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ON THE NUCLEATION AND GROWTH OF AL<sub>2</sub>CU (S') IN AL-LI-CU-MG AND AL--CU-MG ALLOYS

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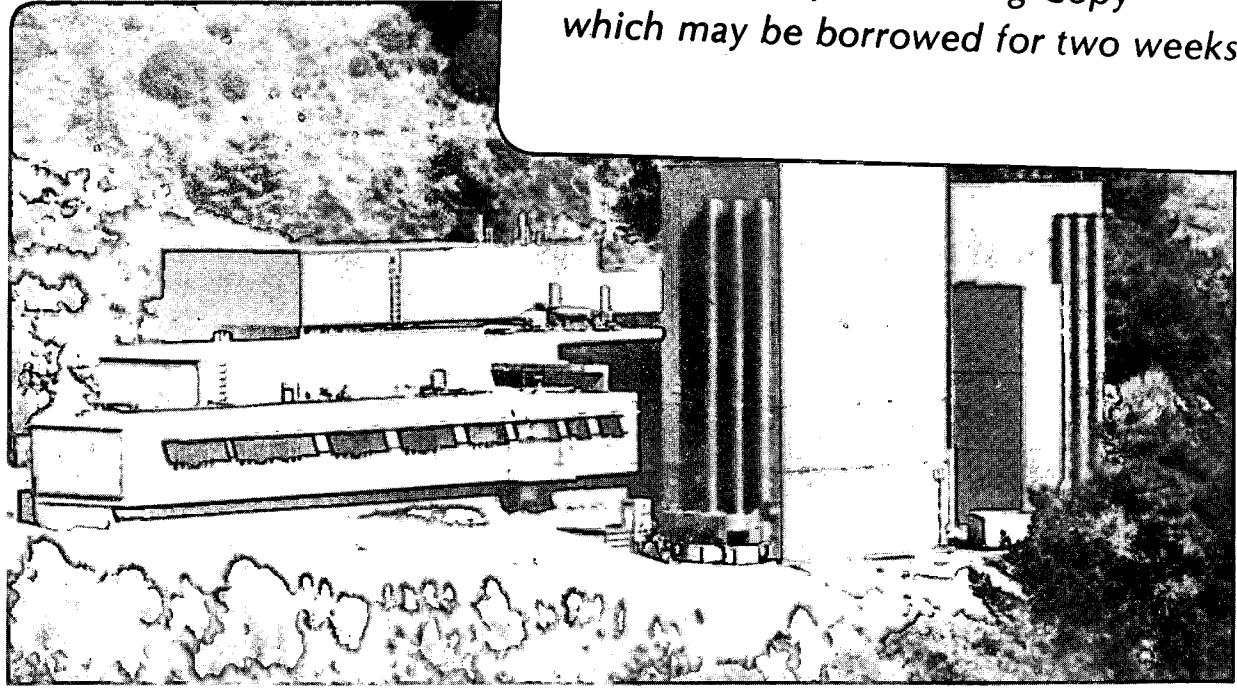
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# ON THE NUCLEATION AND GROWTH OF $\text{Al}_2\text{CuMg}$ (S') IN Al–Li–Cu–Mg AND Al–Cu–Mg ALLOYS

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## Introduction

Improvement of properties in Al–Li–X alloys requires a clear understanding of precipitation in these systems. It has been shown that extensive precipitation of S' ( $\text{Al}_2\text{CuMg}$ ) phase within Al–Li–Cu–Mg alloys significantly affects the deformation path. This has been attributed to extensive cross-slip which prevents localization of strain and promotes less anisotropic properties [1–3]. However, the S' phase can be sheared in localized deformation bands at high cyclic plastic strain [4]. In the pseudo-binary Al– $\text{Al}_2\text{CuMg}$  alloy, the Cu/Mg-rich precipitation zones (GPB) are able to cause considerable hardening of the matrix. The hardening is apparently not very sensitive to the zone size or degree of ordering [5]. According to Silcock [5] these zones are cylindrical, 1–2 nm in diameter and 4 nm long. They are also formed during the early stage of aging at 190C and are followed by nucleation of S' precipitates with a {120} habit plane. Overaging occurs by the further formation and growth of S' with a corresponding re-resolution of GPB zones. S' phase precipitates generally nucleate on dislocations, but have been noted to occur at unidentifiable sites in the matrix [6]. According to Bagaryatsky [7,8], in the ternary Al–Cu–Mg alloy, GPB zones do not act as nuclei for the S' phase. However, Weatherly [9] has found strong evidence for the transformation of the GPB zones to S' precipitates at 190 C in an Al–2.7%Cu–1.5%Mg–0.2%Si alloy. Wilson [10] suggested that Si increases the effective binding energy between the solute atoms, vacancies, and GPB zones, so enhancing the stability of the zones and raising the temperature at which the S' precipitate could form by transformation from GPB zones. Similarly one can expect that Li would behave in a like manner to Si because it also has a high binding energy.

As noted by Flower and Gregson [13], the connection between GP zones and S' formation is not proven. Further, in ternary Li containing alloys there have been no reports of the formation of GPB zones in spite of the use of aging temperatures which result in their formation. In Al–Cu–Mg alloys, heterogeneous nucleation takes place on the dislocation loops and helices which are present at a high density in the as-quenched condition. In Li-containing alloys, the Li atom to vacancy binding is very strong [11,12]. The Li/vacancy binding energy, which is 0.25–0.26 eV, is high enough to allow Li atoms to trap vacancies during the quenching and to prevent loop formation [11]. The only available heterogeneous nucleation sites are grain and subgrain boundaries, and homogeneous nucleation eventually takes place, even in fairly dilute (Mg+Cu) alloys [13]. The precise mechanism of homogeneous precipitation of S' phase is still unknown. A widespread distribution of vacancy clusters may provide sites for the precipitation of S' laths. Alternatively, the clusters may become enriched with copper and magnesium and then develop into S' precipitates via a model of the classic GP zone type [13].

In this paper results using atomic resolution electron microscopy on the nucleation and growth mechanisms of  $\text{Al}_2\text{CuMg}$  (or S') precipitate are reported. Also, an examination is made of Al–Cu–Mg and a Li containing alloy to study the effect of Li atoms and Li/vacancy pairs on S' formation.

## Experimental Procedure

Two alloys, Al–Cu–Mg and Al–Li–Cu–Mg (for analysis see Table 1) were treated as follows: solution treatment at 823K for 2 h, ice brine quenched and aged: Al–Cu–Mg for 72h at 190C and Al–Li–Cu–Mg for 16 and 100 hours at 190C, to produce peak aged and overaged condition respectively. The Al–Li–Cu–Mg alloy was

also deformed 3% prior to aging. 0.125mm thick slices were cut with a slow-speed diamond saw from both the peak-aged and overaged alloys, from which 3mm discs were punched. These samples were jet electropolished with a 1/3 nitric and 2/3 methanol solution below 248K at 15V. Conventional electron microscopy (TEM) was performed on a Philips 400 electron microscope operating at 100kV. High resolution electron microscopy (HREM) images were taken on the JEOL ARM electron microscope operating at 800 and 400kV. An objective aperture of radius 0.06nm was used to filter out high-order spatial frequencies and to improve image contrast. Through-focus series of images were taken automatically in 12nm increments, starting at the minimum contrast condition. With respect to the Gaussian image plane the Scherzer focus value is -60nm and is the same at 400 and 800kV. In order to obtain diffraction information from extremely small volumes of investigated samples the laser optical diffraction procedure, developed for the study of aged alloy by Sinclair et al [14], was employed.

TABLE I  
Alloy Composition (wt.%)

Alloy	Cu	Mg	Li	Zr	Fe
Al-Cu-Mg	2.01	1.06	—	0.14	0.08
Al-Li-Cu-Mg	1.30	1.00	2.5	0.9	—

## Results and Discussion

### I. Ternary Al-Cu-Mg alloy

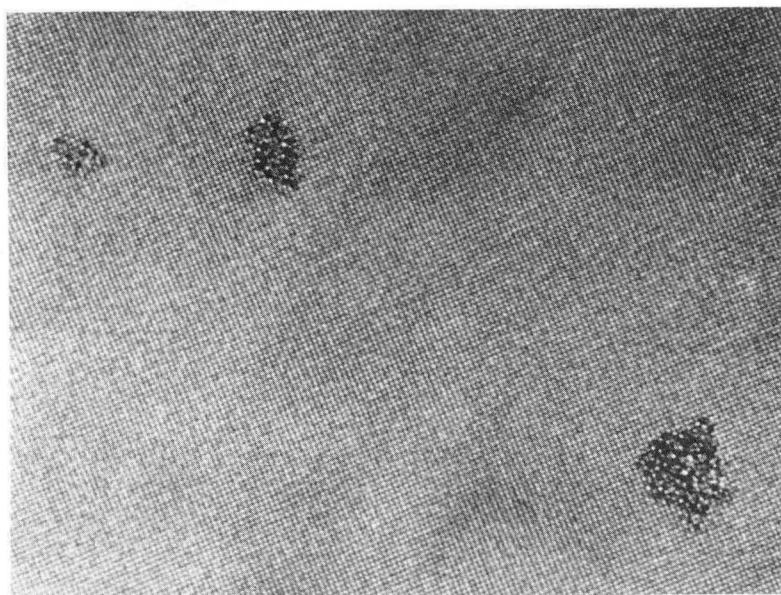
#### A. Nucleation

It was observed that there is continuous nucleation of S' over the investigated transformation times at 463 K. Two primary nucleation mechanisms were observed in the Al-Cu-Mg alloy. The first is clustering of Cu and Mg rich regions between 2 and 4 nm (Fig. 1a). The cluster is slightly larger compared to the zone size (GPB) discussed by Silcock [5]. This could be direct confirmation of the suggestion by Flower and Gregson [13] that the cluster enriched with Cu and Mg might be the nucleus site for S'. Compared to their suggestion that this cluster can develop into S' via the classic GP zone type model [13], our results show that the GPB of spherical, or Silcock's idea [5] of an eventually cylindrical, morphology is more feasible. It is also observed that the ordering degree varies with different clusters. This also has been anticipated by Silcock [5]. Present results further indicate that the clustering is mainly in 110 directions. However, ordering inside the cluster is periodic and in a <102> direction. It may be possible that ordering within the cluster along <102> can represent the initiation of the S' phase. These clusters could be stabilized by a high Mg content, as has been suggested by Vietz and Polmear [15]. Our results indicate that the clusters may be a precursor to nucleation of S' which would be in disagreement with Bagaryatsky [7] who stated that GPB zones do not act as nuclei for the S' phase. The optical diffraction pattern reveals little difference between the cluster and matrix crystal structure in this orientation with some distortion of the aluminum lattice parameter.

The second nucleation site of S' in the ternary alloy is at subgrain or grain boundaries as shown in Fig. 2. Here all of the S' particles are aligned along the subgrain boundary which is established by a small misorientation of the 200 Al atomic planes.

#### B. Growth

Fig. 3 clearly illustrates that ledge migration [16] is the mechanism of growth of S' precipitates. Close examination reveals that the ledges



XBB 888-7745

FIG. 1 HREM of aluminum matrix and Cu/Mg rich clusters.  $\underline{B} = [001]$  Al, Al-Cu-Mg alloy.

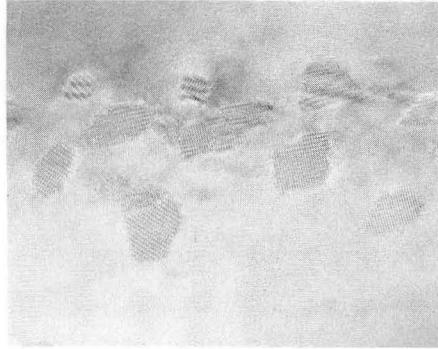


FIG. 2. S' precipita-  
tion at Al sub-grain  
boundary.  $\underline{B}=[001]$   
Al, Al-Cu-Mg alloy

XBB 888-8145

grow along the  $10\bar{2}$  direction (arrowed). In the region labeled 'A' the early stages of new ledge formation is apparent. The similarity between this new ledge and the areas immediately in front of other well developed ledges indicates that nucleation of new steps or the advancement of mature steps involves some disorder of Cu and Mg atoms. Therefore, it seems possible that the limiting step in the advancement of a ledge is the correct attachment of solute at the appropriate position in S' and not volume diffusion to the particle. It is also observed that nearly all of the atomic habit planes are of the  $(10\bar{2})$  type (with respect to the matrix). Fig. 4 illustrates the final stages of S' aging. Here impingement of precipitates has occurred which have different  $(10\bar{2})$  variants.

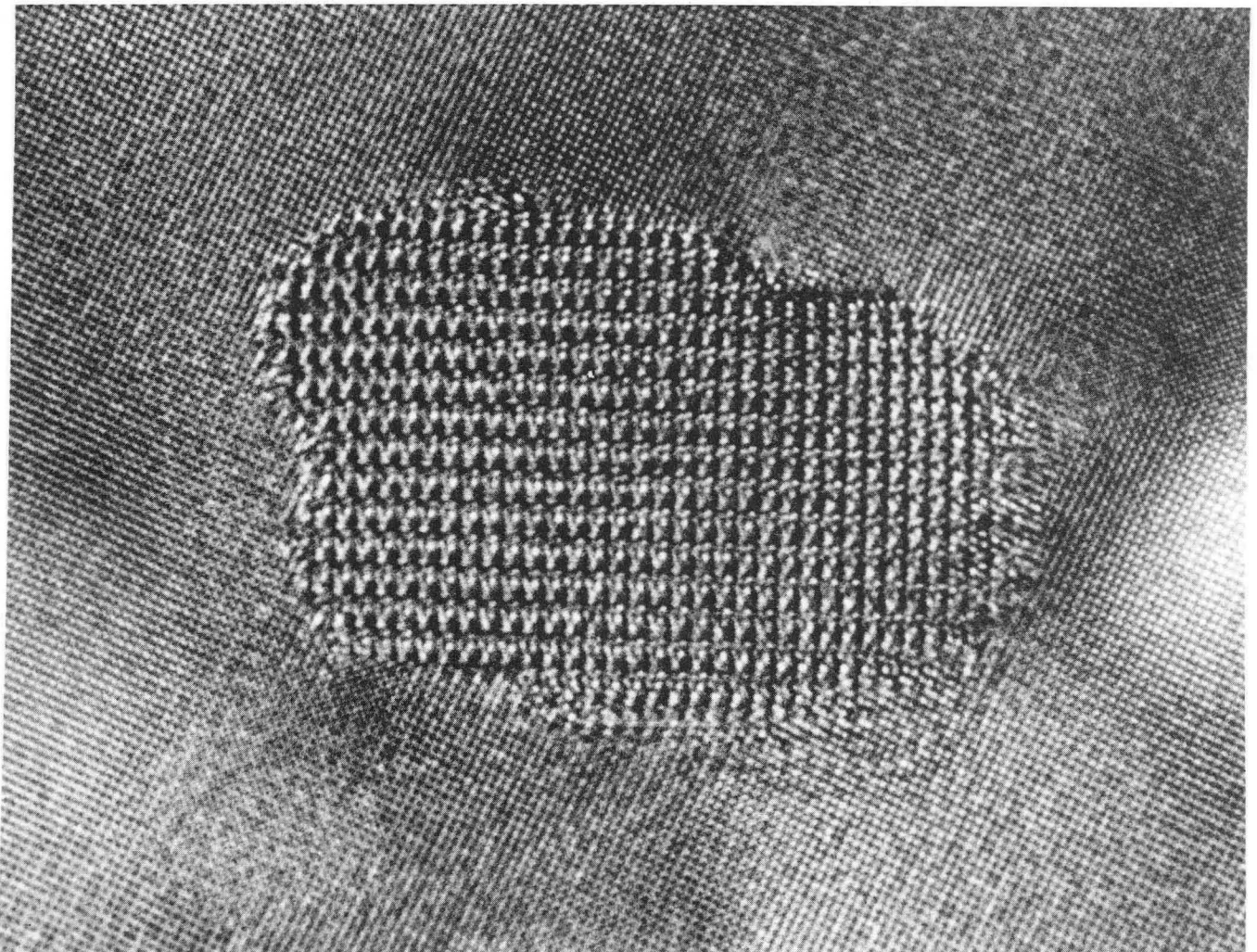


FIGURE 3. Growth ledges associated with S' precipitate in Al-Cu-Mg alloy.  $\underline{B}=[001]$  Al.

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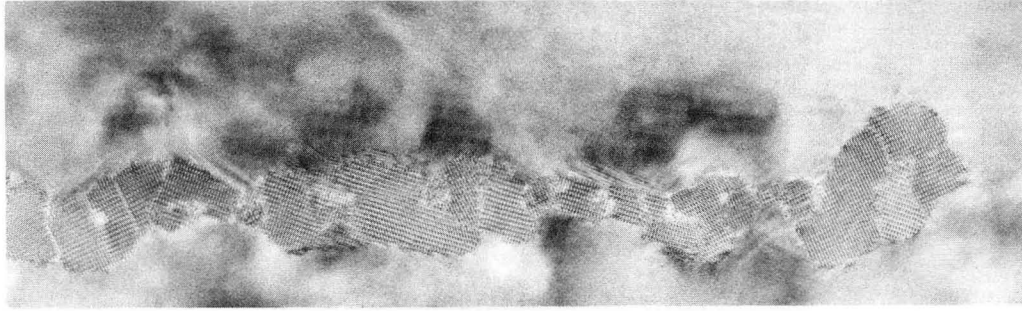


FIG. 4. Later stages of growth showing impingement of S' precipitates along Al matrix grain boundary.  
 $\underline{B}=[001]$  Al, Al-Cu-Mg alloy. XBB 888-8135

## II. Al-Li-Cu-Mg (8090) Alloy

### A. Nucleation

Compared to the Al-Cu-Mg alloy, in Al-Li-Cu-Mg there are significant differences in nucleation mechanisms of S' phase. They are of two types. The first is nucleation on the  $\delta'$ /matrix interface (Fig. 5 at A & Fig. 6). Because of the negligible misfit between the matrix and  $\delta'$ , this interface would not be expected to serve as a favorable site for S' nucleation. However, during the growth of  $\text{Al}_3\text{Li}$  ( $\delta'$ ) excess Cu and Mg concentrations occur at the growth front. This coupled with the excess vacancies released when Li adds to the  $\delta'$  particle result in favorable conditions for S' nucleation.

The second mechanism is nucleation on matrix dislocations (Fig. 5 at B), in this case, induced during stretching immediately after quenching, or nucleation on subgrain boundary dislocations as shown in Fig. 7. The ledge growth mechanism is also operating in this case as in the Al-Cu-Mg alloy (Fig. 7). Apparent in Fig. 7 are both rod-like and plate-like S' (i.e. impinged rectangular rods along a line) morphologies on the same sub-boundary where each is associated with a different  $\langle 102 \rangle$  habit. This is clearly associated with the change in the subgrain boundary orientation. Our results are in disagreement with the statement of Gupta et al [17] that rods or plate morphology depends on the net concentration of Cu+Mg solutes.

In the 8090 alloy the cluster nucleation mechanism for S' was not observed. This might be explained by the high binding energy of Li to vacancies [11] which prevents supersaturation and collapse into loops and dislocation climb to helices [18] which favor cluster formation sites.

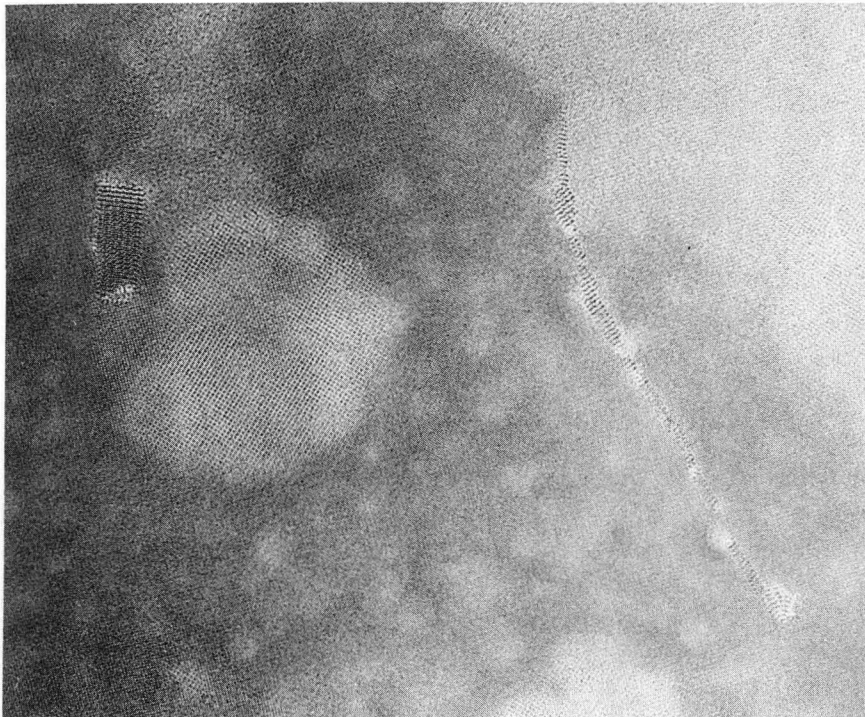


FIG. 5. S' precipitate which nucleated at the  $\delta'$ /Al matrix interface (at A) and on a matrix dislocation (at B).  $\underline{B}=[001]$  Al, Al-Li-Cu-Mg alloy. XBB 888-8144

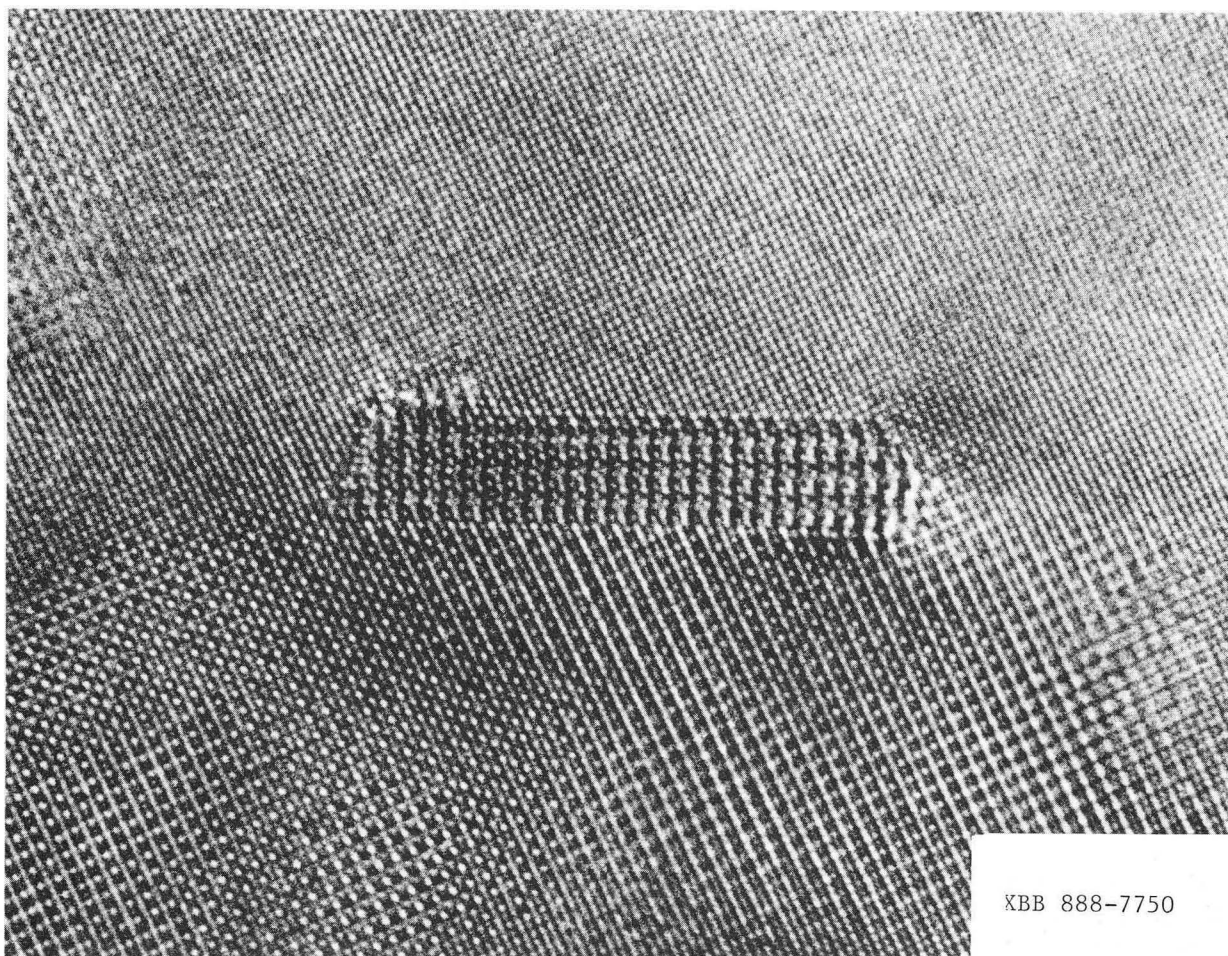


FIG. 6. S' precipitate at  $\delta'/\text{Al}$  matrix interface in Al-Li-Cu-Mg alloy.  $\underline{B}=[001]$  Al. Note also the superstructure period along  $y$   $\langle 102 \rangle$  similar to ordered phases in Ni-Mo found by Das and Thomas (19).

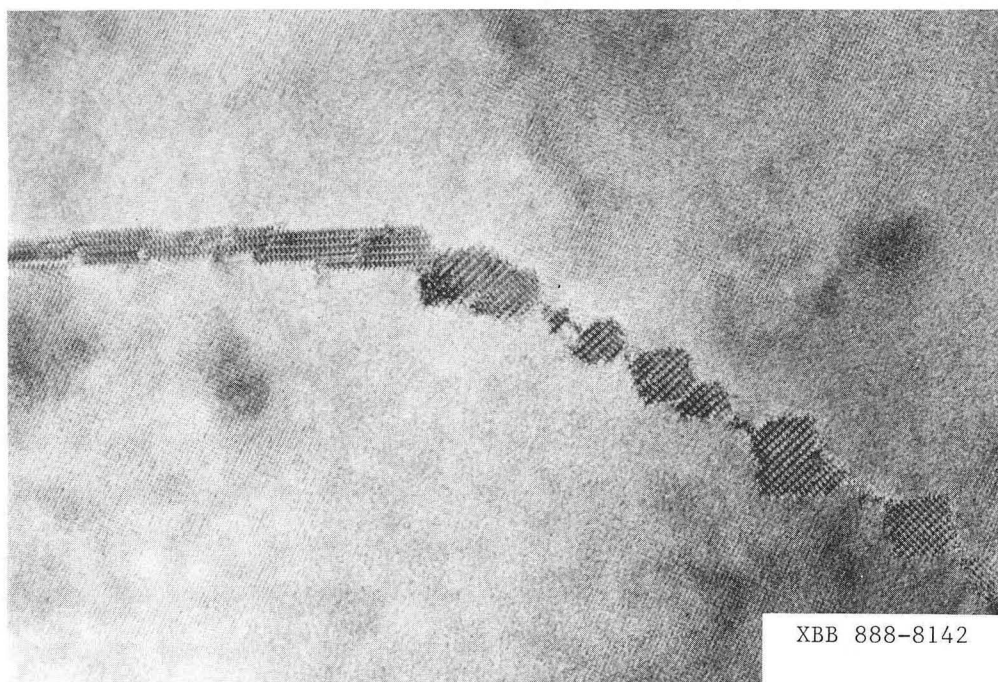


FIG. 7. S' precipitates along subgrain boundary dislocations in Al-Li-Cu-Mg alloy.  $\underline{B}=[001]$  Al.



Finally, detailed inspection of our atomic resolution micrographs, from alloys with and without Li, did not reveal two types of S-type precipitates (i.e. S and S'). This further reinforces the statement by Gregson and Flower [13] that unless a difference is noted between S and S', the notation should be dropped.

### Conclusions

The primary nucleation mechanisms of S' in Al-Cu-Mg alloy are associated with clustering of Mg and Cu at vacancy loops and helices and heterogeneous nucleation at subgrain boundaries.

In the Li containing alloy the dominant nucleation sites are the  $\delta'$ /aluminum matrix interphase boundary and dislocations.

In both alloys the growth mechanism is controlled by ledge migration, and ordered periodicities along  $\langle 102 \rangle_{\text{matrix}}$  develop.

Two different S-type precipitates, i.e. S and S', were not observed.

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### References

- 1 P.J. Gregson and H.M. Flower, *Acta Met.*, 33, 527 (1985).
- 2 H.M. Flower, P.J. Gregson, C.N.J. Pite, and A.K. Mukhopadhyay, *Aluminum Alloys, Their Physical and Mechanical Properties*, eds. E.A. Starke and T.H. Sanders, p. 743, Eng. Mater. Advisory Services (1986).
- 3 W.S. Miller, J. White and D.J. Lloyd, *ibid*, vol. III, p. 1799.
- 4 D. Khireddine, R. Rahouadj, and M. Clavel, *Scripta Met.*, 22, 167 (1988).
- 5 J.M. Silcock, *J. Inst. Met.* 89, 203 (1960-61).
- 6 N. Sen and D.R.F. West, *J. Inst. Met.*, 97, 87 (1969).
- 7 Yu.A. Bagaryatsky, *Zhur. Tekhu. Fiziki*, 18, 827 (1948).
- 8 Yu. A. Bagaryatsky, *Doklady Akad. Nauk SSSR*, 87, 397 (1952).
- 9 G.C. Weatherly, Ph.D. thesis, Univ. Cambridge (1966).
- 10 R.N. Wilson, *J. Inst. Met.*, 97, 80 (1969).
- 11 S. Ceresara, A. Giarda, and A. Sanchez, *Phil. Mag.* 35, 97 (1977).
- 12 K.S. Ranian, E.S.D. Das, and K.I. Vasu, *Scripta Met.*, 4, 291 (1970).
- 13 H. M. Flower and P.J. Gregson, *Mat. Sci. and Tech.*, 3, 83 (1987).
- 14 R. Sinclair, R. Gronsky and G. Thomas, *Acta Met.* 24, 789 (1976).
- 15 J.T. Vietz and I.J. Polmear, *J. Inst. Met.* 94, 410 (1966).
- 16 H.I. Aaronson, in *Decomposition of Austenite by Diffusional Processes*, eds. V. Zackay and H.I. Aaronson, p. 387 (1962).
- 17 A.K. Gupta, P. Gaunt and M.C. Chaturvedi, *Phil Mag. A*, 55, 375 (1987).
- 18 G. Thomas and M.J. Whelan, *Phil. Mag.* 4, 511 (1959).
- 19 S.K. Das and G. Thomas, *Phys. Stat. Sol.*, 21, 177 (1974).

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