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July 1988

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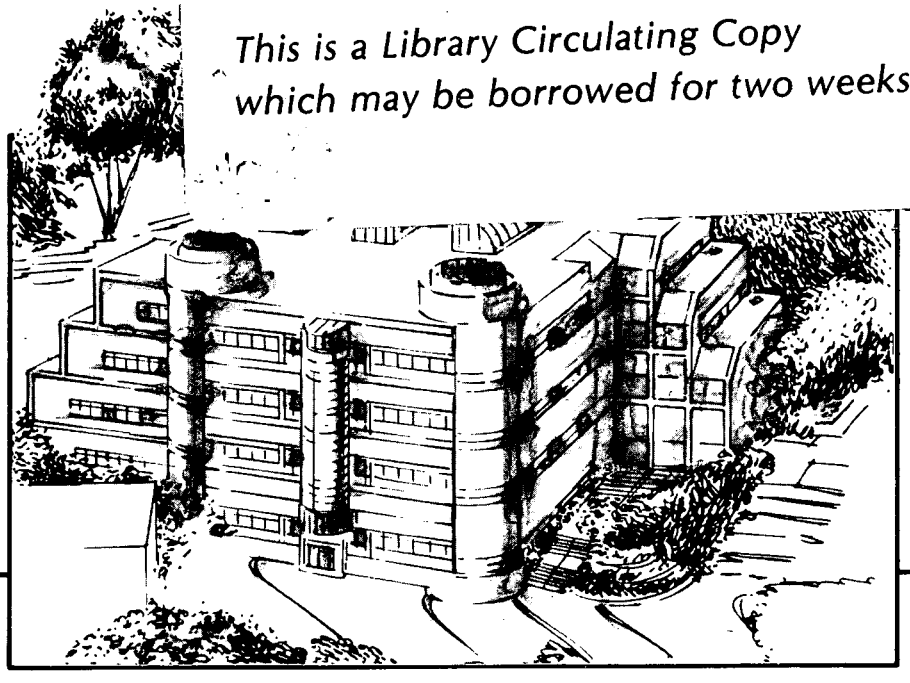

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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LITHIUM DEPLETION IN PRECIPITATE FREE ZONES(PFZ's) IN Al-Li BASE ALLOYS

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Introduction

Since the effects of precipitate free zones(PFZ's) were first examined in high strength Al-Mg-Zn alloys [1,2] much attention has been paid to PFZ's and their deleterious effects, especially with respect to the mechanical behaviour, fracture and stress-corrosion cracking, in a wide range of conventional high strength Al-base alloys[3-9], as well as in the newer high strength Al-Li alloys for aerospace applications[10-14]. In terms of complexities and mechanisms of precipitate nucleation and growth, including considerable non-uniformity due to heterogeneous nucleation, conventional Al base alloys are very similar to the Al-Li-base alloys. The optimization of properties requires uniformity of precipitation with suitable volume fractions of appropriate precipitates. Heterogeneous nucleation may modify the desired morphology, but this mode can also be utilized to increase nucleation rates[2], e.g. by mechanical deformation as in the complex thermomechanical treatments(TMT) currently being pursued. The phenomenon of PFZ's in high strength Al-Li-base alloys has been extensively studied[10,11,15]. In order to establish the mechanism of formation of PFZ's, it is important to determine whether the PFZ's are a result of vacancy or solute depletion (or both) leading to low nucleation rates due to low supersaturations. Possible lithium depletion is indicated from the early analytical work of Williams and Edington[15]. Such lithium depletion could of course cause a reduction in the volume fraction of fine δ' precipitates near the grain boundaries which would adversely affect the mechanical and stress-corrosion properties.
Williams and Edington[15] measured lithium depletion at grain boundaries in an Al-12.9at.%Li alloy by electron energy loss spectroscopy(EELS) using a specially modified Siemens electron microscope. With this device they measured the energy shift of the first plasmon loss peak as a function of lithium content. The difficulties of spectroscopic analysis for Li(mainly because of its low atomic number) are well known. An alternative technique for compositional analysis, although indirect, which can be utilized by high voltage microscopy(HVEM) is that of the so called "critical voltage" effect[16,17]. Specifically Fox and Fisher[18,19] have detected changes of ~ 3at.% lithium in binary Al-Li alloys by the critical voltage(V_C) effect, which

can be measured to within ±5kV[17] by appropriate attention to detail[18]. Thus it should be possible to detect lithium depletion in PFZs in Al-Li alloys by this method, and such is the object of the present work. The 1.5 MeV HVEM with liquid nitrogen stage available at the National Center for Electron Microscopy is necessary for such analyses.

Experimental procedure

Two alloys A(binary Al-Li) and B (ternary Al-Li-Cu) have been investigated (for analysis details see Table 1). These alloys were heat treated as follows: solution treatment at 823K for two hours, ice brine quenched and aged 5 minutes at 573K to produce overaged material with relatively large PFZ's(~2μm across). Alloy B was also deformed 6% prior to aging. 0.125mm slices were cut with a slow-speed diamond saw from both the as-quenched and overaged alloys from which 3mm discs were punched. These samples were jet electropolished with a 3% perchloric acid/35% n-butoxy ethanol/62% ethanol solution below 248K at 40V. In the case of alloy B which contains Cu, severe copper redeposition during electropolishing was encountered which resulted in poor Kikuchi patterns (essential for accurate critical voltage measurements) and so a two-stage technique was adopted where the final thinning was performed by ion milling at 77K.

Table I- Chemical composition[wt.%]

Alloy	Alloying elements			
	Li	Cu	Zr	Al
A	2.45	0.02	0.11	bal.
B	2.37	2.49	0.13	bal.
A1*	1.40	---	0.12	bal.
A2*	2.20	---	0.12	bal.

*Alloys used by Fox and Fisher[16]

Calculations based on the work of Fox and Fisher[19] and Shirley and Fisher[21] were performed to produce theoretical 222 and 400 critical voltage values(V_c^{222} and V_c^{400}) for the as-quenched alloys A and B. These are shown in Table 2 together with the experimental results and the results of Fox and Fisher.

Large PFZ's(about 2μm across) at the grain boundaries were obtained in alloy B(as shown in figure 1) with a high density of $\delta'+T_1$ phases in the center of the grains. Because of the difficulties of obtaining sharp Kikuchi patterns in the TMT treated alloys due to diffuse scattering from the high density of dislocations, the results to be reported here were obtained from measurements of the critical voltages in the PFZ's in alloy B, and critical voltages in the precipitate free regions near the center of the grains in alloy A.

Both V_c^{222} and V_c^{400} were measured at 293K and below room temperature in the center of the grains of alloy A. V_c^{222} was measured at 293K in alloy B in both the center of the grains and in the PFZ shown in figure 1. Attempts were made to measure V_c^{400} in alloy B, but it was immediately evident that because of the poor diffraction patterns (particularly in the center of the grains) sufficient accuracy would not be obtained with those measurements to search for possible lithium depletion. The experiments were performed using convergent beam diffraction at a beam spot size of ~ 0.7μm at 400 to 500kV reducing to about 0.5μm at 900 to 1000kV in the Kratos EM 1500 HVEM. The results thus have these spatial resolution limitations. It should be noted

that the low temperature measurements made on alloy A were performed by maintaining the microscope voltage constant and reducing the temperature until the appropriate Bragg reflection disappeared i.e. a "critical temperature" technique, originally adopted by Sellar et al.[22]. This approach leads to improved accuracy.

Results and discussion

The chemical analyses of alloys A and B shown in Table 2 indicate that the lithium contents of the center of the grains in both alloys are very nearly the same in both the as-quenched and overaged conditions. This allows a comparison between the critical voltage measurements made on the two alloys so that possible Li depletion at PFZ's can be confirmed. In spite of the unavoidably large errors, the V_c^{222} measurements on alloy B suggest that there is lithium depletion at PFZ's(see Table 2), which is in agreement with Williams and Edington[15]. It is very satisfying to note that all the critical voltages measured in this work agree in a consistent way with those made by Fox and Fisher[16].

Table 2 - Calculated and Experimental Critical Voltages (V_c) for Al-Li Alloys

Sample	Temp. [K]	V_c^{222} [kV]	V_c^{400} [kV]	%Li [at]	%Li (wt.)
Alloy A as quenched(calculated)	293	478	994.5	[8.9]	(2.45)
Alloy B as quenched(calculated)	293	477	990	[8.7]	(2.37)
Alloy B(overaged; in PFZ)	293	465±15	----	[5.3]	(1.40)
Alloy B(overaged; in grain center)	293	475±30	----	[8.3]	(2.30)
Alloy A(overaged; in grain center)	293	480±10	1000±25	[9.8]	(2.70)
Alloy A(overaged; in grain center)	253	500±7.5	----		
A1 (as quenched)*	293	465±10	975±15	[5.3]	(1.40)
A1 (as quenched)*	92	535±10	1110±15		
A2 (as quenched)*	293	475±10	990±15	[8.1]	(2.20)
A2 (as quenched)*	92	550±10	1140±15		

* Data from ref. [16]

The most striking confirmation of the lowering of V_c^{222} in the PFZ's is the comparison of the 111 systematic convergent beam patterns(CBDP) taken at 460kV in both the center of grains in alloy A and in the PFZ's in alloy B. Examples are shown in figures 2 and 3, respectively. It is clear from these figures that the CBDP taken from the PFZ in alloy B is close to V_c^{222}, since the 222 reflection and Kikuchi lines are absent in figure 3, whereas that taken from the center of the grain in alloy A is obviously well below V_c. From these

results it can be estimated that the lithium content of the PFZ's in alloy B is about 5.25 at.%(1.4wt.%) and just a little higher than the solubility limit at 436K. On the other hand the lithium content of the grain centers is close to that of the overall analysis shown in Table 1.
In addition to these studies on grain boundaries, a similar exercise was performed on subgrain boundaries in overaged alloy A and a dark field micrograph is shown in figure 4. It is clear that small PFZ's are also formed next to these subgrain boundaries. However because they are so narrow it was not possible to perform V_c measurements there and hence no conclusion can yet be drawn about the Li content. In addition, precipitates which are encountered at the subgrain boundary dislocations are δ' (Al_3Li), rather than δ(AlLi) which occur on grain boundaries. This is clearly shown in figure 4 where the δ' precipitates in the center of the grains are of the usual spherical morphology, whereas those at the subgrain boundary dislocations are constrained in shape by the presence of the dislocation, as has been explained by Cassada et al.[23]. It is likely that these PFZ's at subgrain boundaries also contribute to non-uniform mechanical and corrosion properties in these alloys.

Conclusions

1. The critical voltage effect provides a unique method for estimating the lithium content in Al-alloys with a spatial resolution of ~0.5 mm and accuracy of about 3 at.%Li.
2. Such critical voltage measurements confirm that there is lithium depletion near grain boundaries in the investigated alloys.
3. PFZs of ~ 0.2 to 0.5μm width can also occur at subgrain boundaries in Al-Li base alloys, and the precipitates which form on the subgrain boundary dislocations are of δ' (Al_3Li) rather than δ (AlLi) which occur mainly on the grain boundaries.

Acknowledgements

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, U.S. Department of Energy, under Contract DE-AC3- 76SF00098.The authors gratefully acknowledge critical discussions with Ms J. Glazer.. The alloys were supplied by ALCOA (Aluminum Company of America). G. Thomas and V. Radmilovic also gratefully acknowledge a grant from Allied Signal Inc. and the latter also acknowledges partial financial support from the Council for Basic Sciences of Serbia(RZNS), Belgrade, Yugoslavia.

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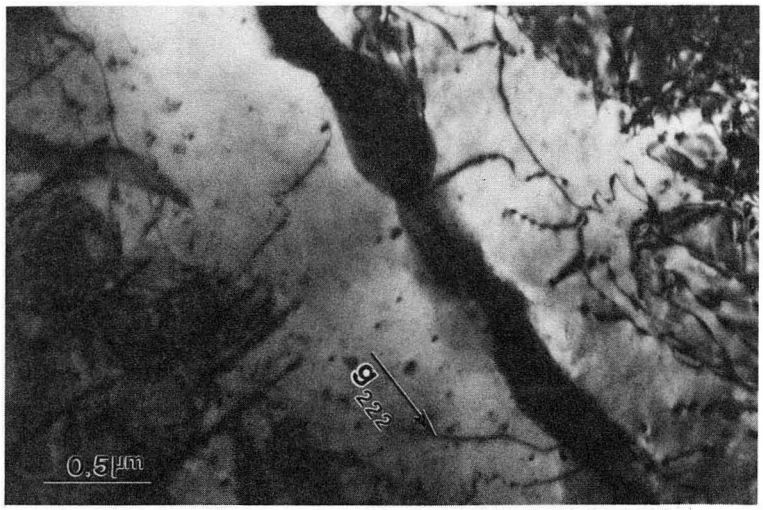

Fig.1- TEM bright field image of PFZ at a grain boundary in an Al-Li-Cu alloy produced after aging 5min at 573K.

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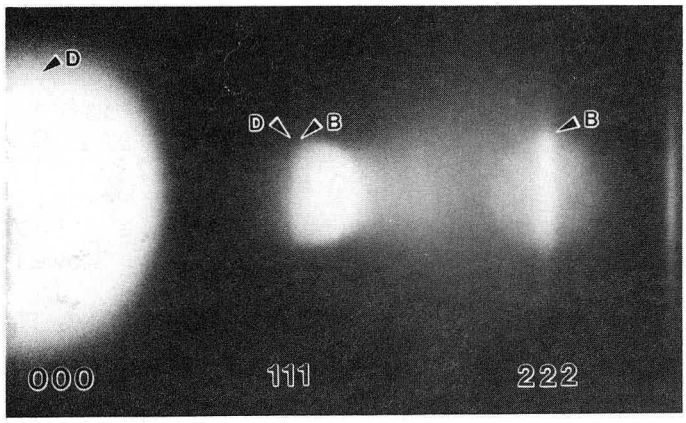

Fig. 2- CBDP image using 111 systematic reflections, from the center of the grain in Al-Li binary alloy. Note the 222 reflection and contrast at the Kikuchi lines. Since the bright contrast from the Kikuchi line in the 111 reflection lies to the 222 side of the origin then the voltage is below that of the critical value.

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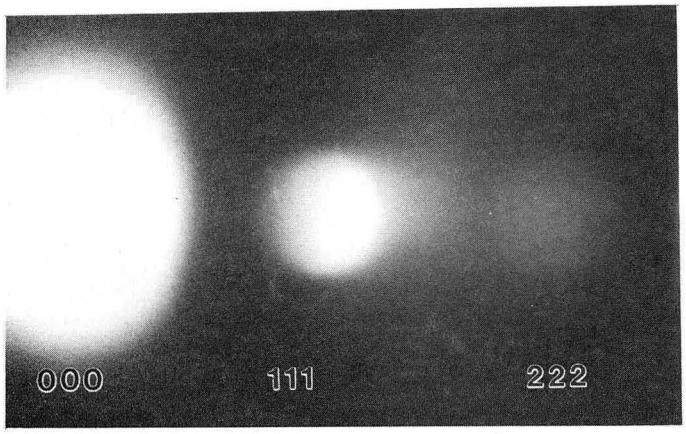

Fig. 3- CBDP image using 111 systematic reflections from a PFZ in Al-Li-Cu alloy. The absence of Kikuchi line intensity at the 222 reflection indicates the voltage is at the critical value.

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Fig. 4- TEM centered dark field image taken using a [111]. Heterogeneous precipitation of δ' produced after aging 5min at 573K. Note PFZ and nonspherical morphology of δ' precipitates along subgrain boundary.

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