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AGING OF Al-Li ALLOYS - PART I

by

Carl L. Angerman
Pile Materials Division

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ABSTRACT

Aluminum-lithium alloys are subject to precipitation from solid solution, and may be age hardened by the same techniques used for more common aluminum alloys. Spherical particles of precipitate were observed with the electron microscope in 1.5% and 2.8% Al-Li alloys after aging for times comparable to those required to produce maximum hardness. Rod-shaped particles that were oriented parallel to either the (110) or the (111) planes of the aluminum matrix were observed in overaged specimens.

CONTENTS

	<u>Page</u>
INTRODUCTION	6
SUMMARY	6
DISCUSSION	6
Background	6
Materials	7
Experimental techniques	8
Heat treatment	8
Metallographic preparation	8
Replicas for electron microscopy	8
Microstructural changes during aging	9
Orientation of the precipitate	12
Hardness measurements	12
BIBLIOGRAPHY	15

LIST OF FIGURES

Figure

1	Aluminum-rich portion of the Al-Li phase diagram	7
2	Microstructural changes during aging of 2.8% Li alloy	10
3	Microstructural changes during aging of 1.5% Li alloy	11
4	Rod-shaped particles in overaged specimens	13
5	Orientation of precipitated particles	14
6	Aging curves for Al-Li alloys	14

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AGING OF Al-Li ALLOYS · PART I

INTRODUCTION

Precipitation from a supersaturated solid solution is one of the important reactions in the solid state of metals, and has been widely exploited in commercial aluminum-base alloys. Precipitation reactions are responsible for age-hardening effects, which have been studied exhaustively in the fabrication and application of high strength aluminum alloys. Similar precipitation reactions also occur in the aluminum-lithium alloys that are used as control rods in nuclear reactors.

Information on the changes in the microstructure of Al-Li alloys during age hardening is of interest in the fabrication of control rods and in the study of irradiation damage to these rods.

This report describes the examination with both the optical and electron microscopes of both Al-1.5% Li and Al-2.8% Li alloys. The use of the electron microscope in such a study is necessary to resolve the very small particles formed in the early stages of precipitation.

SUMMARY

In both the Al-1.5% Li and the Al-2.8% Li alloys, particles of the precipitating intermetallic compound, LiAl, were observed with the electron microscope after aging for periods approximately the same as required to produce maximum hardness. In aging treatments at 275°C, the precipitate was visible after 16 hours in the 1.5% alloy and after 15 minutes in the 2.8% alloy. The particles were first observed at the grain boundaries, and became visible within the grains as aging progressed. Within the grains the precipitate was found to occur as rods oriented parallel to either the (110) or the (111) planes of the aluminum matrix.

In addition to the metallographic examinations, hardness measurements were made as a function of aging time. The maximum hardness was found to be 12 Rockwell "E" for the 1.5% alloy and 98 Rockwell "E" for the 2.8% alloy.

DISCUSSION

BACKGROUND

The phenomenon of age hardening occurs in an alloy system if the following two requirements are satisfied; (a) the solubility of one metal in the other must increase with increasing temperature, and (b) the precipitate must have a crystallographic relationship to the matrix, e.g., in the present case, the precipitate forms as rods where axes are parallel to the (110) or the (111) planes of the Al matrix. When an alloy within the solubility range is heated to a temperature

at which solution occurs and is then rapidly quenched, the second phase is retained in solid solution. Upon subsequent heating to some intermediate temperature, precipitation of the second phase occurs. This precipitation is characterized by a rapid increase in hardness of the alloy, followed by a decrease in hardness as the heating at the intermediate temperature, or "aging", continues. An alloy aged past the point of maximum hardness is termed "overaged". An alloy that does not satisfy condition (b) would exhibit only a continuous increase in hardness with precipitation; the maximum would not be present. A comprehensive review of the theory of precipitation from solid solutions of metals may be found in Reference 1.

The aluminum-rich portion of the phase diagram for the Al-Li alloy (Figure 1) shows that Al-Li alloy meets the solubility requirement for an age-hardening alloy. The solubility limits of lithium in aluminum are taken from the measurements of Nowak⁽²⁾.

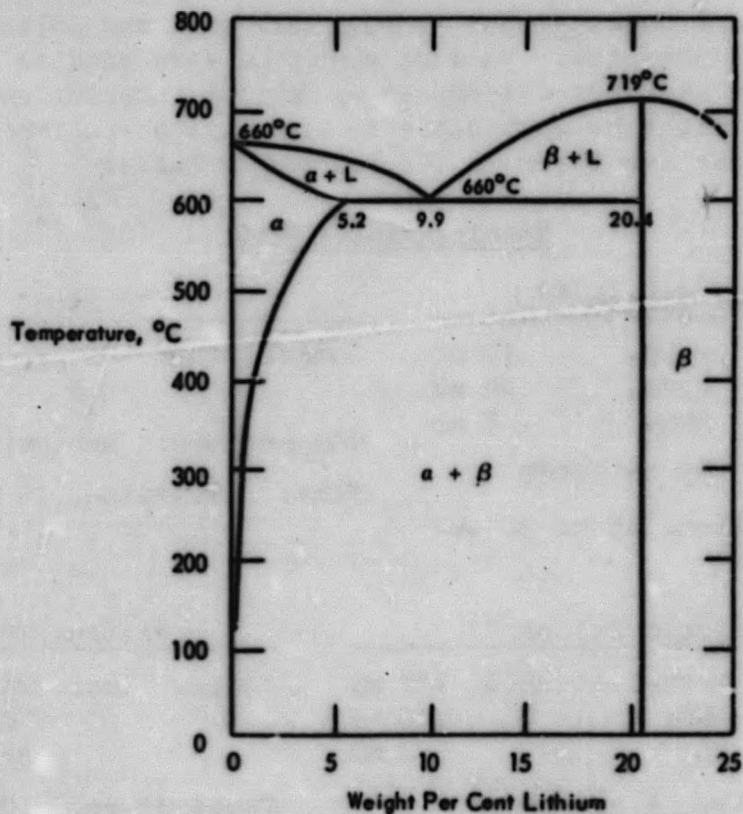


FIGURE 1 - ALUMINUM-RICH PORTION OF THE Al-Li PHASE DIAGRAM

MATERIALS

The specimens used in this study were cut from as-extruded rod, 0.8 inch in diameter. The extrusion billets were 8 inches in diameter, and were made from 99.95% aluminum and 99.98% lithium. The nominal lithium contents were 1.5 and 2.8% by weight.

EXPERIMENTAL TECHNIQUES

HEAT TREATMENT

The temperatures of the heat treatments were the same for both the Al-1.5% Li and the Al-2.8% Li alloys. Solution treatment was accomplished by heating at 525°C for two hours and rapidly quenching in water at room temperature. The specimens were aged at 275°C in air in a resistance-heated muffle furnace, and were quenched in water after the desired time at this temperature. The specimens, 3/8-inch wafers, were cut in half longitudinally after heat treatment, and only the central portion of the piece was examined. This precaution was necessary, since lithium diffused out of the specimen forming a depleted zone 0.050 inch wide around the periphery of the specimen.

METALLOGRAPHIC PREPARATION

All specimens were rough ground through 600 grit and polished through 1-micron diamond abrasive. Various etchants were used to ensure that spurious effects were not introduced by any one etchant and to develop techniques that might be applicable to irradiated specimens. The etching procedures are given in the following table:

Etching Procedures

<u>Chemical Polish⁽⁶⁾</u>			<u>HF Etch</u>		
Composition:	H ₃ PO ₄	70 ml	Composition:	HF	1 ml
	H ₂ SO ₄	25 ml		H ₂ O	99 ml
	HNO ₃	5 ml	Temperature:	Ambient	
Temperature:	85 to 100°C		Time:	Immersion, 10 sec	
Time:	Immersion, 15 to 30 sec				
<u>Electrolytic Polish⁽⁶⁾</u>			<u>Pitting Etch⁽⁷⁾</u>		
Composition:	Methyl Alcohol	100 ml	Composition:	HNO ₃	50 ml
	HNO ₃	100 ml		HCl	48 ml
	HCl	4 ml		HF	2 ml
Current Density:	4 amp/cm ²		Temperature:	10°C	
Temperature:	Ambient		Time:	Swab, 5 sec	
Time:	15 to 30 sec				

REPLICAS FOR ELECTRON MICROSCOPY

Two different replication techniques were employed. The first was the oxide film technique, which is widely used for aluminum and its alloys.⁽³⁾ The specimen was anodized in a solution of disodium

phosphate and sulphuric acid at 40 volts. The oxide film developed by the anodization was stripped by immersion, first in a saturated solution of mercuric chloride, and then in water. The film was released from the surface by amalgamation of the underlying aluminum. After stripping, the replicas were washed in a 10 volume per cent solution of HCl. Shadowing of the replicas was not necessary.

In the second technique, the replica was formed by evaporating carbon directly onto the surface. No parting layer was used. The replica was stripped by immersion, first in a 1 volume per cent solution of HF, and then in water.

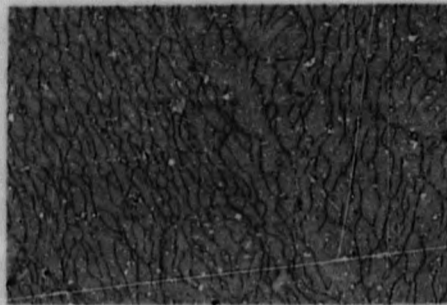
MICROSTRUCTURAL CHANGES DURING AGING

As aging progressed, the same general changes in microstructure were observed in both the 1.5 and 2.8% lithium alloys. The particles of the precipitate were first observed at the grain boundaries and became visible within the grains as aging progressed. This sequence is shown in Figure 2 for specimens of the 2.8% alloy that were chemically polished and replicated by the oxide film technique.

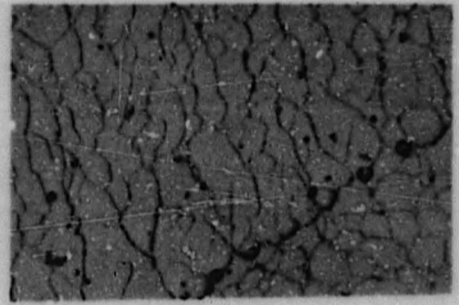
The "mounds" shown in Figures 2b and 2d are believed to be pits caused by the attack on the particles of the precipitate by the chemical polish and the anodization. This attack on second phase particles has been observed by other investigators.⁽³⁾ As shown in the photomicrographs, the concentration of small "mounds" increases with aging time, and then decreases. Simultaneously, isolated rod-shaped particles grew. This sequence of events corresponds to the classical picture of aging, in which the precipitate first occurs as small particles which increase in number to a maximum and then decrease.

The "mounds" visible at the early stages of aging may possibly be attributed to a transitional precipitate similar to that which occurs in Al-Cu alloys. In Al-Cu alloys, the first precipitate to form is the metastable, transitional phase, θ' , which, upon further aging, transforms to the CuAl_2 phase.⁽¹⁾ The θ' particles are barely resolvable even with the electron microscope and are usually detected by X-ray diffraction techniques. If such a transitional phase exists in the Al-Li alloys, it may be more readily observable because the lithium reacts more readily with the chemical etchants. The rods observed in the later stages of aging would then be the final form of the precipitate, LiAl.

The network of subgrain boundaries that was observed in all specimens was also observed by Hunter and Robinson⁽⁴⁾, who used the Alcoa R-5 "Bright Dip" as a chemical polish during metallographic preparation. The term "chemical polish" refers to a solution which polishes rather than etches the sample and does not employ an external potential, as in electrolytic polishing. The chemical polish used in this study was similar to that used by Nowak⁽²⁾ in his study of the solubility of lithium in aluminum.

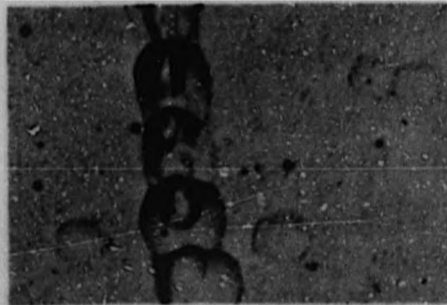


2a Solution treated 5500X

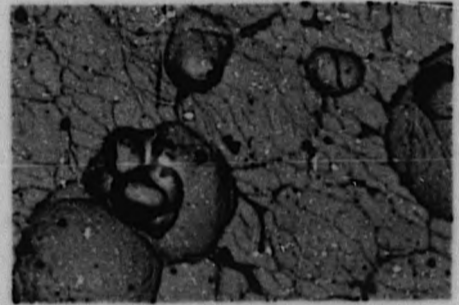


2b Aged 15 minutes 5500X

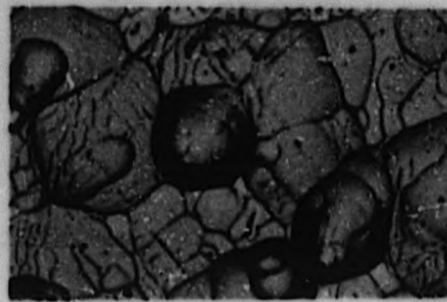
Samples were solution treated for 2 hours at 525°C, quenched in water, and aged at 275°C.



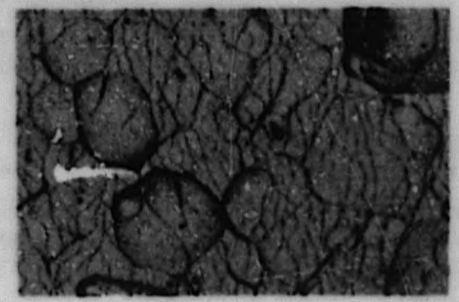
2c Aged 45 minutes 5500X



2d Aged 1 hour 5500X



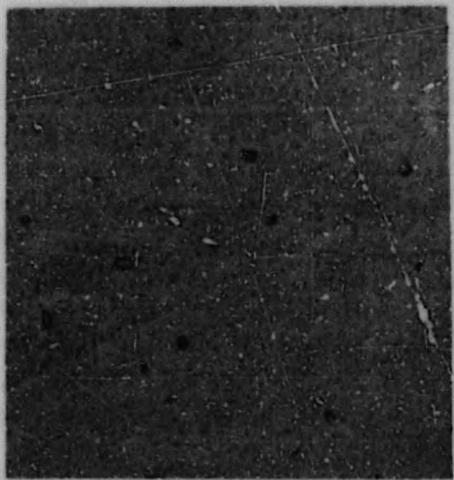
2e Aged 2 hours 5500X



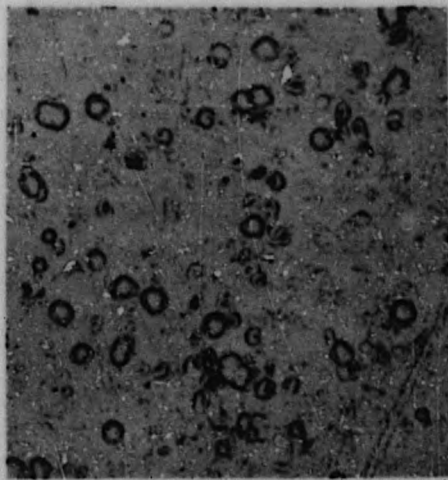
2f Aged 4.5 hours 5500X

Precipitation was first observed as the formation of "mounds" at grain boundaries (Figures 2b and 2c). As aging progressed these mounds and rods appeared within the grains (Figures 2d through 2f). The white dots in Figure 2a are artifacts in the replica.

FIGURE 2 - MICROSTRUCTURAL CHANGES DURING AGING OF 2.8% LI ALLOY
(Specimens chemically polished. Oxide film replicas.)

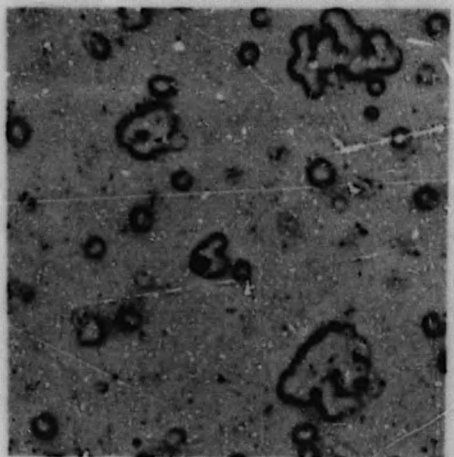


3a Solution Treated 5500X

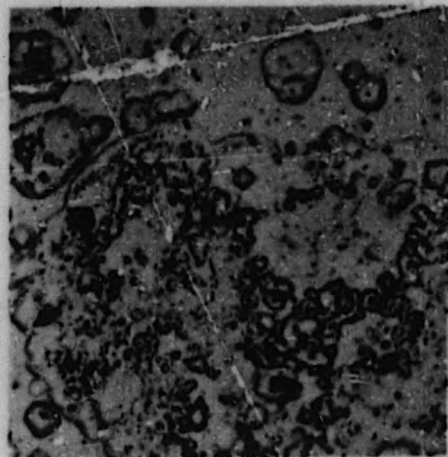


3b Aged 16 hr 5500X

Samples were solution treated for 2 hours at 525°C, quenched in water and aged at 275°C.



3c Aged 26 hr 5500X



3d Aged 44 hr 5500X

The concentration of the precipitate (round particles) followed the same variation with aging time as it did in the 2.8% alloy. Rod-shaped particles were not observed. Particles agglomerated (Figure 3d) during overaging. The round dots in Figure 3a are artifacts.

FIGURE 3 - MICROSTRUCTURAL CHANGES DURING AGING OF 1.5% LI ALLOY
(Specimens etched in HF. Oxide film replicas)

Specimens of 1.5% lithium alloys were aged and examined after etching in a 1% HF solution. Examples of these microstructures are shown in Figure 3. The microstructures follow the same pattern of development as those of the 2.8% alloy. As overaging occurs, the precipitate agglomerates into large clusters, as shown in Figure 3d. Although the variation in the precipitate concentration with aging time was similar to that of the 2.8% lithium alloy, more particles were observed in the 1.5% lithium specimens etched with HF. It is believed that this observation resulted from a combination of differences in the type of attack between the chemical polish and the etch and the depth of focus of the electron microscope. The chemical polish dissolves the LiAl particle, leaving a shallow pit which, in some cases, cannot be seen because no sharp edges exist in the replica. The HF etch attacks the interface between the LiAl particle and the matrix, producing a sharp ring depression which is easily seen in the microscope. Comparison of Figures 2 and 3 illustrates this difference in type of attack. No explanation can be given at this time for the lack of rod-shaped particles in specimens etched with HF.

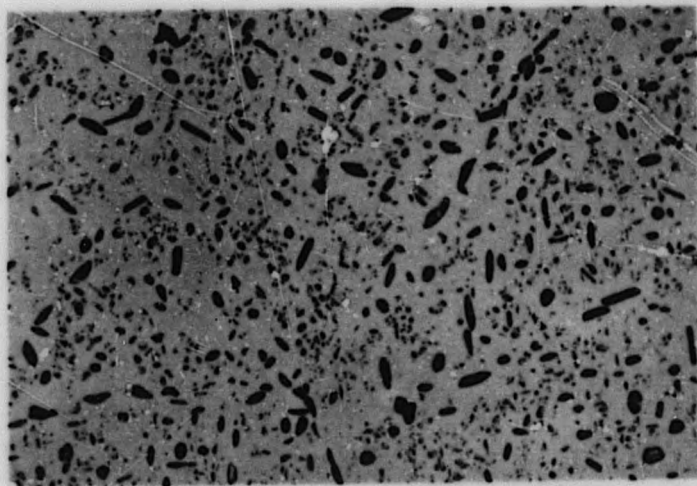
In overaged specimens, rod-shaped particles were observed in electro-polished specimens, as shown in Figure 4 on page 13. The particles were known to be rods, rather than plates, since only rods and small dots, which were the ends of rods, were seen, as shown in Figure 4a. No large round particles corresponding to the surface of a plate particle were observed. This structure was observed in both longitudinal and transverse sections.

ORIENTATION OF THE PRECIPITATE

In all age-hardening systems, a crystallographic relationship exists between the precipitating phase and the matrix. Such a relationship was found in the Al-Li system. Specimens of the 2.8% alloy were aged for four hours to develop the rod-shaped particles, and then were etched in aqua regia containing HF. This reagent is known to produce etch pits in which the sides are parallel to the (100) planes of the aluminum. As can be seen from Figure 5 on page 14, the rods of the precipitate were approximately parallel to the diagonals of the square etch pits, thus making an angle of 45° with the (100) planes. There are two planes in aluminum that intersect the (100) planes at angles close to 45° ; these are the (110) and (111) planes. This relationship between the precipitate and either the (110) or the (111) planes of the matrix has been observed in the Al-Ag, Al-Zn, and Cu-Sn systems⁽⁵⁾.

HARDNESS MEASUREMENTS

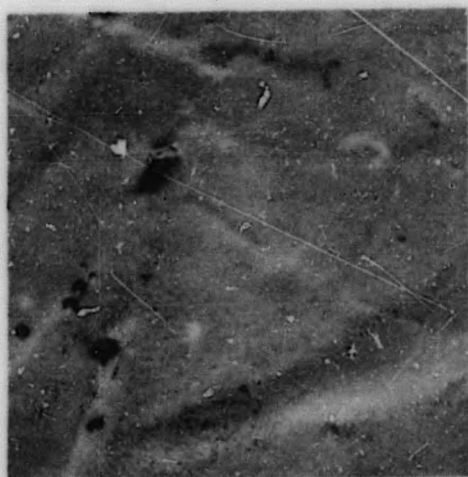
The hardness of both the 1.5 and 2.8% alloys was measured as a function of the aging time on those specimens that were used for metallographic examination. The curves, shown in Figure 6 on page 14, summarize the results of these measurements. For the 1.5% alloy the maximum hardness



4a

Optical photomicrograph

Mag. 250X



4b

Mag. 5500X

Electron photomicrograph (carbon replica). Rod-shaped particles within the grains.



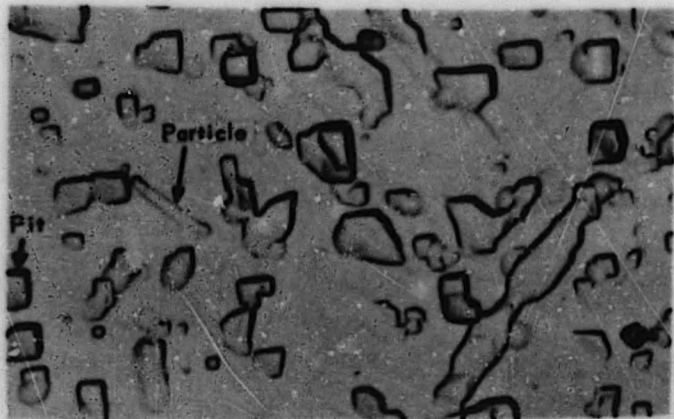
4c

Mag. 5500X

Electron photomicrograph (carbon replica). Precipitation at a grain boundary.

Specimen of 2.8% alloy was solution treated and aged for 12 hours at 275°C.

FIGURE 4 - ROD-SHAPED PARTICLES IN OVERAGED SPECIMENS
(Specimens electrolytically polished)



Mag. 3200X

The precipitate formed on planes parallel to the diagonals of the etch pits, whose sides are the (100) planes of the aluminum matrix.

FIGURE 5 - ORIENTATION OF PRECIPITATED PARTICLES
(Specimen chemically polished and etched in pitting etch. Oxide film replica.)

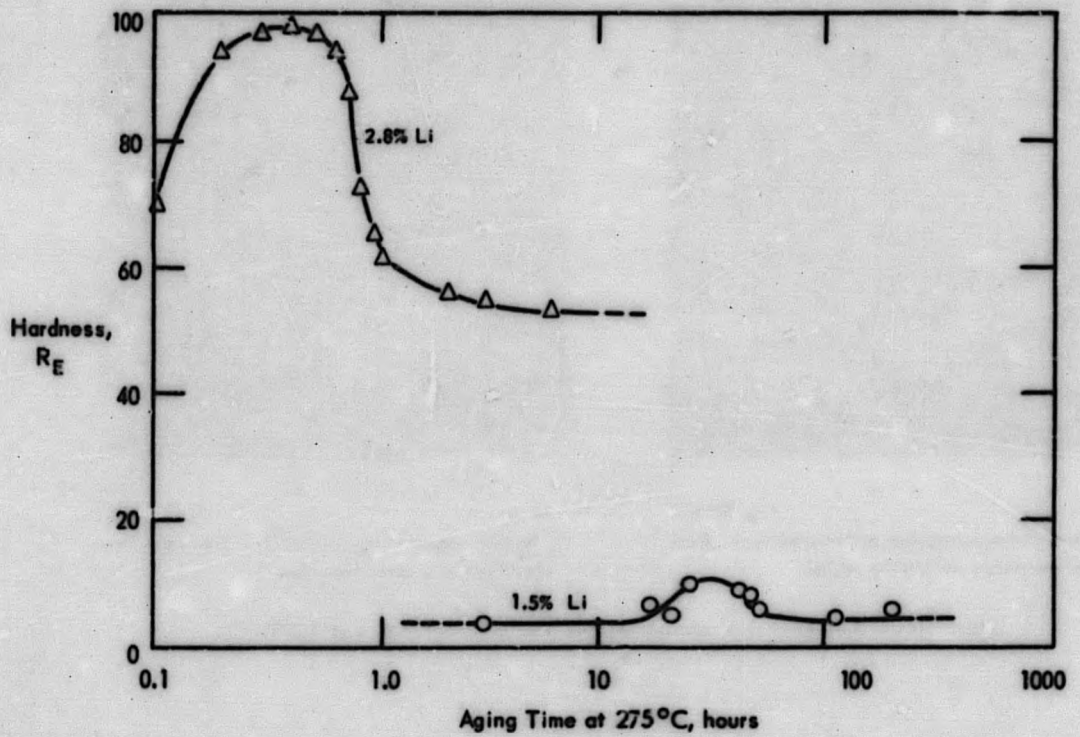


FIGURE 6 - AGING CURVES FOR Al-Li ALLOYS
(1.5% and 2.8% Li)

was 12 Rockwell "E", and occurred after aging for 28 hours. For the 2.8% alloy, the maximum hardness was 98 Rockwell "E", and occurred after aging for 25 minutes. These hardnesses apply only for the aging temperature of 275°C. The times required to achieve maximum hardness agreed closely with the times required to produce the first visible particles of precipitate, as seen by the electron microscope. The occurrence of the maximum in the curves shown in Figure 6 indicates that the Al-Li alloy is a true age-hardening alloy.

C. L. Angerman
C. L. Angerman
Pile Materials Division

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