

# QUANTITATIVE ANALYSIS OF ELASTIC PROPERTY OF AL-LI ALLOYS USING ULTRASONIC VELOCITY MEASUREMENT AND TEM

S. M. Jeon, J. D. Kim and J. K. Park  
Department of Material Science and Engineering  
Korea Advanced Institute of Science and Technology  
Taejon 305-701, Korea

S. S. Lee  
Center for Materials Characterization and Evaluation  
Korea Research Institute of Standards and Science  
Taejon 305-606, Korea

## INTRODUCTION

Al-Li alloys have been recently subject to intensive researches mainly because of their lightness and high elastic stiffness. Addition of Li has a unique property to increase the elastic modulus of the alloy by decreasing its density at the same time.

Young's modulus of Al-Li binary alloy in metastable two-phase region consists of the contribution from the matrix and that from the metastable  $\delta'$  phase of  $Al_3Li$ . Recent measurement in single crystal showed that the elastic modulus of  $\delta'$  phase is quite large as compared to that of solid solution[1]. This suggests that the presence of  $\delta'$  phase can significantly influence the elastic property of Al-Li binary alloy in metastable two-phase region, although its volume fraction is usually small, 10~15%.

The purpose of the present study was to investigate the variation of the elastic property of polycrystal of Al-Li alloys and to investigate its relationship with the microstructural evolution, particularly of  $\delta'$  phase during the aging treatment.

## EXPERIMENTS

Two alloys with a different Li composition, 2.39wt% and 3.43wt%Li (both contain 0.12wt%Zr), have been casted in a vacuum induction melting furnace. The alloys were homogenized at high temperature and the surface layer of 3mm has been machined out to avoid a layer of Li depletion. The cubes having side of 20mm have been machined from the homogenized slab in order to measure the elastic modulus and also for the TEM work. No mechanical working has been applied in order to get rid of the texture problem which is serious in this alloy system.

Cube samples have been solutionized at  $520^{\circ}\text{C}\pm 2^{\circ}\text{C}$  for 30 min. in a salt bath and then quenched to the water at room temperature. Subsequent aging treatment has been performed in either salt bath or Si-oil bath controlled to  $\pm 1^{\circ}\text{C}$ .

Modified ultrasonic pulse echo overlap method[2] has been used to determine the propagation rate of ultrasonic waves(10MHz) in longitudinal and transversal modes, which allows to calculate the elastic moduli. Density of the alloy has been determined using Archimedes principle.

For TEM work, thin sheets of ~2mm thickness has been sliced out from the cube sample and have been mechanically ground. Thin foils have been prepared using electropolishing technique in a solution of 30%  $\text{HNO}_3$  and 70%  $\text{CH}_3\text{COOH}$  at  $\sim -20^{\circ}\text{C}$ . Observation has been made at 200KeV using Philips CM 20. Foil thickness was determined using contamination spot technique. Correction was made for the truncation and overlapping effect[3].

## RESULTS AND DISCUSSION

The results of the measurement of Young's moduli are illustrated in Fig.1. As-quenched state of 2.4 alloy(2.39wt%Li) indicates Young's modulus of 78.5 GPa. On aging isothermally, the elastic modulus of the alloy first increases rapidly and then approaches a limiting value, ~80 GPa. The variation of modulus occurs slowly at  $160^{\circ}\text{C}$ , whereas it occurs rapidly at temperatures higher than  $\sim 180^{\circ}\text{C}$ . As-quenched 3.4 alloy (3.43wt%Li) indicates Young's modulus of ~80 GPa. Aging treatment at  $200^{\circ}\text{C}$  results in an increase of elastic modulus up to ~82 GPa. Present results in the 2.4 alloy are quite similar to those of Broussaud & Thomas [4] using the pulse-echo overlap method in an Al-2.5wt%Li alloy. Present results are however somewhat smaller than those of Noble et al.[5] using tensile test method in Al-2.4wt%Li and Al-3.4wt%Li alloys. The behavior of the variation of elastic property in Fig.1 resembles the age hardening behavior of the alloy. This suggests that the elastic property of the alloys is influenced by the microstructural evolution during the aging treatment.

Fig.2 illustrates an example of the dark field images of the  $\delta'$  particles which are the main constituent in this system.  $\delta'$  particles are seen to be growing with the aging time. The variation of the  $\delta'$  particle sizes is measured and results are summarized in Fig.3. The cubes of particle sizes are observed to be fairly proportional to the aging time. This

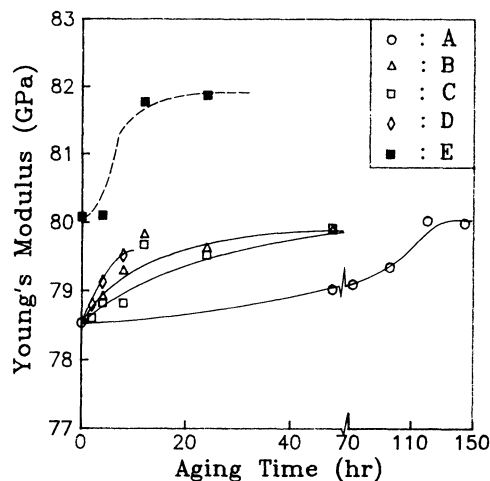


Fig. 1. Variation of Young's modulus as a function of aging time in an alloy of 2.39wt%Li(A:  $160^{\circ}\text{C}$ ; B:  $180^{\circ}\text{C}$ ; C:  $200^{\circ}\text{C}$ ; D:  $220^{\circ}\text{C}$ ) and in an alloy of 3.43wt%Li (E:  $200^{\circ}\text{C}$ ).

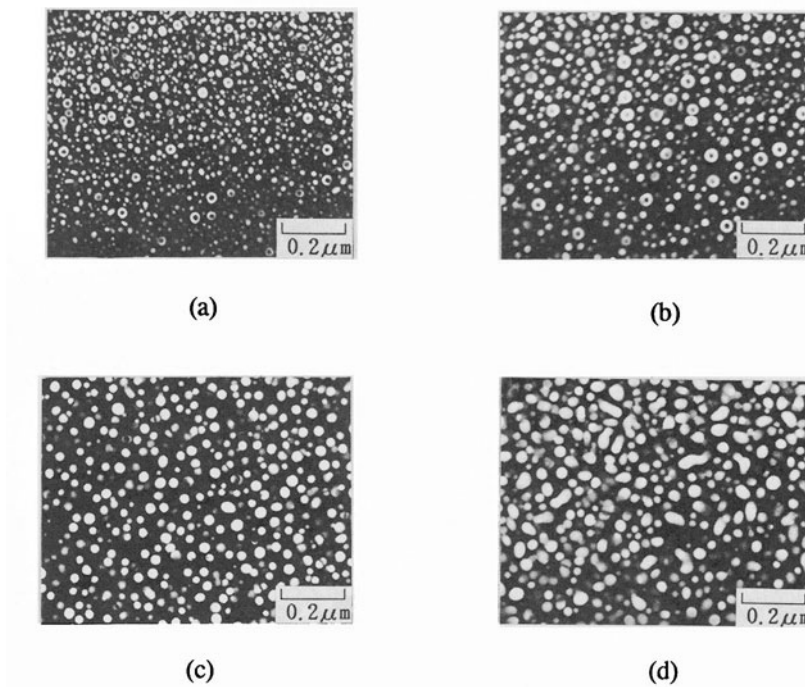


Fig. 2. Dark field images taken using a superlattice reflection in an alloy of 2.39wt%Li (a: aging at 160°C for 48hr; b: aging at 160°C for 144hr; c: aging at 200°C for 48hr) and in an alloy of 3.43wt%Li (d: aging at 200°C for 24hr).

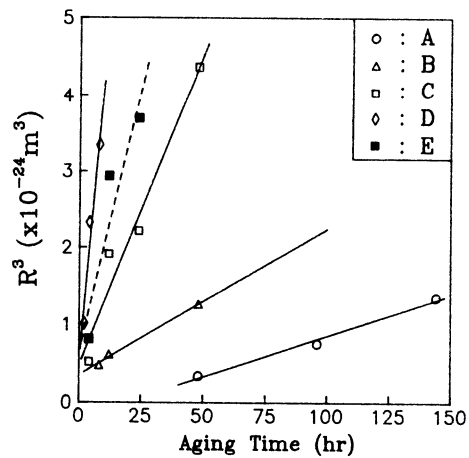


Fig. 3. Variation of the cubes of particle sizes of  $\delta'$  phase as a function of aging time in an alloy of 2.39wt%Li (A: 160°C; B: 180°C; C: 200°C; D: 220°C) and in an alloy of 3.43wt%Li (E: 200°C).

Table 1. Analysis of  $\delta'$  coarsening kinetics

Alloy	Aging Temp.(°C)	$C_\alpha$ (at%Li)	$C_{\delta'}$ (at%Li)	$K(\varphi)$ mea. (m <sup>3</sup> /sec.)	$D_{Li}$ (m <sup>2</sup> /sec.)	$\sigma$ (J/m <sup>2</sup> )
2.4 Li	160	6.00	23.0	$2.93 \times 10^{-30}$	$2.3 \times 10^{-20}$	0.007
	180	6.25	22.6	$5.26 \times 10^{-30}$	$1.1 \times 10^{-19}$	0.003
	200	6.33	21.8	$2.26 \times 10^{-29}$	$4.3 \times 10^{-19}$	0.003
	220	6.51	21.2	$1.03 \times 10^{-28}$	$1.6 \times 10^{-18}$	0.004
3.4 Li	200	6.33	21.8	$4.80 \times 10^{-29}$	$4.3 \times 10^{-19}$	0.003

is in accordance with the prediction of the LSW coarsening kinetics[6,7]. Further measurements indicate that the coarsening kinetics of the 3.4 alloy is greater than that of the 2.4 alloy by ~2 times at 200°C. This indicates that the  $\delta'$  coarsening kinetics strongly depend on its volume fraction. Analysis showed that the coarsening kinetics in this system could be well described in terms of the MLSW theory[8], in accordance with the previous reports[9,10]. The coarsening kinetics of MLSW theory is given by

$$r^3(t) - r^3(0) = K(\varphi) \cdot t \quad (1)$$

$$K(\varphi) = \frac{6 \cdot \sigma \cdot D \cdot C_e \cdot V m^2 \cdot \rho^3(\varphi)}{RT \cdot v(\varphi)}$$

where  $\rho(\varphi)$  and  $v(\varphi)$  are the parameters depending on the volume fraction,  $\varphi$ . Diffusivity data used were those of Moreau et al.[11] which have been directly measured at low temperature(150~200°C). The results are summarized in Table 1. It indicates that the interfacial energy of  $\delta'$  particles is very small to be ~4mJ/m<sup>2</sup>. This value is somewhat lower than that of Baumann & William[12], but is in good accordance with other reports[10,13]. This low interfacial energy is not unexpected if one considers a very low lattice mismatch of ~0.08% between  $\delta'$  particle and matrix.

Fig. 4 summarizes the results of the measurement of the  $\delta'$  volume fraction. An increase in the volume fraction was observed during the initial period of aging. This time period increases with a decrease in the aging temperature. This suggests that the initial stage of aging is still in the growth stage. The  $\delta'$  volume fraction of the 2.4 alloy varies from ~9% to ~11% depending on the aging condition. The limiting value, ~11% is

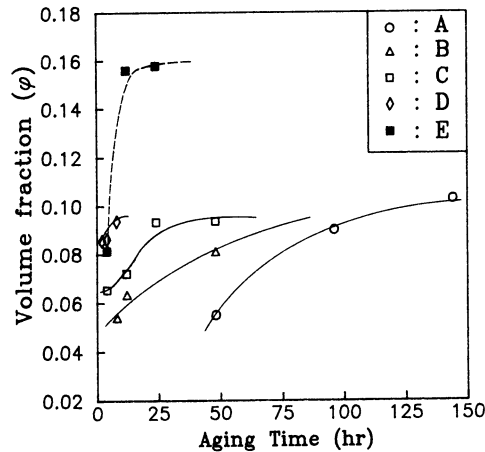


Fig. 4. Variation of the  $\delta'$  volume fraction as a function of aging time in an alloy of 2.39wt%Li (A: 160°C; B: 180°C; C: 200°C; D: 220°C) and in an alloy of 3.43wt%Li (E: 200°C).

somewhat smaller than that expected from the equilibrium phase diagram (which predicts 13%~15%). We believe that this difference is due to the precipitation of the equilibrium  $\delta$  phase.

Comparison suggests that the variation behavior of the  $\delta'$  volume fraction is similar to that of the elastic modulus. The elastic modulus of the alloy consists of two contributions, the one from the matrix and the other from the  $\delta'$  precipitates. The addition rule has two limiting cases, i.e., Voight and Reuss averaging procedures. Voight method assumes uniform strain in both phases, whereas the same stress in both phases is assumed in the Reuss method. However the difference turned out to be small in this system. We have applied Voight averaging method, in which the elastic modulus of the alloy E is expressed by

$$E = \phi E_{\delta'} + (1-\phi) E_m \quad (2)$$

where  $E_{\delta'}$  and  $E_m$  are Young's moduli of the  $\delta'$  phase and of the matrix respectively. Elastic modulus of the  $\delta'$  phase  $E_{\delta'}$  can be evaluated from eq.(2) using known Young's modulus of the solid solution, which is  $E_m = 71 + 1.22at\%Li$  [1]. Matrix was assumed to have an equilibrium composition with the  $\delta'$  phase and SAXS data [14] have been used for the equilibrium composition. Table 2 summarizes the results. The elastic modulus has been evaluated at 4 different aging temperature. The results give rise to a similar value, ~93 GPa, except the case of aging at 220°C, This value is somewhat smaller than that reported in single crystal, ~106 GPa [1]. This is closer to that estimated in polycrystal, ~96 GPa [5]. The case of aging at 220°C indicates a significantly low value. The reason for this discrepancy is not fully understood. However one possibility may be the effect of the precipitation of equilibrium  $\delta$  phase. There are two consequences: The one is the possibility of overestimation of the  $\delta'$  volume fraction because of a large inhomogeneity of  $\delta'$  density at this high temperature. An estimation however indicated that the contribution of this factor is small, i.e., ~10% overestimation in  $\delta'$  volume fraction induces a change in  $E_{\delta'}$  less than ~1%. The other is a possibility of a local variation of the equilibrium concentration of matrix due to the precipitation of  $\delta$  phase. There is a large difference(6.3at%Li vs. 2.8at%Li at 200°C for example) in the equilibrium concentrations of the matrix with respect to the  $\delta'$  and  $\delta$  phases. An estimation indicated that a small change in the equilibrium matrix concentration can induce a large change in  $E_{\delta'}$ . For example, ~10% diminution of the average equilibrium concentration results in ~10% increase of  $E_{\delta'}$ .

Table 2. Estimation of Young's modulus of  $\delta'$  phase from the alloys aged at various temperature

T(°C)	Alloy	Time(hr)	E (GPa)	$E_m$ (GPa)	$E_{\delta'}$ (GPa)	$E_{\delta'}$ (avg.)
160	2.4 Li	48	79.02	78.31	91.23	91.8
		96	79.34		89.77	
		144	79.97		94.47	
180	2.4 Li	8	79.30	78.52	92.99	94.9
		12	79.63		96.06	
		48	79.90		95.58	
200	2.4 Li	4	78.82	78.72	80.25	92.6
		12	79.67		91.91	
		24	79.52		87.30	
		48	79.90		91.34	
	3.4 Li	4	80.10	78.72	95.69	
		12	81.77		98.27	
220	2.4 Li	2	78.78	78.94	77.07	80.7
		4	79.12		81.03	
		8	79.43		84.08	

Similar argument may apply to the explanation of the discrepancy of the present data with those of Müller et al.[1] in single crystal. The result of the volume fraction measurement, as previously discussed, suggests that ~5.5% of Li is used up in the formation of  $\delta$  phase at 220°C. This has an effect to reduce, on average, the overall matrix concentration. The consideration of this effect would make  $E_{\delta'}$  larger and thus closer to the value reported in single crystal.

## CONCLUSIONS

Young's modulus of solid solution significantly increases as a result of Li addition. A further increase of Young's modulus occurs as a result of the precipitation of metastable  $\delta'$  ( $\text{Al}_3\text{Li}$ ) phase. Young's modulus of  $\delta'$  phase is estimated to be ~93 GPa which is somewhat lower than that reported in single crystal. The result in the alloy aged at high temperature, 220°C appears to give rise to a much lower value than ~93 GPa. This was estimated to be due to the influence of the precipitation of equilibrium  $\delta$  phase on the average matrix concentration. We believe that the same argument explains the discrepancy of the present  $E_{\delta'}$  value with that in single crystal. Saturation of the  $\delta'$  volume fraction occurs after a considerable period of aging time, differently from the previous reports. The saturation value is apparently lower than that expected from the equilibrium phase diagram. This was attributed to the formation of equilibrium  $\delta$  phase. Coarsening kinetics of the  $\delta'$  particles have been analyzed. The result indicates a very low value of interfacial energy, ~4mJ/m<sup>2</sup> of  $\delta'$  phase.

## ACKNOWLEDGEMENTS

This work is supported by the cooperation program of the Korea Research Institute of Standards and Science with the Universities.

## REFERENCES

1. W. Müller, E. Bubeck and V. Gerold, Aluminum-Lithium III, edited by C. Baker, C.J. Gregson, S.J. Harris and C.J. Peel ( The Inst. of Metals, London, 1986 ), p.435.
2. E. P. Papadakis, J. Appl. Phys., 35, 1474(1964).
3. E.E. Underwood, Quantitative Stereology(Addison Wesley, Reading, Mass.,1970).
4. F. Broussaud and T. Thomas, Aluminum-Lithium III, edited by C. Baker, C.J. Gregson, S.J. Harris and C.J. Peel (The Inst. of Metals, London, 1986), p.442.
5. B. Noble, S.J. Harris and K. Dinsdale, J. Mat. Sci., 17, 461(1982).
6. I.M. Lifshitz and V.V. Slyozov, J. Phys. Chem. Solids, 19, 35(1961).
7. C. Wagner, Z. Electrochem., 65, 581(1961).
8. A.J. Ardell, Acta Met., 20, 61(1972).
9. K. Mahalingam, B.P. Gu, G.L. Liedl and T.H. Sanders, Jr., Acta Met., 35, 483 (1987).
10. B.P. Gu, G.L. Liedl, T.H. Sanders, Jr. and K. Welpman, Mat. Sci. Eng., 76, 483 (1985).
11. C. Moreau, A. Allouche and E.J. Knystautas, J. Appl. Phys., 58, 4582(1985).
12. S.F. Baumann and D.B. Williams, Scripta Met., 18, 611(1984).
13. J.J. Hoyt and S. Spooner, Acta Met., 39, 689(1991).
14. S. Ceresara, G. Cocco, G. Fagherazzi and L. Schiffini, Phil. Mag., 35, 373(1977).