# **Effect of Stretching on the Precipitation Kinetics of an AI-2.0Li-2.8Cu-0.5Mg(-0.13Zr) Alloy**

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The influence of stretching on the precipitation kinetics of an Al-2.0Li-2.8Cu-0.5Mg(-0.13Zr) alloy has been quantitatively investigated using transmission electron microscopy (TEM) and hardness testing. The microstructure of the alloy consists primarily of  $\delta'$ , S', and  $T_1$  phases. Stretching exerts little influence on the coarsening kinetics of  $\delta'$  phase. The activation energy for coarsening is estimated to be  $\sim$  100 kJ/mole, regardless of whether the alloy is unstretched or stretched. The volume fraction of  $\delta'$  phase, however, is significantly reduced in the stretched condition. The stretching treatment greatly accelerates the nucleation kinetics of  $T_1$  phase at the expense of S' phase; however, the growth rate of  $T_1$  phase (and also of S' phase) is significantly reduced in the stretched condition due to overlapping of the diffusion field. A kinetic model is presented that addresses this problem. The model successfully predicts the effect of stretching on the lengthening rate of  $T_1$  plates. The activation energies for the lengthening of  $T_1$  plates and S' rods are  $\sim$ 100 to 110 kJ/mole and  $\sim$ 110 to 120 kJ/mole, respectively, regardless of the condition of stretch. It is concluded that, for both unstretched and stretched material, the growth of the  $T_1$  and S' phases is controlled by the diffusion of copper along dislocations. The nucleation of S' phase tends to occur at dislocations with a Burgers vector that is nearly parallel to the  $[010]_{S'}$  direction, which is the direction that exhibits maximum misfit.

## I. INTRODUCTION

AL-Li-Cu-Mg alloys are of great commercial interest because they offer high stiffness and lightness. The principal strengthening agents in ternary A1-Li-Cu alloys are the  $\delta'$  (Al<sub>3</sub>Li) and  $T_1$  (Al<sub>2</sub>CuLi) phases, particularly in the stretched condition.  $[1,2]$  The addition of magnesium is advantageous from a density standpoint and offers the possibility of utilizing additional precipitation of S'  $(Al<sub>2</sub>CuMg)$  phase.

The  $\delta'$  phase has an ordered L1<sub>2</sub> structure. T<sub>1</sub> phase has a hexagonal crystal structure ( $a = 0.497$  nm,  $c =$ 0.935 nm), with an orientation relationship with the matrix  $of^{[3]}$ 

$$
(0001)_{\text{T}_1} \parallel (111)_{\text{Al}}; \qquad [10\bar{1}0]_{\text{T}_1} \parallel [\bar{1}10]_{\text{Al}} \parallel
$$

S' phase in A1-Li-Cu-Mg alloys has an orthorhombic crystal structure, with  $a = 0.404$  nm,  $b = 0.925$  nm, and  $c = 0.718$  nm. The growth direction of S' lath is [100]s,, and it has the following orientation relationship:[4]

$$
\begin{aligned} [100]_{S'} \parallel [100]_{Ai}; & [010]_{S'} \parallel [021]_{Ai}; \\ [001]_{S'} \parallel [01\bar{2}]_{Ai} \end{aligned}
$$

The equilibrium S phase in ternary A1-Cu-Mg alloys has the same crystal structure and orientation relationship, but slightly different lattice parameters.<sup>[4]</sup> It is difficult to distinguish between S' and S in AI-Li-Cu-Mg alloys, and no distinction has been attempted in this article.

The  $T<sub>i</sub>$  phase is an equilibrium phase and is known to nucleate heterogeneously in A1-Li-Cu alloys within the composition range of commercial interest, probably *via*  a stacking fault mechanism<sup>[5]</sup> or *via* the dissociation of perfect dislocations in the vicinity of jogs.<sup>[6]</sup> Stretching is known to accelerate greatly the nucleation kinetics of  $T_1$  phase,  $[7]$  probably through the promotion of dense areas of dislocation jogs.

The S' precipitation is also known to occur primarily by heterogeneous nucleation in alloys of medium magnesium content ( $\sim$ 0.7 wt pct) and low copper content  $(-1.2 \text{ wt } \text{pc})$  (a typical composition of 8090 Al-Li alloy).<sup>[8]</sup> The stretching treatment encourages heterogeneous precipitation of fine S' particles at the expense of  $T_1$  phase.<sup>[9,10,11]</sup> Homogeneous precipitation of S' phase is promoted in alloys of either high magnesium content  $(-1.0 \text{ wt } \text{pc})$  or medium copper content  $(\sim 2.0$  wt pct). <sup>[12,13]</sup> However, a predominant precipitation of  $T_1$  phase is observed in low-magnesium  $(\sim 0.5$  wt pct) alloys.<sup>[10]</sup> The high-copper ( $\sim 2.5$  wt pct) alloys that contain a significant amount of magnesium  $(>-0.5$  wt pct) have received comparatively little attention: increasing the copper content tends to promote  $\theta'$  $(Al<sub>2</sub>Cu)$  and T<sub>1</sub> precipitation in place of S' precipitation. The stretching treatment suppresses  $\theta'$  precipitation in favor of  $T_1$  precipitation. The high magnesium content  $(>\sim 1$  wt pct) tends to promote S' precipitation. However, this case can lead to the precipitation of  $T_2$  $(Al<sub>6</sub>CuLi<sub>3</sub>)$  phase, particularly in alloys with very high copper contents ( $>$  -3 wt pct). [14,15] T<sub>2</sub> phase exerts little hardening effect. Stretching alters the precipitation kinetics of both the  $T_1$  and S' phases in these high-copper alloys and can significantly affect the balance of the two phases. However, no detailed investigation of this effect has been reported. Furthermore, most previous investigations of precipitation in A1-Li-Cu-Mg alloys have been strictly qualitative. Only a few studies have focused on detailed precipitation kinetics, particularly of  $T_1$  and S' phases.

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The present investigation was undertaken to measure quantitatively the precipitation kinetics of  $\delta'$ ,  $T_1$ , and S' phases in an A1-2.0Li-2.8Cu-0.5Mg (wt pct) alloy and to evaluate the effect of stretching on the precipitation kinetics of the three phases.

# **II. EXPERIMENTS**

The alloy, with a composition of A1-2.02Li-2.78Cu-0.48Mg-0.13Zr (wt pct), was cast in a vacuum induction furnace under an argon atmosphere using high-purity metals. It was homogenized, then hot- and cold-rolled to 2-mm-thick sheet. Samples were solution-treated at 530  $\degree$ C for 30 minutes, quenched, and subsequently aged at elevated temperatures in either a silicon-oil bath or a salt bath controlled to  $\pm 1$  °C. The aging behavior was measured using a Vickers hardness tester. Thin-foil specimens for transmission electron microscopy (TEM) were prepared by electrolytic polishing in a solution of 30 pct HNO<sub>3</sub> and 70 pct CH<sub>3</sub>OH at  $\sim$  -20 °C. The TEM observations were made at 200 keV using a PHILIPS CM20\* microscope outfitted with scanning transmission electron microscopy (STEM) equipment. The foil thick-

\*PHILIPS CM20 is a trademark of Philips Electronic Instruments Corporation, Mahwah, NJ.

ness was measured using the contamination spot technique.

Correction for the effect of particle overlapping and truncation<sup>[16]</sup> was applied for the  $\delta'$  volume fraction measurement in the underaged condition. In the overaged condition, only the truncation effect was taken into account. No correction for truncation was applied to the measurement of  $\delta'$  particle sizes, because they were very small in comparison to the foil thickness. Maximum sizes of  $T_1$  plates and S' rods were measured to investigate their growth kinetics. In this case, no correction for truncation was required if the particles inclined with respect to the foil surface were embedded within the foil. The edge-on variants were actually used to measure the  $T_1$  plate sizes. There are four variants in the  $T_1$  phase, and it was assumed that all had equal populations. There are three types of S' rods, corresponding to the three  $\langle 100 \rangle$ <sub>AI</sub> growth directions. In the unstretched condition, the population of each type was observed to be approximately the same size. However, only one type of rod was frequently observed in material in the stretched condition. The populations of  $T_1$  and S' phases differed from location to location. To minimize error, measurements were performed on several different grains.

# III. **RESULTS**

Hardness measurements indicated that stretching significantly increases alloy hardness during the early stage of aging (Figure 1). This increase can be attributed not only to the strain hardening effect but also to an acceleration of aging kinetics brought on by the stretch treatment.

The microstructure of the alloy studied is complex because of the simultaneous presence of S' and  $T_1$  phases, in addition to  $\delta'$  phase. The S' phase has 12 variants,



Fig. 1 -- Variation of Vickers hardness as a function of aging time at  $190 °C$ .

four of which belong to the same growth direction, *i.e.,*   $(100)_{Al}$ . The T<sub>1</sub> phase has four  $\{111\}$  variants. To help characterize the microstructure, a mixed diffraction pattern containing all the variants of the  $S'$  and  $T_1$  phases must be constructed. Figure 2 illustrates an example of the procedure in the presence of S' phase. Figure  $2(a)$ represents a mixed stereogram showing one of 12 S' variants:  $[100]_{S'}$  ||  $[100]_{Al}$ ;  $[010]_{S'}$  ||  $[012]_{Al}$ ;  $[001]_{S'}$  ||  $[0\overline{2}1]_{Al}$ . The zone axis [110] of S' phase becomes parallel (within 0.51 deg) to the [112] matrix zone axis. This is rotated to bring the [112] matrix zone axis to the projection center (Figure 2(b)). The mixed diffraction pattern for this variant is then constructed (Figure  $2(c)$ ). The structure factors for S' phase are calculated using the atomic structure proposed by Mondolfo. [17] Figure  $\bar{3}$ summarizes the result of the complete construction, including all the S' phase variants.

A similar approach has been employed to construct the mixed diffraction pattern in the presence of  $T_1$  phase. The result (Figure 4) is consistent with a previous report.<sup>[18]</sup> Figure 5 illustrates a final mixed diffraction pattern that includes S',  $T_1$ , and  $\delta'$  phases. An example of the observed diffraction pattern is shown in Figure 5(b), which is consistent with the calculated pattern in Figure 5(a), except for the presence of streaks. Four streaks are visible in Figure  $\overline{5(b)}$ —along [111], [201],  $[02\overline{1}]$ , and  $[1\overline{1}0]$ . The streak along  $[11\overline{1}]$  is due to the edge-on  $T_1$  plates on the (111) plane. The other streaks are due to three S' laths grown along [010], [100], and [001] in the matrix. The  $\bar{S}'$  laths grown along [010] and [100] are gradually inclined with respect to the foil surface, whereas the one grown along [001] is steeply inclined.

Figure 6 illustrates  $\delta'$  dark-field (DF) images in various conditions of stretch. Homogeneous nucleation is evident in all cases. Several  $\theta'$  plates coated by  $\delta'$  phase at low temperature are visible in the unstretched condition (Figure  $6(a)$ ). Stretching, however, tends to suppress  $\theta'$  plates (Figure 6(b)). No  $\theta'$  plates are observed



Fig. 2-Procedure for constructing a mixed diffraction pattern including S' phase: (a) mixed stereogram showing the orientation relationship  $[100]_{S'}$  ||  $[100]_{A}$ ;  $[010]_{S'}$  ||  $[012]_{A}$ ;  $(b)$  mixed stereogram resulting from rotation of the zone axis  $[112]_{A1}$  to the projection center; and (c) mixed diffraction pattern corresponding to the  $[112]_{\text{Al}}$  zone axis.



Fig. 3-Mixed diffraction pattern of  $z = [112]_{A1}$  in the presence of S' phase:  $+$ , reflections from the matrix;  $\blacksquare$ , reflections from the S' phase;  $\Box$ , reflections arising from the double diffraction effect.



Fig. 4-Mixed diffraction pattern of  $z = [112]_{A1}$  in the presence of  $T_1$  phase: +, reflections from the matrix;  $\bullet$ , reflections from the  $T_1$ phase. Includes the effect of extension of reciprocal lattice points due to the thinness of  $T_1$  plates.

when the alloy is aged at temperatures above  $\sim$ 175 °C (Figure 6(c)).

The  $\delta'$  particle sizes have been measured using DF images such as those shown in Figure 6. It was shown $f<sup>[19]</sup>$ that the  $\delta'$  coarsening kinetics are best described by modified Lifshitz-Slyozov-Wagner theory,<sup>[20]</sup> apart from the particle distribution function. The theory predicts that

 $r^{3}-r_{0}^{3}=K(\phi)\cdot t$ 

and

$$
K(\phi) = \left(\frac{8\gamma C_{\rm e}DV_{\rm m}^2}{9RT}\right)\left(\frac{\rho(\phi)}{\rho(0)}\right) \tag{1}
$$

where  $\phi$  is the volume fraction,  $\gamma$  is the interfacial energy,  $C_{\rm e}$  is the equilibrium concentration, D is the lithium diffusivity, and  $\rho(\phi)$  is the volume-fractiondependent function. The cube of particle size plotted against aging time (Figure 7) shows a good linear relationship from the early stage of aging, suggesting an early start of the coarsening stage in agreement with previous reports. [21,22,231 Note, in particular, that stretching treatment has no significant influence on the  $\delta'$  coarsening kinetics. Measurement of particle sizes showed them to be similar in both conditions.



Fig. 5--Mixed diffraction pattern of  $z = [112]_{A1}$  including S', T<sub>1</sub>, and  $\delta'$  phases: (a) constructed pattern; (b) observed selected-area diffraction pattern (SADP). Note in (b) the presence of a streak *along*  [111] due to  $T_1$  phase and streaks along three directions--[021], [201], and  $\overline{[110]}$ —due to S' phase.

The results of  $\delta'$  volume fraction measurements (Table I) indicate a nearly constant value  $(\sim 2.7 \text{~pot})$ from the early stage of aging at temperatures near 175  $\degree$ C, confirming the early onset of a coarsening stage. The volume fraction tends to decrease at a later stage, particularly at high temperature ( $\sim$ 190 °C). This can probably be attributed to the increasing precipitation of  $T_1$  phase and possibly also of  $\delta$  phase. Results further show that stretching reduces the  $\delta'$  volume fraction by  $\sim$ 10 pct. This is due to an increase in the volume fraction of  $T_+$  phase.

Equation [1] can be rearranged to give

$$
\ln\left(\frac{K(\phi)\cdot T}{C_e}\right) = \ln\left(\frac{8\gamma D_0 V_m^2 \rho(\phi)}{9R\rho(0)}\right) + \left(\frac{-Q}{RT}\right)
$$
 [2]

where  $\hat{Q}$  is the activation energy for lithium diffusion. Figure 8 shows the plot  $\ln (K(\phi) \cdot T/C_e)$  vs 1/T. The activation energies can be estimated from the slope: 102.9 kJ/mole and 105.8 kJ/mole in the unstretched and stretched conditions, respectively. These energies are somewhat lower than those in an A1-Li-Cu ternary alloy ( $\sim$ 120 to 130 kJ/mole)<sup>[24,25]</sup> and in Al-Li binary alloys (~120 to 140 kJ/mole). [22,26,27,28]

Figure 9 illustrates examples of  $S'$  and  $T_1$  phases in the unstretched and stretched conditions. Both cases contain S' and  $T_1$  phases. The proportion of each phase changes drastically as a result of stretching. In the unstretched condition (Figure 9(b)), there are significant amounts of edge-on  $T_1$  plates and of S' rods grown along [010] (projection direction:  $\overline{152}$ ]). In the stretched condition (Figure 9(d)),  $T_1$  plates become much finer and more numerous, whereas S' rods tend to be finer but scarce. This indicates that stretching promotes the  $T_1$  nucleation rate at the expense of  $S'$  precipitation---an observation that is in direct contradiction with previous reports regarding low-copper quaternary alloys.<sup>[9]</sup> The discrepancy probably arises from the dependence of the relative stability of the two phases on the coppermagnesium ratio.

Examination of SADPs indicates, in the unstretched condition (Figure 9(a)), the presence of three streaks (along  $[0\overline{2}1]$ ,  $[\overline{2}01]$ , and  $[\overline{1}10]$ ) due to S' rods grown along three  $(100)_{\text{Al}}$  directions. However, in the stretched condition (Figure 9(c)), only one streak appears along  $[201]$ , which is due to rods grown along  $[010]_{Al}$ . Numerous observations frequently have indicated that S' rods grow along only one of three  $(100)_{A1}$  directions, the other two being nearly absent. This is in clear contrast to the unstretched case, where the rods grown along three (100) directions have nearly equal populations.

The volume fraction of  $T_1$  plates has been measured (Table I) using DF images such as those shown in Figure 9. The volume fraction gradually increases with aging time, which suggests that  $T_1$  precipitation and  $\delta'$ precipitation have different growth stages. Stretching abruptly increases the  $T_1$  volume fraction--e.g., from  $\sim$ 2 pct to  $\sim$ 4 pct at 175 °C. This effect is less pronounced at a high temperature of 190  $^{\circ}$ C. At this temperature, the volume fraction tends to increase rapidly even in the unstretched condition, probably because of a high diffusion rate.

The sizes of  $T_1$  plates and S' rods have been measured using DF images. According to the Zener-Hillert theory, $^{[29]}$  the lengthening rate of solute-rich plate edges (of  $\beta$  phase) is linear as long as the radius of curvature, r, remains constant:

$$
\frac{dL}{dt} = \frac{D(C_0 - C_\alpha^{\alpha\beta})}{2kr(C_\beta^{\beta\alpha} - C_\alpha^{\alpha\beta})}
$$
 [3]

where  $C_0$  is the initial alloy composition,  $C_\alpha^{\alpha\beta}$  is the equilibrium composition in the matrix with respect to the  $\beta$  $(T_1)$  phase,  $C^{\beta\alpha}_{\beta}$  is the equilibrium composition of  $\beta$ phase, and k is a constant. Figure 10 plots the maximum plate diameter *vs* aging time. The stretched condition exhibits a much slower growth rate, an observation in agreement with a previous report on an AI-Li-Cu ternary alloy.<sup> $[7]$ </sup> Because the volume fraction is large in the stretched condition, the number density per unit volume, *Nv,* is expected to be larger in this condition as well. Measurement indicated that *Nv* is promoted by an order of magnitude, *i.e.*, from  $\sim 10^2/\mu m^3$  in the unstretched condition to  $\sim 10^3/\mu m^3$  in the stretched condition (near peak aging condition at 175  $^{\circ}$ C). Figure 10 indicates a







(b)



(c)

Fig. 6-Dark-field images taken using superlattice reflection due to  $\delta'$  phase: (a) sample aged at 160 °C for 96 h in the unstretched condition; (b) sample aged at 160  $^{\circ}$ C for 96 h in the 5 pct stretch condition; and  $(c)$  sample aged at 190 °C for 8 h in the unstretched condition.

significant deviation from the linear growth rate expected from Eq. [3]. This discrepancy is more pronounced in the stretched condition, suggesting that it is primarily due to the effect of overlapping diffusion field.

In an attempt to solve this problem,  $C_0$  in Eq. [3] has been replaced with time-dependent  $C_0(t)$  as a first approximation, *i.e.,* 

$$
\frac{dL}{dt} = \frac{D(C_0(t) - C_\alpha^{\alpha\beta})}{2kr(C_\beta^{\beta\alpha} - C_\alpha^{\alpha\beta})}
$$
 [4]

It was further assumed that the supersaturation,  $C_0(t)$  –  $C_{\alpha}^{\alpha\beta}$ , varies sinusoidally with distance, as in the case of ingot homogenization.  $[30]$  The supersaturation at the center of the diffusion field becomes

$$
C_0(t) - C_{\alpha}^{\alpha\beta} = (C_0 - C_{\alpha}^{\alpha\beta}) \exp\left(\frac{-\pi^2 Dt}{\lambda^2}\right) \qquad [5]
$$

where  $\lambda$  is a linear measure of the diffusion field length. Note that Eq. [5] differs only slightly from the first-term approximation of the complete solution of diffusion equation at the boundary conditions, which are similar to those in the decarburization problem. $[31]$  Equation  $[4]$ is then

$$
\frac{dL}{dt} = K_1 \cdot D \cdot \exp\left(\frac{-\pi^2 Dt}{\lambda^2}\right) \tag{6}
$$

where

$$
K_1 = \frac{C_0 - C_{\alpha}^{\alpha\beta}}{2kr(C_{\beta}^{\beta\alpha} - C_{\alpha}^{\alpha\beta})}
$$

Integration gives

$$
L = K_0 \left[ 1 - \exp\left(\frac{-\pi^2 Dt}{\lambda^2}\right) \right]
$$
 [7]

where

$$
K_0 = K_1 \cdot \frac{\lambda^2}{\pi^2}
$$

If the exponent in Eq. [6] is small  $(<0.5)$ ,

$$
\frac{dL}{dt} \cong K_1 \cdot D\left(1 - \frac{\pi^2 Dt}{\lambda^2}\right) \tag{8}
$$

Integration yields

$$
\frac{L}{t} = K_1 \cdot D - K_2 \cdot D^2 \cdot t \tag{9}
$$

where

$$
K_2 = K_1 \cdot \frac{\pi^2}{2\lambda^2}
$$

Equation 9 predicts a linear decrease of  $L/t$  with t. The negative slope of the line is proportional to the square of the diffusion coefficient, and the intercept is directly proportional to the diffusivity. Figure 11 replots the data according to Eq. [9]. The result shows that a linear relationship is satisfied during the initial stage at high temperatures and that it extends to a longer time at low temperatures. The logarithms of the slopes and of the intercepts are plotted as a function of the inverse of absolute temperature in Figure 12. Analysis of the intercepts yields activation energies of 107.4 kJ/mole and 111.6 kJ/mole in the unstretched and stretched conditions, respectively. The corresponding activation energies from the slopes are 104.0 kJ/mole and 110.9 kJ/mole, respectively. The two results are in good agreement, which partly justifies the present model. There is no significant difference in activation energy



Fig. 7-Variation of the cubes of  $\delta'$  particle radii as a function of aging time at various temperatures, depending on the condition of stretch.

regardless of the condition of stretch, which suggests that the diffusion mechanism is the same in both conditions.

Figure 13 shows a similar plot for the case of S' rods in the unstretched condition. The activation energies are 113.3 kJ/mole and 123.1 kJ/mole from the intercepts and from the slopes, respectively. Measurement indicated that the number density in the stretched condition decreases to only  $\sim$ 10 pct of that of the unstretched condition. This is due to an acceleration of  $T_1$  precipitation in the stretched condition. It was difficult to test the stretching effect because of the scarcity of S' rods.

#### IV. DISCUSSION

The activation energy for  $\delta'$  coarsening is estimated to be  $\sim$ 100 kJ/mole, regardless of the condition of stretch. This value is somewhat lower than that reported for an Al-Li-Cu ternary alloy  $(\sim 120 \text{ to } 130$ kJ/mole)<sup> $[24,25]$ </sup> and for Al-Li binary alloys ( $\sim$ 120 to 140 *kJ/mole). 122,26,27,28]* This could simply be due to the difference in the  $\delta'$  volume fraction. However, the present



Fig. 8--Arrhenius plot of the coarsening rate of  $\delta'$  particles in both the unstretched and stretched conditions.

results appear to indicate that activation energy is nearly independent of the condition of stretch, although the  $\delta'$ volume fraction is decreased by  $\sim$  10 pct in the stretched condition. Furthermore, the principal microstructural constituents in the stretched condition are similar to those in A1-Li-Cu ternary alloys, except for the presence of a minor amount of S' phase. This leads us to conclude that there is a small difference in the activation energy between the quaternary and ternary alloys and that the difference is due to the presence of magnesium. Magnesium is reported to be incorporated into  $\delta'$  particles,  $^{[32]}$ although its precise role is unknown at the present time.

The intercept  $K_1D$  in Eq. [9] is the coefficient of the linear growth rate of the original Zener-Hillert equation, which represents the situation in the absence of the problem of overlapping diffusion field, The effect of overlapping diffusion field is incorporated in the slope of the plot  $K_2D^2$ . Thus, Eq. [9] predicts the same intercept regardless of the condition of stretch. At the same time, it predicts a steeper slope when the alloy is stretched, because the interparticle distance  $\lambda$  is expected to decrease as a result of stretching.

Results for  $T_1$  plates (Figure 11) indicate that taking

Table I. Volume Fraction of  $\delta'$  and  $T_1$  Phases in Various Aging Conditions

Aging Condition	$\delta'$ Phase		T. Phase	
	Unstretched	5 Pct Stretch	Unstretched	5 Pct Stretch
175 °C				
24 hours	0.028	0.025	0.010	0.022
48 hours	0.027	0.024	0.014	0.032
72 hours	0.025	0.023	0.022	0.040
190 $^{\circ}$ C				
8 hours	0.028	0.023	0.008	0.016
12 hours	0.025	0.022	0.015	0.027
24 hours	0.023	0.022	0.022	0.032



Fig. 9-Selected-area diffraction patterns of the zone axis near  $[112]_{\text{Al}}$ and DF images taken using reflections including both the  $T_1$  and S phases in a sample aged at 160 °C for 96 h:  $\alpha$ ) SADP in the unstretched condition;  $(b)$  DF image in the unstretched condition;  $(c)$  SADP in the stretched condition;  $(d)$  DF image in the stretched condition. Particles seen along  $[\bar{1}10]_{A1}$  are edge-on T<sub>1</sub> plates and particles seen along  $[\overline{152}]_{A1}$  are S' rods. Note the presence of streaks due to S' rods along all three directions  $(i.e., [021], [201],$  and  $[110])$  in (a), but of a streak along only one direction  $([201])$  in (c).



Fig. 10-Variation of maximum plate diameter  $(D_{\text{max}})$  of  $T_1$  phase as a function of aging time at various temperatures, depending on the condition of stretch. The lengthening rate of  $T<sub>i</sub>$  plates is significantly reduced in the stretched condition.

the data during the initial stage of aging leads to similar intercepts under the two different conditions, in agreement with the prediction. It is also evident that the initial slope of the data in the stretched condition is somewhat larger than that in the unstretched condition, *i.e.,* by



Fig. 11-Variation of  $D_{\text{max}}/$ time of T<sub>1</sub> phase as a function of aging time according to Eq. [9] at various temperatures, depending on the condition of stretch. A significant deviation from linearity occurs at a later stage of aging at 190 °C.

 $\sim$ 1.5 times for all temperatures. The condition for the approximation within  $\sim$ 10 pct error in Eq. [9] is  $\pi^2Dt/\lambda^2$  < 0.5. An estimation using  $\lambda \sim 120$  nm indicates that the condition holds at times of less than  $\sim$ 20 hours at  $\sim$ 190 °C. Thus, the use of data obtained during the initial stage of aging is a necessary condition at comparatively high temperatures. Examination of the  $T_1$  dispersion indicated that  $\lambda$  is typically  $\sim$ 120 nm and  $\sim$ 85 nm in the unstretched and stretched conditions, respectively. The ratio of the slope in Eq. [9] is thus predicted to be  $\sim$ 2.0, which is in reasonable agreement with the observed ratio. These results strongly support the contention that the present model can be used as a reasonable approximation for treating the problem of overlapping diffusion field.

The activation energies for the growth of  $T_1$  plates are estimated to be in the range of  $\sim$ 100 to 110 kJ/mole, regardless of the condition of stretch, suggesting that the growth of  $T_1$  plates occurs by the same diffusion mechanism in both the unstretched and stretched conditions. Comparison with the literature indicates that the activation energy is very close to that reported for the case of grain-boundary diffusion of copper in aluminum<sup>[33]</sup>  $(-105 \text{ kJ/mole})$ . The activation energy for the growth of S' rods in the unstretched condition is estimated to be a similar value ( $\sim$ 110 to 120 kJ/mole). This leads us to conclude that the growth of both  $T_1$  and S' phases is controlled by the diffusion of copper through dislocations. The activation energy along a dislocation is expected to be similar to that along a grain boundary.

The present model has several deficiencies, however. The first is the exaggeration of the linear gradient approximation for the diffusion field. The second is the lack of consideration of the effect of decreasing  $\lambda$  with time due to plate lengthening. Fortunately, the first approximation generally leads to a slower growth rate,  $[34]$ 



Fig. 12--Arrhenius plots of (a) the intercepts and (b) the slopes using the data in Figure 11 obtained during the early stage of aging. Note the close correspondence of the two intercepts depending on the condition of stretch in (a).

whereas the second leads to a faster growth rate. The model also oversimplifies the concentration profile during initial aging time. This treatment is therefore more appropriate in a situation where the overlapping of diffusion field begins to occur.

The stretching treatment tends to facilitate the growth of S' rods in only one of three possible  $\langle 100 \rangle_{\text{at}}$  directions, probably due to the strain energy effect on S' nucleation. The misfit parameters of the S' phase differ depending on the three principal crystal  $axes$ ;  $[35]$  the maximum misfit occurs along the b crystal axis. One would then expect a maximum release of strain energy when the S' phase nucleates on dislocations with a Burgers vector that is parallel to its b axis. Examination of the orientation relationship indicates that if the Burgers vector is parallel to [110], for example, only one growth direction  $(i.e., [001]_{Al})$  can make the **b** axis of S' phase nearly parallel  $(\sim 18.4 \text{ deg})$  to the given Burgers vector. This is true only for the two of four variants that belong to this growth direction. Those S' precipitates grown along the other directions  $(i.e., [010]_{Al})$ and  $[001]_{Al}$  always make the angle larger than 50.8 deg.



Fig. 13-Variation of  $D_{\text{max}}/$ time of S' phase as a function of aging time according to Eq. [9] at various temperatures in the unstretched condition.

This thus explains why the S' rods grow in only one of three  $(100)_{\text{Al}}$  directions in the stretched condition, if one assumes that the dislocations controlling the plastic flow have the same Burgers vector in a given grain. It is in fact reported that these dislocations are predominantly screw type in this alloy system.  $[36]$  Thus, it is quite possible that these parallel dislocations have the same Burgers vector. In the unstretched condition, the types of dislocations or their Burgers vectors are not necessarily the same. One can therefore anticipate equal populations of S' phase in the three (100) growth directions.

## V. CONCLUSIONS

The microstructure of an A1-2.0Li-2.8Cu-0.5Mg (-0.13Zr) alloy consists primarily of  $\delta'$ , S', and  $\overline{T}_1$ phases. Stretching exerts little influence on the coarsening kinetics of the  $\delta'$  particles. The activation energy for  $\delta'$  coarsening is estimated to be  $\sim$ 100 kJ/mole, regardless of the condition of stretch, which is somewhat lower than that in an A1-Li-Cu ternary alloy. The volume fraction of  $\delta'$  phase, however, is significantly reduced (by  $\sim$ 10 pct) in the stretched condition. The stretching treatment greatly accelerates the nucleation kinetics of  $T_1$  phase at the expense of S' phase; however, the growth rate of  $T_1$  phase (and also of S' phase) is significantly reduced in the stretched condition due to the effect of overlapping diffusion field. A model has been presented to accommodate this problem. The effect of stretching on the lengthening rate of  $T_1$  plates can be successfully predicted. The activation energy for the lengthening of  $T_1$  plate is estimated to be  $\sim$ 100 to 110 kJ/mole, regardless of whether the alloy is unstretched or stretched. A similar activation energy value  $(\sim 110$  to 120 kJ/mole) is observed for the growth of S' rods. It is concluded that the growth of both  $T_1$  and S' phases in

**any condition of stretch is controlled by the diffusion of copper along dislocations. The nucleation of S' phase is greatly influenced by misfit strain energy and tends to occur at dislocations with a Burgers vector that is nearly**  parallel to the  $[010]_{s'}$  direction, which is the direction **that exhibits maximum misfit.** 

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