  is the mean diameter of particles. Therefore, particle growth kinetics of the forms  $d \propto t^{0.22}$  and  $d \propto t^{0.26}$  would be expected from eq.(5) and eq.(8), respectively.

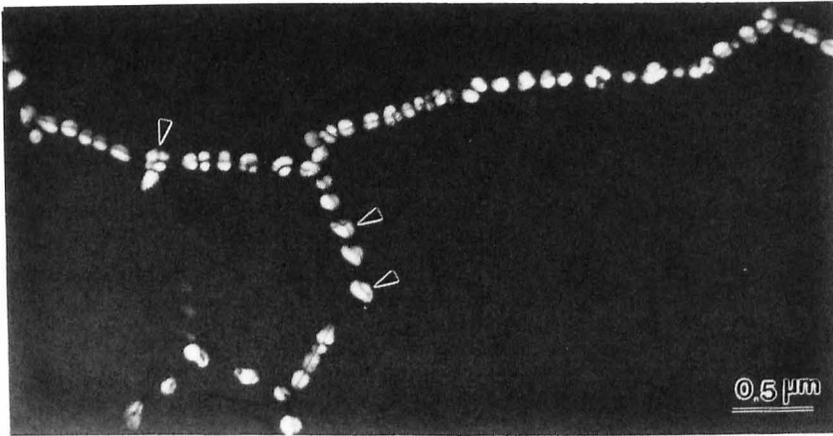
Ham considered the influence of an individual dislocation line on diffusion in an array of dislocations with density  $\rho_d$  by taking the distance  $R_o = (\pi\rho_d)^{-1/2}$ .  $R_o$  was compared to the characteristic bulk diffusion distance at time  $t$ ,  $(Dt)^{1/2}$ . If  $(Dt)^{1/2} \ll R_o$ , the diffusion to any one dislocation is independent of the matrix diffusion to other dislocations; if  $(Dt)^{1/2} \geq R_o$ , i.e. at longer aging times, interference is expected to occur between neighboring dislocations. In this study, the dislocation density of the samples was estimated to be  $\rho \cong 10^9$  cm<sup>-2</sup>. This would give  $R_o \cong 1.784 \times 10^{-5}$  cm as a lower bound radius for an average dislocation's interference field. Using the largest aging time  $t = 180$  min and highest temperature diffusivity  $D= 8.96 \times 10^{-15}$  cm<sup>2</sup>/s, the diffusion length  $(Dt)^{1/2} = 9.837 \times 10^{-6}$  cm which is much less than  $R_o$ . Therefore, dislocations can essentially be treated as "isolated cylinders" in our present work.

## Results and Discussion

### $\delta'$ Growth on Dislocations

Experiments were performed to observe  $\delta'$  nucleation on dislocations for early stages of aging (i.e.  $\leq 3$  hours) and at small undercooling heat treatment conditions where homogeneous nucleation does not occur. TEM investigation revealed that  $\delta'$  particles nucleate solely on dislocations. For example, the  $\delta'$  centered dark-field micrograph in Fig. 1 shows  $\delta'$  particles associated with dislocation lines in a sample aged at 230°C for 30 minutes. As the precipitate has a coherent interface with the matrix,  $\delta'$  nucleates and grows on dislocations without destroying

the core structure as indicated by arrows in Fig. 1. Using two-beam analysis techniques at the orientation close to the [110] zone of Al, it has been shown that  $\delta'$  preferentially nucleates on dislocations with strong edge character. Further, since the strain associated with the formation of  $\delta'$  is negative,  $\delta'$  always occurs at the compressive side of the dislocations [4].



**Figure 1.**  $\delta'$  centered dark field image where the sample was aged at 230°C for 30 minutes.

In order to analyze the kinetics of growth of  $\delta'$  particles at the dislocations, an average of 200 particle diameters were measured at each aging time  $t$  and temperature  $T$ . The relationship between the logarithm of the mean diameter,  $\log d$ , and the logarithm of the time,  $\log t$ , was determined to be linear. Table 2 shows the good agreement between the experimental points and a linear regression fitted curve, and suggests a relationship of the form

$$d = c't^n, \tag{10}$$

where  $n$  is in the range from 0.51 to 0.56, with an average value of 0.54.

**Table 2. The linear regression results of  $\log d$  vs.  $\log t$  at different temperatures (the average of  $n$  is 0.541)**

Aging temperature (°C)	Index $n$	R (chi - square)
210	0.566	0.99
230	0.551	0.98
240	0.537	0.99
250	0.511	0.98

Fig. 2 shows the volume fraction of  $\delta'$  per unit length of dislocation obtained by multiplying the mean particle volume,  $V(t)$ , i.e.  $\frac{\pi}{6} d^3$ , by the number density of  $\delta'$ , as a function of aging time. The positive slope of the data points for each temperature condition (except for the last two points at 250 °C) indicates that  $\delta'$  is still in the growth stage for the aging time period analyzed. If

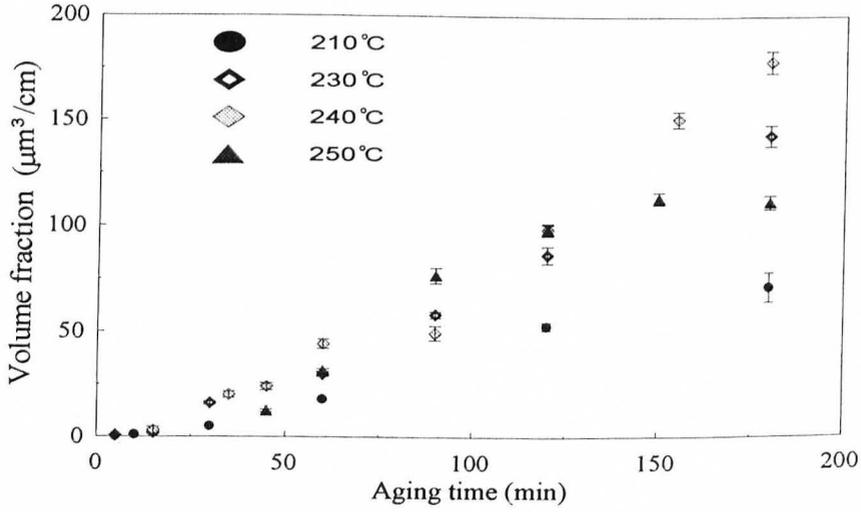
$\delta'$  growth kinetics are diffusion-controlled, rather than only taking into account a drift under a dislocation stress field, it is reasonable to suppose that  $c''$  in eq.(10) is proportional to a diffusion coefficient  $D$ . Therefore, we have

$$d = c'Dt^n \tag{11.1}$$

and

$$D = D_0 \exp\left(-\frac{Q}{kT}\right), \tag{11.2}$$

where  $Q$  is the activation energy for Li diffusion occurring during  $\delta'$  growth,  $D_0$  is the pre-exponential diffusion coefficient, and  $c'$  is a temperature independent coefficient. From eq.(11),  $Q$  can be found from the plot of  $\log(d/t^n)$  vs.  $1/T$ . The slope obtained indicates an activation energy of  $\sim 0.517$  eV; this is much lower than the reported activation energy of 1.25 eV for volume diffusion of Li in an Al matrix [5].



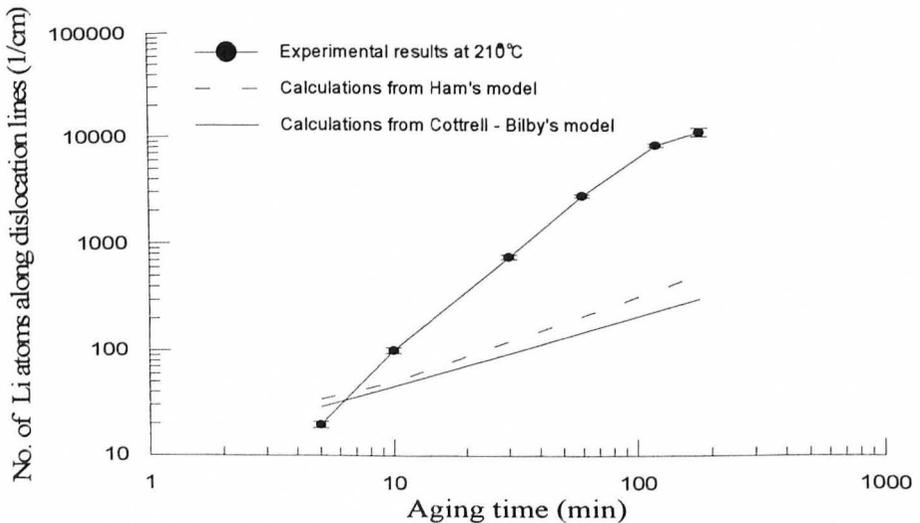
**Figure 2.**  $\delta'$  volume fraction along dislocations for temperatures used in the present work.

Discussion

The two time regimes, i.e.  $\tau = \left(\frac{Dt}{R_c^2}\right) \sim 10 - 10^4$  and  $(Dt)^{1/2} \ll R_0$ , hold for the aging time used in

this experiment so that the theories by Cottrell-Bilby and Ham stated above are expected to explain the experimental results. In Fig. 3, calculations based upon those theories for the aging temperature of 210°C are shown and compared with the corresponding experimental data. Several important features from this plot should be pointed out: 1) The initial kinetics show close agreement with either the pure drift treatment by Cottrell-Bilby or the longer time approach by Ham. 2) The calculations based on the present experimental measurements reveal that the number of Li atoms accumulated per unit length of dislocation increases more rapidly than calculated from either theory at longer times. 3) The subsequent kinetic growth rate reflected by the estimated

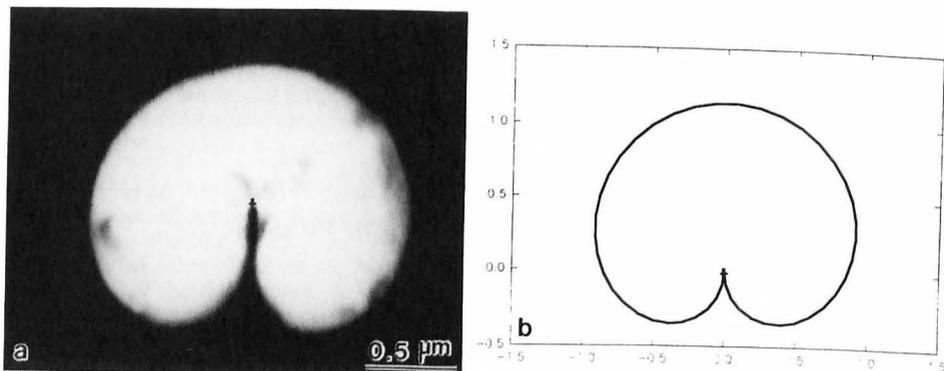
value of the activation energy for Li, is much faster than one controlled only by volume diffusion to the dislocation pipes [2,3].



**Figure 3. A comparison between experimental results and theoretical calculations for the aging temperature of 210°C.**

The disagreement between the two models and the experimental results imply that the assumptions of drift flux under the interaction potential by Cottrell-Bilby and dislocation-sink pipe by Ham do not account for the experimental measurements and suggest that the assumptions may not always be justified. Consider a growing spherical precipitate of  $\delta'$  lying on a dislocation, the growth rate depends on the total number of Li atoms arriving at the surface of the particle from the bulk plus the number arriving from the dislocation pipe region. Within short range or early aging times the strain effect due to dislocations needs to be taken into account. As shown in Fig. 4, the calculated Li atom depleted area by Cottrell-Bilby's model can be compared with the unique  $\delta'$  morphology associated with an edge dislocation core where the sample was aged at 260°C for 30 minutes. The pipe diffusion coefficient is much larger than the volume diffusivity but the area of intersection of the dislocation with  $\delta'$  represents only a small fraction of the total surface area. At high temperatures, i.e. 210 °C - 250 °C, the two contributions to the flux, bulk and dislocations, may be comparable. Under this circumstance, a finite rate limitation for solute transfer into the precipitated phase must be considered. It is suggested that during the  $\delta'$  growth process both dislocation pipe and volume diffusion are operative.

Furthermore, the formation of a second phase may involve a change in volume which could then lead to transient changes in the potential interaction of the dislocation with solutes still in solution. The dislocation which is a source or sink for vacancies may climb at longer aging times, and so move a short distance away from the precipitates already formed which we have also observed. The interaction between solute atoms and dislocations will therefore be changed.



**Figure 4. (a)  $\delta'$  centered dark-field image shows the unique precipitate morphology associated with the dislocation which is located in the micrograph center and is indicated by the mark. (b) Calculated solute depleted region profile around an edge dislocation according to Cottrell-Bilby theory [2].**

#### Conclusions

The theories on growth kinetics of heterogeneous nucleation on dislocations have been assessed experimentally in the Al-Li system in which  $\delta'$  nucleates on dislocations at small undercooling. The experimental results show that there is a disagreement with existing theories. The  $\delta'$  growth rate on dislocations discovered in this work is much faster than that predicted by theories at longer aging times. It is suggested that at high temperatures, i.e. 210 °C - 250 °C, since volume diffusion and pipe diffusion are comparable, the solute flux which assists  $\delta'$  growth is due to the contribution from both pipe diffusion and volume diffusion. The rate limiting diffusion along dislocations has to be taken into account. The details of our modified model will be presented in a later publication.

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#### References

1. H.B. Aaron and H.I. Aaronson, Acta Metall. **16**, (1968), 789.
2. A.H. Cottrell and B.A. Bilby, Proc. Phys. Soc. (London) **A62**, (1949), 49.
3. F.S. Ham, J. Appl. Phys. **30**, (1959), 915.
4. W.A. Cassada, G.J. Shiflet and W.A. Jesser, Acta Metall. **40**, (1992), 2101.
5. M. A. Krishtal, M.A. Vyboyshchik and V.A. Sudnik, Fiz. metal. metalloved. **36**, No.5, (1973), 1103.