Variations of elastic moduli during ageing process of Al–Li solid solutions treated at high pressure

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Supersaturated Al–10 and 15 mol % Li solid solutions were prepared by means of heat treatments under high pressure and high temperature, and the variations of elastic modulus, electrical resistivity and micro-Vicker's hardness in these solid solutions during isochronal ageing up to 673 K were investigated. The maximum shear modulus was observed during the precipitation of the δ′ phase at 453 K ageing. The difference in the decomposition behaviour of several specimens obtained by high-pressure solid solutioning and the conventional one is discussed based on the results of elastic moduli measurements.

1. Introduction
Al–Li alloys present a combination of a low density and a high specific modulus which make it an attractive structural material for aerospace use. This alloy type, similar to Duralumin, is age hardenable, and its decomposition process is considered to be as follows. A δ′ unstable intermediate phase precipitates from the supersaturated alloy by disorder–order transformation, and then this δ′ phase transforms into a stable δ phase [1]. The structures of these two phases are shown in Fig. 1. The decomposition of the δ′ phase occurs rapidly, and it is reported to be unavoidable even under extremely rapid quenching conditions [2]. The precipitation of the δ′ phase increases the hardness and produces a higher elastic modulus, although the ductility is relatively low in its early stage of development [3]. Recent research has indicated that an optimum heat treatment or adding other elements to the alloy that improve the precipitation of the δ′ phase, can result in precipitations that are small in size and uniformly distributed. The control of the production of the δ or δ′ phase is important from the technological standpoint if the full potential of the Al–Li alloys is to be exploited. We have reported the phase diagram for Al rich Al–Li alloys at the high pressure of 5.4 GPa [4] and also on the variation in elastic moduli of alloys treated at a high pressure and high temperature [5]. In these articles we indicated that supersaturated solid solution by high pressure heat treatment has little or no δ′ phase because the change in elastic moduli in the alloys is linear up to 17.5 mol % Li. It may be possible to prevent the precipitation of the δ′ phase by high pressure solid solutioning. In fact, the mean volume fraction of atomic defects is greatly reduced by adding pressure [6], which leads to a slower diffusion speed for the solute atom which in turn prevents reordering of the supersaturated solid solution. Therefore, the ageing character of Al–Li alloys treated at high-pressure can be expected to differ from that of the conventional one, although the research on this point remains to be done. Further, we have discovered a unique elastic behaviour of this alloy, in that, adding Li to the solid solution causes a higher Young's modulus and shear modulus but a lower bulk modulus, and it is of interest to determine whether or not the nature of this effect would change.

In the present study, we investigated the variations in the elastic constants of Al–10 and 15 mol % Li solid solution treated at high pressure during isochronal ageing, and the elastic moduli of the δ′ phase were estimated. The results are compared with those of conventionally processed alloys, and the effects of high pressure solid solutioning are elucidated.

2. Experimental procedure
Al–10 and 15 mol % Li alloy solid solutions were prepared by the high pressure solid solutioning method described in the previous paper [4]. These alloys were prepared from Al (99.99 wt %) and an Al–Li master alloy. After casting the mixture using LiCl as a flux, specimens were heat treated under a pressure of 5.4 GPa at 960 K for the 10 mol % Li and 1060 K for the 15 mol % Li and were then quenched to room temperature after heating for 36 ks.

Specimens were also prepared by a conventional process, alloys were heated in an Ar atmosphere at

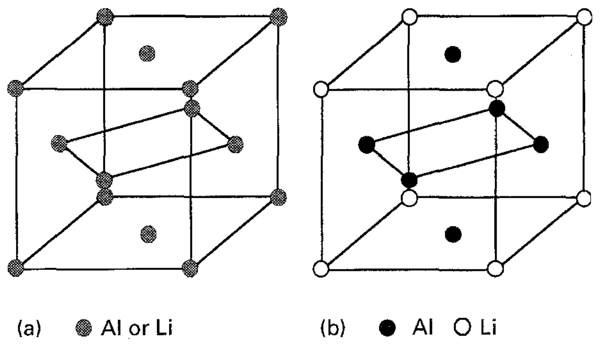

Figure 1 Schematic decomposition process of the Al–Li alloy. (a) shows the supersaturated solid solution, atoms of Al and Li are arranged in an f.c.c. matrix at random. (b) shows the ordered structure of the δ′ phase metastable intermetallic Al_3Li. Their structure is the same as that of Al, and the lattice constant is also almost the same. This phase appears in the process by which the supersaturated solid solution is quenched. The decomposition of the δ′ phase reportedly started very quickly at an early stage in the quenching, so the manner in which precipitation occurs remains unclear.

823 K for the 10 mol % Li and 873 K for the 15 mol % Li, then quenched in iced water after heating for 1.2 ks.

The phase peaks of these alloys was checked by X-ray diffraction (XRD), and all specimens were identified as being single α-phase. Isochronal ageing was performed at temperatures between 303–573 K in 30 K steps in air, or at 623 K and 673 K in an argon atmosphere. All the heat treatments were for a time period of 18 ks. The three-dimensional resonance method of multiple modes [7] was used in order to determine the elastic moduli, the density was measured by Archimedes method and the electrical resistivity was observed by the four-probe method.

3. Results and discussion

3.1. Variations in the XRD pattern

Fig. 2 shows the evolution of the XRD patterns of Al–15 mol % Li (high pressure treated) during isochronal ageing. All patterns contained sharp diffraction peaks from the α phase, and also the (1 0 0) and (1 1 0) peaks of the δ′ phase were found in the patterns for the samples aged at 483 and 513 K. These peaks were derived from ordering of the δ′ phase and the width and low intensity of the peaks were attributed to the extra-fine precipitate size. Schmitz and Hassen [8] reported that the amount of the δ′ phase in the early stage of decomposition is too small to observe using XRD.

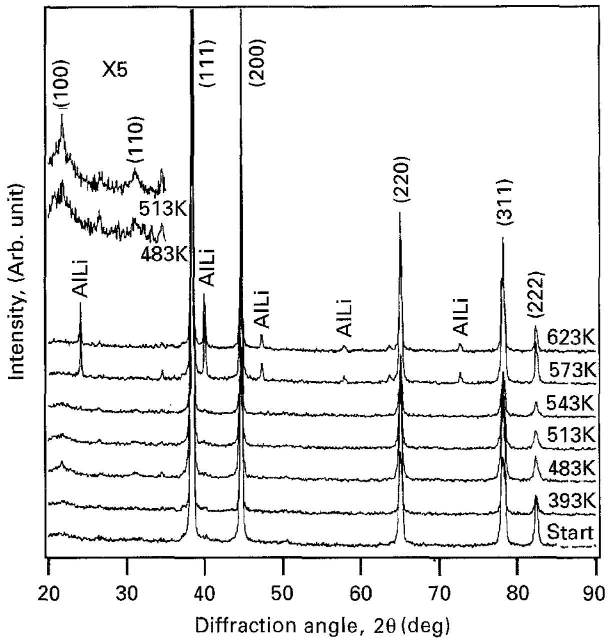

Figure 2 X-ray diffraction patterns of Al–15 mol % Li alloy during the ageing process. The prohibited peak of the f.c.c. matrix in the measurement for 483 K and 513 K ageing is barely visible because of the extremely small particles of the unstable θ′ phase [8].

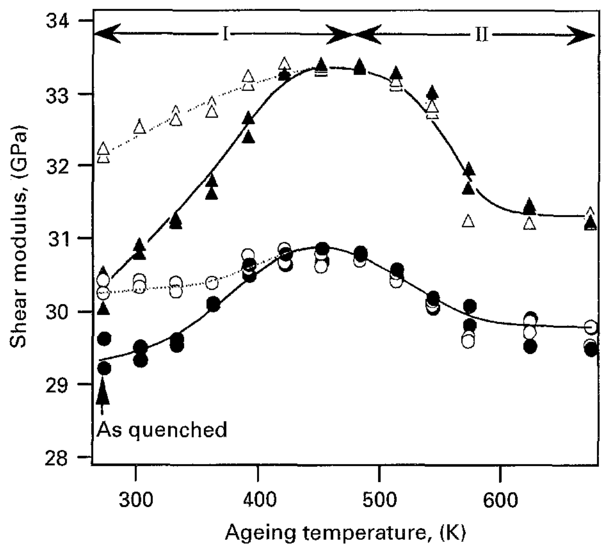

Figure 3 Variation of shear modulus in Al–Li alloys during the ageing process. The data are taken for samples that were; (●) 10% Li high pressure synthesis, (○) 10% Li conventional synthesis, (▲) 15% Li high pressure synthesis and (△) 15% Li conventional synthesis.

3.2. Variations of the elastic modulus

Figs 3, 4 and 5 show the variation in the shear modulus *G*, the Young's modulus *E* and the bulk modulus *B* as a function of temperature during isochronal ageing. The dotted lines show the data for conventionally treated alloys and solid lines indicate the data for high pressure treated alloys. The trends in the variations can be separated into two stages, i.e., *E* and *G* increase from 363–483 K for 10 mol % Li and to 483 K for 15 mol % Li (Stage I) and then they decrease above 513 or 573 K (Stage II). Each stage corresponds to the precipitation of either the δ′ or the δ phase as observed in the XRD patterns. In terms of ageing, the maximum *G* and *E* reached 2% and 5% for 10 mol % Li and, 10% and 8% for 15 mol % Li, respectively. These increases are mostly derived from the precipitation of the δ′ phase. Therefore, the elastic moduli of the δ′ phase can be estimated using these values. The calculation was carried out using Voigt's law because of the good coherence of the δ′ phase with the α matrix [9]. Moreover, the volume fraction of the δ′ phase was estimated from the equilibrium phase diagram [10]. The resultant elastic moduli of the δ′ phase are listed in Table I with the theoretical values

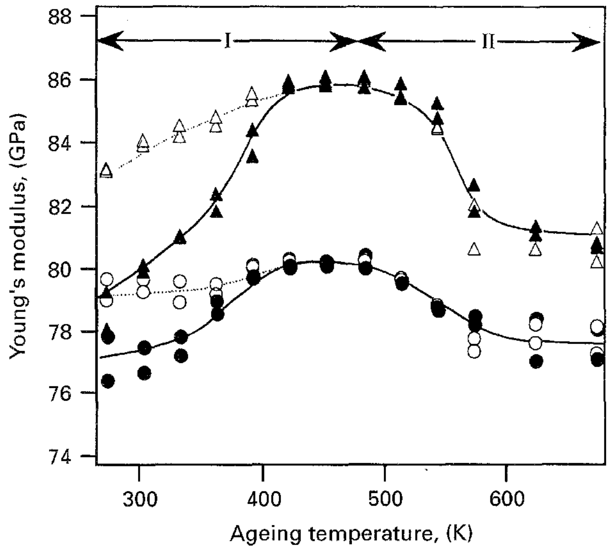

Figure 4 Variation of Young's modulus in Al–Li alloys during the ageing process. The samples were; (●) 10% Li high pressure synthesis, (○) 10% Li conventional synthesis, (▲) 15% Li high pressure synthesis and (△) 15% Li conventional synthesis.

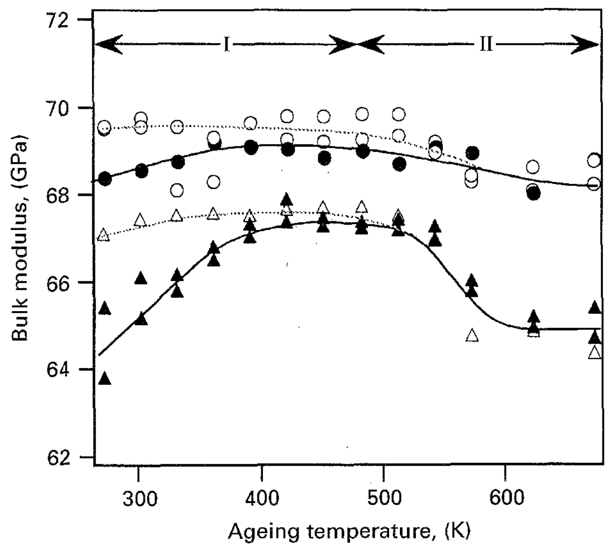

Figure 5 Variation of bulk modulus in Al–Li alloys during the ageing process. The data were taken on the samples, (●) 10% Li high pressure synthesis, (○) 10% Li conventional synthesis, (▲) 15% Li high pressure synthesis and (△) 15% Li conventional synthesis.

calculated by Mehl [11]. The theoretical values are higher than our results, as is the case for the calculated elastic modulus for Al which is 10–20% higher than our actual measurements. Hence, we think that our results are reasonable.

We now discuss the variation of B with the Li concentration in the alloys. The values of B in Al–15 mol% Li are always lower than those in Al–10 mol% Li during the ageing process. On the other hand, E and G increase with increasing Li concentration, so the unique elastic property of Al–Li alloy [5] is found to be maintained during the ageing process.

Fig. 6 shows the variation in density of the bulk specimens. There was a small decrease in stage II in which the stable δ phase precipitates, though no

TABLE I Resultant elastic moduli of the δ′ phase (Al_3Li)

	This work	Mehl [11]
C_{11} (GPa)	114.7	139.8
C_{12} (GPa)	39.1	33.7
C_{44} (GPa)	37.8	40.7
E (GPa)	94.8	111.5
ν	0.254	0.230

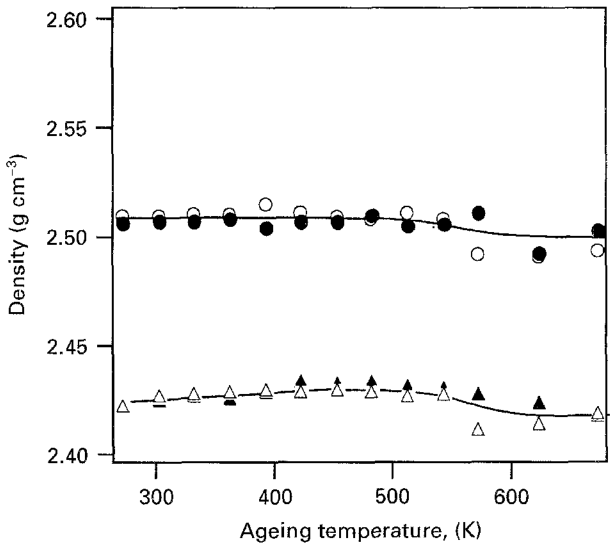

Figure 6 Variation of bulk densities in Al–Li alloys during the ageing process. The data were taken on the samples, (●) 10% Li high pressure synthesis, (○) 10% Li conventional synthesis, (▲) 15% Li high pressure synthesis and (△) 15% Li conventional synthesis.

change was found during stage I where the δ′ phase precipitates grow in size and become larger. The misfit ε between the α matrix and the δ′ phase is very small.

$$\varepsilon = \Delta a/a$$

Where, a is the lattice constant of the matrix and Δa is the difference in the lattice constant between the δ′ phase and the α phase, ε is reported to be 0.08% or 0.2% [12].

The small reduction in density observed during the ageing process at higher temperature is understood as follows. The density of a specimen that contains both α and δ phases was estimated from the individual densities of each of the components that were calculated from the lattice constants obtained by X-ray diffraction. Thus, the calculated density of a specimen that separates into α and δ phases is 0.1% smaller than that of the supersaturated α phase, which is in good agreement with the observed variation of the resultant density. Therefore, it is thought that there are no voids in the specimen, so the variation in resultant density is the same as the true density calculated from X-ray diffraction.

Variations in the micro Vickers hardness (H_v) and electrical resistivity (ρ) during the ageing process are shown in Fig. 7 and Fig. 8. H_v increases in stage I, and simultaneously the electrical resistivity is decreased by the ordering phenomenon in the specimen and reaches its lowest value at 483 K, which is the

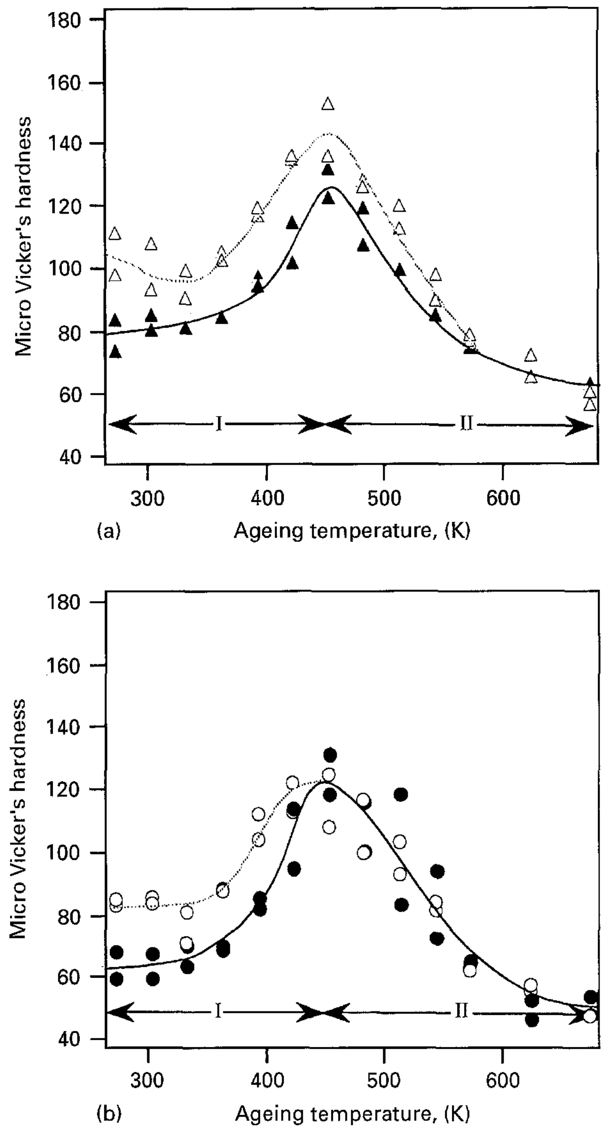

Figure 7 Variation of micro Vickers hardness in Al–Li alloys during the ageing process. The data were taken on the samples (▲) 15% Li high pressure synthesis and (△) 15% Li conventional synthesis, (●) 10% Li high pressure synthesis, (○) 10% Li conventional synthesis.

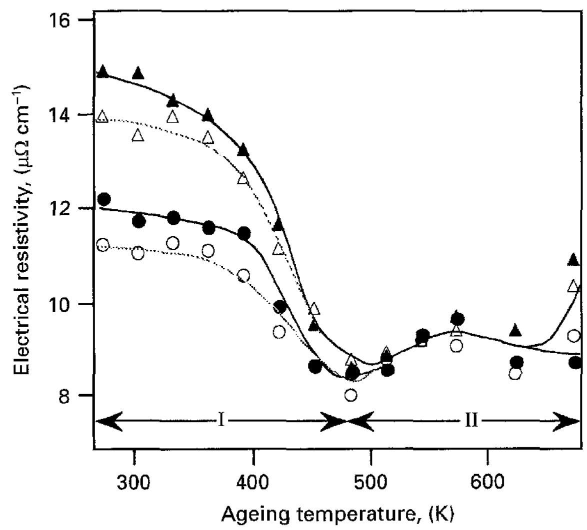

Figure 8 Variation of electronic resistivity of Al–Li alloys during the ageing process. The data were taken at room temperature on the samples, (●) 10% Li high pressure synthesis, (○) 10% Li conventional synthesis, (▲) 15% Li high pressure synthesis and (△) 15% Li conventional synthesis.

same temperature for which the values for E and G reach a maximum. Thus, these changes are associated with the precipitation of the δ' phase.

3.3. Effect of high pressure processing

In this section, we discuss the effect of pressure during solid solutioning on the ageing character of the Al–Li alloy. The variation in material properties of specimens that were conventionally processed are shown by the dotted line in the figures discussed earlier. The E and G values (shown in Figs 3 and 4) in stage I for samples that were processed under high pressure were higher than those conventionally processed, but the values were essentially the same when processed at temperatures greater than 483 K. The increases in E and G in stage I were derived from the precipitation of the δ' phase, so the difference in the elastic modulus in the as quenched state indicates a difference in the amount of the δ' phase, i.e., there is little if any δ' phase in specimens processed at high pressure. In stage II the segregation goes further and equilibrium is achieved so the effect of high pressure processing vanishes. Differences were found in the resultant H_v and ρ values for each processing condition, whether by high-pressure or the conventional method. In the case of ρ, a reverse behaviour to that for E and G is observed since ρ is observed to decrease with the reduction in the level of disordering in the specimen, whereas the precipitation of the δ' phase means an increase in order of the specimen. Thus, the specimens treated at normal pressure have some δ' phase as quenched, and the high pressure treated solid solution includes little or no δ' phase.

Why was precipitation of the δ' phase interrupted by adding pressure? Firstly the δ' phase is relatively unstable at high pressure, secondly, the mean concentration of atomic voids is drastically reduced by adding pressure. The latter case, in which the volume fraction of atomic voids decreases compared to the case at normal pressure the Al atomic void volume at 5.4 GPa reportedly decreases several hundred-fold [6]. This is the ostensible reason for the interruption by increasing the pressure.

4. Conclusion

In this study, we investigated the variation of material properties (mainly elastic modulus) in Al–Li alloys treated at a pressure of 5.4 GPa during isochronal ageing. The effect on segregation of the δ' phase by the addition of pressure during solid solutioning was studied. The results were as follows; (i) The elastic modulus, micro Vicker's hardness and electrical resistivity of Al –10 and 15 mol % Li alloys heat treated at a pressure of 5.4 GPa during isochronal ageing were measured. The Young's modulus and shear modulus were increased during ageing at 303–483 K for the 10 mol % Li and for temperatures between as quenched to 483 K for the 15 mol % Li. They showed decreased values for annealing in the temperature range 483–513 K or 573 K. These variations proved to be derived from the precipitation of the δ' and δ phases as shown in X-ray diffraction experiments. In addition it was also shown that the micro Vickers hardness and electrical resistivity changed at almost the same temperature as at which the elastic modulus changes. (ii) These variations were compared with those for specimens that were conventionally processed. An obvious difference was seen in the ageing processes at relatively low temperatures. This means more δ′ phase was contained in the specimen processed at atmospheric pressure, and the control of the segregation of the δ′ phase by the use of pressure is suggested from these results.

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