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The elastic modulus of aluminium-lithium alloys

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Young's modulus measurements have been made on Al–Li alloys containing up to 32 at % lithium, in an attempt to determine the cause of the high modulus that characterizes this potentially important alloy system. In alloys of commercial interest (7–11 at %, 2–3 wt % lithium) the modulus is in the range 79 to 83 GPa, the actual value depending on heat-treatment conditions. The major contribution to this increased modulus arises from lithium in solid solution. The Young's moduli of the Al_3Li and AlLi intermetallic phases are estimated to be 96 GPa and 105 GPa respectively. Additions of magnesium to the Al–Li system produce a small decrease of the modulus, e.g. 4.5 at % (4 wt %) magnesium reduces the modulus by approximately 2 GPa.

1. Introduction

The addition of lithium to aluminium produces an age-hardenable alloy with the precipitation sequence [1]:

$$\text{supersaturated solid solution} \rightarrow \delta' (Al_3Li) \rightarrow \delta (AlLi).$$

After suitable heat-treatment, the transition phase δ' forms as spherical particles which have an ordered $L1_2$ structure and this results in considerable strengthening [1–3]. Additional strengthening can be achieved by the presence of further elements, e.g. magnesium produces solid-solution strengthening [4].

Alloys of the Al–Li system have a high stiffness and a low density, e.g. a 10.5 at % (3 wt %) addition of lithium increase the specific Young's modulus by some 30% [4]. It is this characteristic that has aroused interest in Al–Li alloys for aerospace applications [5].

The general strengthening of Al–Li alloys results from the presence of a large volume fraction of the coherent δ' phase, but the cause of the high modulus is not known. It has been suggested [6, 7] that the δ' phase may have a high intrinsic modulus due to its ordered nature, and that this is producing the high values of Young's modulus observed in the alloys, but no systematic study appears to have been carried out.

The present work has been concerned with the determination of elastic modulus in a range of Al–Li alloys spanning the single-phase α, $\alpha + \delta'$ and $\alpha + \delta' + \delta$ regions. These phase regions are defined in Fig. 1. In addition, the effect of magnesium on the modulus of Al–Li alloys has been evaluated.

2. Experimental procedure

A range of alloys up to 32 at % lithium and 0–4 at % magnesium was prepared by melting and casting high-purity materials under an argon atmosphere. Compositions of the alloys are given in Table I. Unless otherwise stated, all alloy compositions in this paper are expressed in atomic percentages. In addition to the elements listed, all alloys contained 0.05 % zirconium; this element reduces the grain size and therefore improves the strength and fracture resistence. Preliminary work showed that the zirconium addition did not affect the value of the elastic modulus.

All alloys were homogenized near their solidus temperature, extruded and rolled to 2.0 mm strip. Tensile samples were machined from this strip, solution treated at 20° C above the solvus temperature and water quenched. Some alloys were tested in this quenched condition; others after ageing at 170 and 200° C. Modulus measurements were made statically using strain gauges attached to each side of the specimen. Particular attention was paid to axiality of loading in the tensile machine, and it is estimated that errors in the modulus value due to non-axiality of loading did not exceed 0.5 %.

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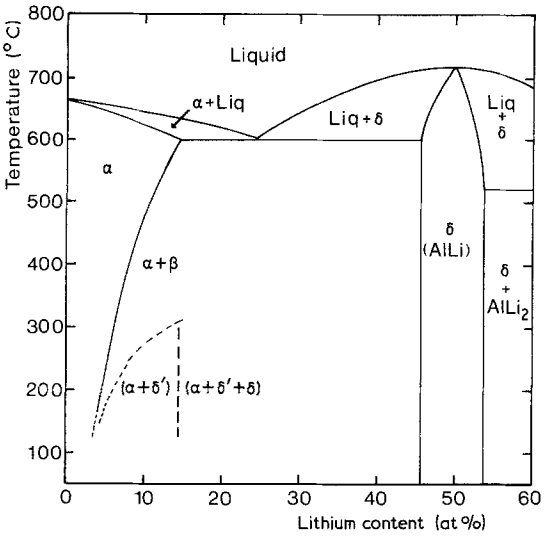


Figure 1 Phase diagram of Al–Li system.

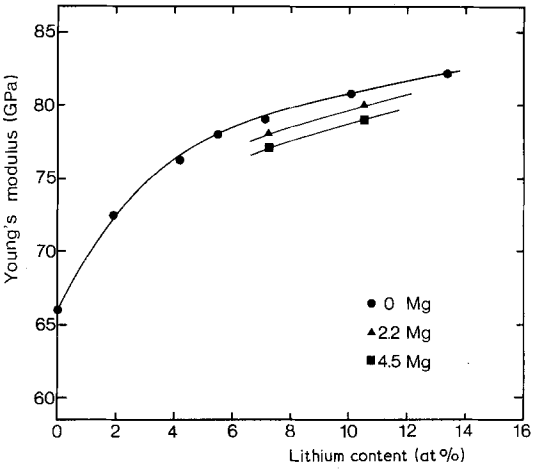


Figure 2 Variation of Young's modulus with lithium in solid solution.

3. Experimental results

Young's modulus determinations have been made on alloys where the lithium is in solid solution, present as δ' (Al_3Li) and present as δ (AlLi).

3.1. Solid-solution alloys

The limit of solid solubility of lithium in aluminium is 14.4 at % (4.2 wt %) at 600° C. A series of alloys containing 0, 2, 4, 5, 7, 10 and 14 at % lithium has been produced in the single-phase α state by rapid quenching from above the δ solvus temperature. Electron microscopy showed that a very small quantity of fine δ' is produced during the quenching of the more concentrated alloys, but as will become apparent later this will not have had a large effect on the measured modulus values.

TABLE I Composition of alloys*

Alloy code	Lithium (at %)	Magnesium (at %)
Al	0	-
Al-2Li	1.9	-
Al-4Li	4.2	-
Al-5Li	5.5	-
Al-7Li	7.1	-
Al-10Li	10.1	-
Al-14Li	13.4	-
Al-17Li	16.8	-
Al-19Li	18.9	-
Al-32Li	32.0	-
Al-7Li-2Mg	7.2	2.2
Al-7Li-4Mg	7.2	4.5
Al-10Li-2Mg	10.4	2.2
Al-10Li-4Mg	10.5	4.5

*All alloys contained 0.05 % zirconium for grain refinement.

The results of the Young's moduli determinations are shown in Fig. 2, where it can be seen that the presence of lithium in solid solution significantly increases the modulus. The increase is rapid over the first few atomic per cent addition but thereafter the rate of increase falls. Alloys for commercial interest contain between 7 and 11 at % (2–3 wt %) lithium and for these alloys the lithium in solid solution has increased the modulus from 66 GPa to 79–81 GPa, i.e. a 20 % improvement.

3.2. Alloys aged to produce δ'

The alloys containing 0, 2, 4, 5, 7, 10 and 14 at % lithium were aged at 170° C. The δ' solvus occurs at approximately 5.5 % lithium for this ageing temperature, so that alloys containing 5.5–14.0 % lithium contained increasing amounts of the δ' phase. Electron microscopy on these alloys showed the size and volume fraction of δ' to vary between 20 and 30 nm and 0.01 and 0.30, respectively. Fig. 3a and b show typical microstructures at 7 and 14 at % Li. No δ phase was detected in any of the alloys containing less than 14 % lithium.

The effect of ageing on the modulus values of the alloys is shown in Fig. 4. No change occurred in alloys containing less than 5.5 % lithium, but in those alloys containing the δ' phase a small increase in modulus occurred relative to the solution-treated value. The value of the modulus in alloys containing δ' increased in a linear manner with lithium concentration, from a value of 80 GPa at 7 % lithium to 86 GPa at 14 % lithium. Modulus determinations

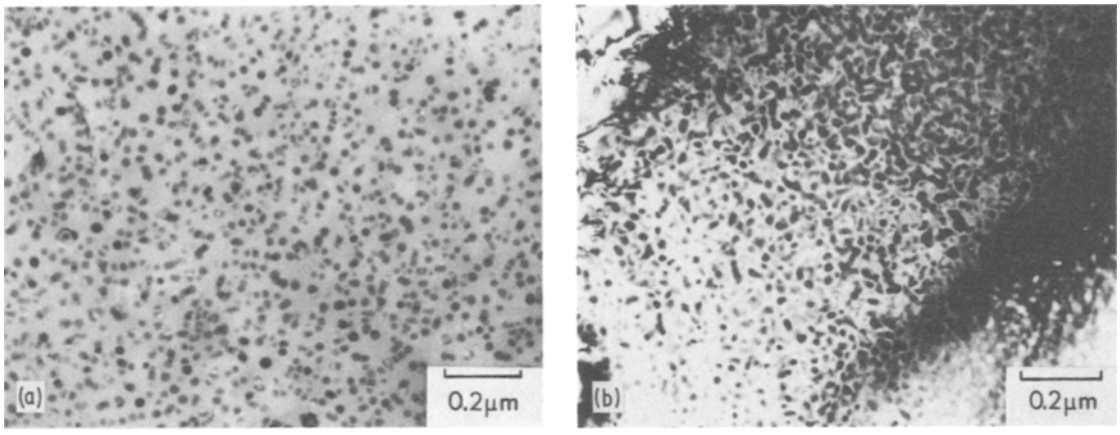


Figure 3 δ′ precipitate dispersions in (a) Al–7 at% Li and (b) Al–14 at% Li.

were also made on alloys that had been aged at 200° C and the values found to be the same as those aged at 170° C thus indicating that the equilibrium fraction of δ′ has been closely approached at the lower ageing temperature. This being the case, the contributions that the δ′ phase and the solid-solution α make to the modulus can be estimated (see Fig. 4). For alloys of commercial interest the contribution from δ′ is approximately 14% at 7% lithium and 30% at 11% lithium.

3.3. Alloys containing the δ phase

Alloys with more than 14.2% lithium contain the δ phase formed directly from the melt. Fig. 5a–c show typical optical micrographs of high-lithium alloys in both cast and extruded forms. In the case of the 20% lithium alloy dendrites of aluminum-rich solid solution (α) are surrounded by a eutectic of (α + δ). At 32% lithium, δ is present as the pro-eutectic phase, again surrounded by (α + δ) eutectic. Modulus measurements were made on alloys containing 17, 19 and 32 at% lithium (aged condition) and the results are shown in Table II. A small increase was detected at large volume fractions (~0.50) of δ and a rule-of-mixtures calculation (see Discussion) indicates a modulus for the intermetallic AlLi of approximately 105 GPa. The hardness of the intermetallic was measured at 160 VPN.

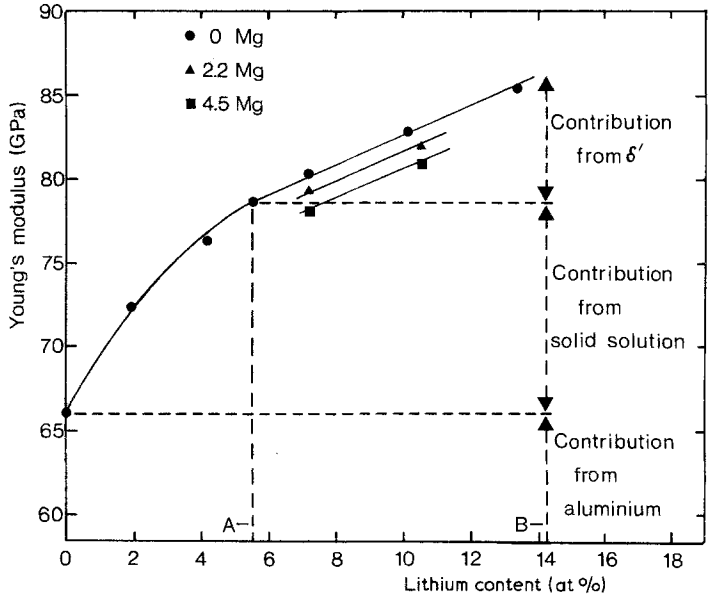
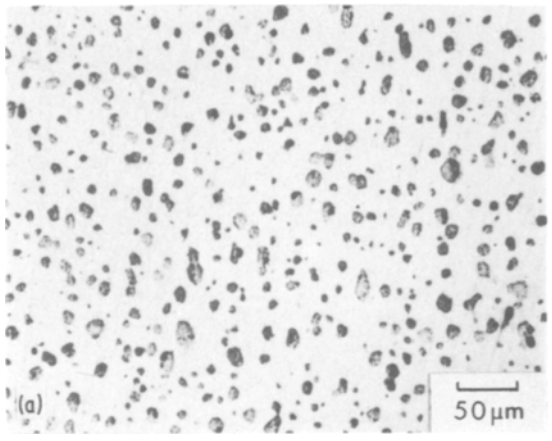
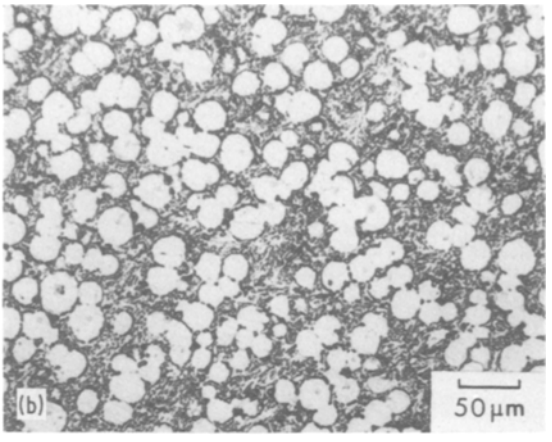


Figure 4 Variation of Young's modulus with lithium in aged alloys.





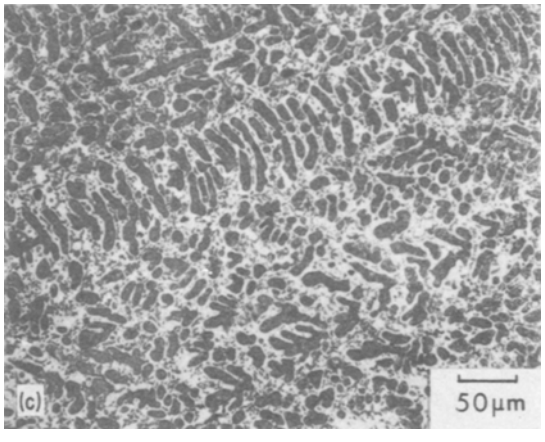


Figure 5 δ precipitation in alloys containing (a) 19% lithium (extruded), (b) 19% lithium (as-cast) and 32% lithium (as-cast).

3.4. Density and specific modulus measurements

Density measurements were carried out on the as-cast alloys containing up to 20% lithium; the results are plotted in Fig. 6. The plot of density versus lithium concentration is linear and indicates a reduction of almost 1% in density for each 1 at% lithium addition. Extrapolation of this plot to 50% lithium produces a value of 1600 $kg\,m^{-3}$ for the density of the δ phase. This should be compared with a value of 1725 $kg\,m^{-3}$ quoted by Mondolfo [8].

Using the modulus data for the aged alloys and the above density measurements, values of specific modulus were calculated and these are plotted in Fig. 7. At 7% lithium the specific modulus has been increased by 18% relative to aluminium, and increased by 34% at 11% lithium.

TABLE II Elastic modulus and volume fraction of δ in alloys containing 17–32 %Li

Lithium content (at %)	Volume-fraction of δ	Young's modulus (GPa)
17	11	87
19	20	88
32	53	94

3.5. Alloys containing magnesium

Various magnesium additions have been made to alloys containing 7 and 10% lithium; the results are shown in Figs 2 and 4. In both the solution-treated and the aged conditions the effect of magnesium is to reduce the modulus, the extent of the reductions being approximately 0.5% per at% Mg. From a modulus point of view, therefore, magnesium additions are not at first sight a desirable addition. However, at the same time the density of the alloy is reduced by the addition of magnesium (measured at −0.55% per at% Mg) so that the specific modulus of the alloy is not adversely affected (see Fig. 7).

4. Discussion

4.1. The modulus of δ′ (Al_3Li) phase

Theoretical models [9] have shown that the elastic modulus of a composite material containing a particulate phase should be between minimum and maximum bounds given by

$$E_pE_m/[(1-V_p)E_m + V_pE_p] \leqslant E_c \leqslant (1-V_p)E_m + V_pE_p \quad (1)$$

where the E and V terms are elastic moduli and volume fraction terms relating to composite alloy, c, precipitate, p, and solid-solution matrix, m. The left-hand side of the above equation, i.e. the lower

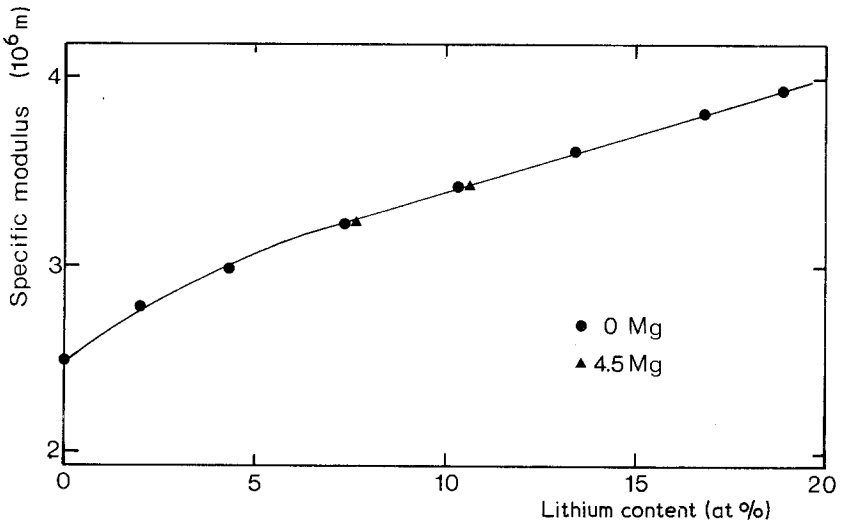


Figure 6 Variation of density with lithium concentration.

bound, refers to the condition where both matrix and precipitate are equally stressed, whilst the right-hand part is for the situation where both are equally strained. Where the ratio E_p/E_m is less than three, the separation between the bounds is small.

The right-hand side of Equation 1 (often referred to as the rule of mixtures) was applied to the modulus data for Al–Li alloys containing various amounts of δ' phase. For the aged alloys a value for $E_m = 78.5$ GPa was taken at 5.5% lithium. Calculations using the data given in Fig. 4 produce a value of 96 GPa for the Young's modulus of Al_3Li. Such a value is not exceptional for intermetallics based on aluminium, and therefore the contribution from the Al_3Li phase to the modulus will be relatively small unless the volume fraction is very high. For alloys of commercial importance the volume fraction of Al_3Li is in the range 0.04 to 0.10 and therefore the maximum contribution that δ' can make to the modulus is about 30% at 11% lithium. This contribution is even less (approximately halved) if the value for the aged alloy is compared with that for the alloy in the solution-treated condition.

The relatively low modulus of the Al_3Li phase is in accord with many ordered A_3B compounds with $L1_2$ structures. For example, the modulus of ordered Cu_3Au is only about 5% higher than that of copper, and the moduli of Ni_3Fe, Ni_3Mn are about the same as pure nickel.

It can be concluded that for alloys being developed for aerospace applications (7–11 at% Li, 2–3 wt% Li) the major contribution to the modulus does not come from $\delta'(Al_3Li)$.

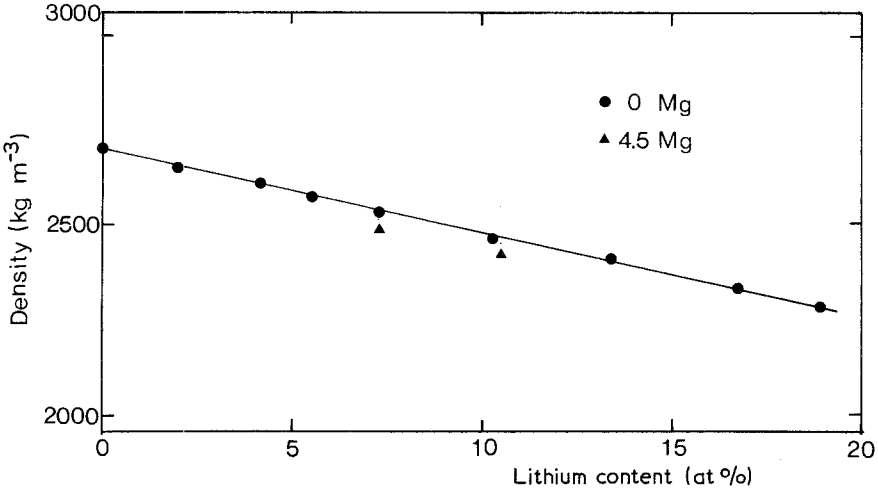


Figure 7 Change in specific modulus with increasing lithium concentration in aged alloys.

TABLE III Properties of various intermetallic phases

Compound	Hardness (VPN)	Young's modulus* (GPa)	Heat of formation (kJ mol^{-1})
AlLi	160	105	30
Al_2Cu	400–600	100	13
Al_7Cr	500–700	130	13
Al_6Mn	550	125	15
Al_3Fe	700	130	25
Al_3Ti	400–700	150	35
Al_3Ni	700	115	40

*Modulus values extrapolated for data for dilute two-phase alloys.

4.2. The modulus of δ (AlLi) intermetallic

A similar analysis to that employed in Section 4.1 was adopted for the data obtained on alloys containing > 14.4% lithium. A rule-of-mixtures equation involving three components was adopted, i.e.

$$E_{\text{aged alloy}} = E_m V_m + E_{\delta'} V_{\delta'} + E_\delta V_\delta$$

where δ' refers to the Al_3Li phase and δ refers to the AlLi phase.

Assuming E_m at 5.5% Li = 78.5 GPa and $E_{\delta'}$ = 96 GPa and taking the experimental data given in Table II a value of 105 GPa may be estimated for the AlLi phase. Such a value is within the range normally found for intermetallics in aluminium alloys, i.e. approximately 100 to 150 GPa. Similar comments apply to the heat of formation of AlLi, which is 30 kJ mol^{-1}; typical compounds in aluminium alloys are in the range 13 to 49 kJ mol^{-1} (see Table III). The hardness of AlLi at 160 VPN is considerably lower than other intermetallics which are commonly in the range 400 to 700 VPN.

It can be concluded that the intermetallic AlLi does not have exceptionally high intermetallic bond energies and, therefore, can play little or no part in the remarkably high modulus values observed in the Al–Li alloy system.

4.3. The modulus of solid-solution alloys

The results in Fig. 2 show that lithium in solid solution produces a very large increase in Young's modulus. In fact, many of the common alloying elements added to aluminium produce an improvement in modulus, magnesium being the notable exception. It is of interest to compare the effect of lithium on elastic modulus with other elements that form solid solutions with aluminium to see if the observed increase is exceptional or if it fits a general trend in aluminium-based alloys. Data on the modulus of various aluminium alloys are available [8] or have been determined as part of the present work.

Earlier workers [10] have measured the Young's modulus of quenched aluminium alloys and noted an increase with increased solute concentrations. In particular the moduli of quenched Al–Ag alloys were measured over the range 0 to 15% silver, i.e. a range similar to that used in the present work on Al–Li alloys. The general trend in the two alloy systems is similar, i.e. an initial rapid increase in modulus over the first few atomic per cent addition, followed by a gradual levelling-off. The explanation proposed [10] for the initial increase of modulus in the Al–Ag system was based on the locking of dislocations by solute atoms, which prevents flexing of the dislocation lines between their anchoring points. The argument against such an explanation for the series of alloys described in the present work is that there is no evidence of dislocation locking by lithium alloys. Also, in the Al–Mg system, where evidence of solute–dislocation interaction does exist, the modulus decreases rather than increases. Modulus values in the literature [8] indicate a decrease of 0.5 GPa per atomic per cent of magnesium, which compares favourably with the value of 0.5 GPa obtained in the current work using Al–Li as the base material.

As a means of comparison, the modulus results for the Al–Li system will be compared to those of other solid-solution aluminium alloys on the basis of their atomic size factors [11] This is defined as

$$(\Omega_S^* - \Omega_{Al})/\Omega_{Al}$$

where Ω_{Al} is the mean atomic volume of the aluminium atom, and Ω_S^* the effective volume of the solute atom as calculated from lattice parameter data [11]. The change in modulus per atomic per cent of solute in solid solution is plotted against this parameter in Fig. 8. The large amount of scatter indicates little, if any, correlation be-

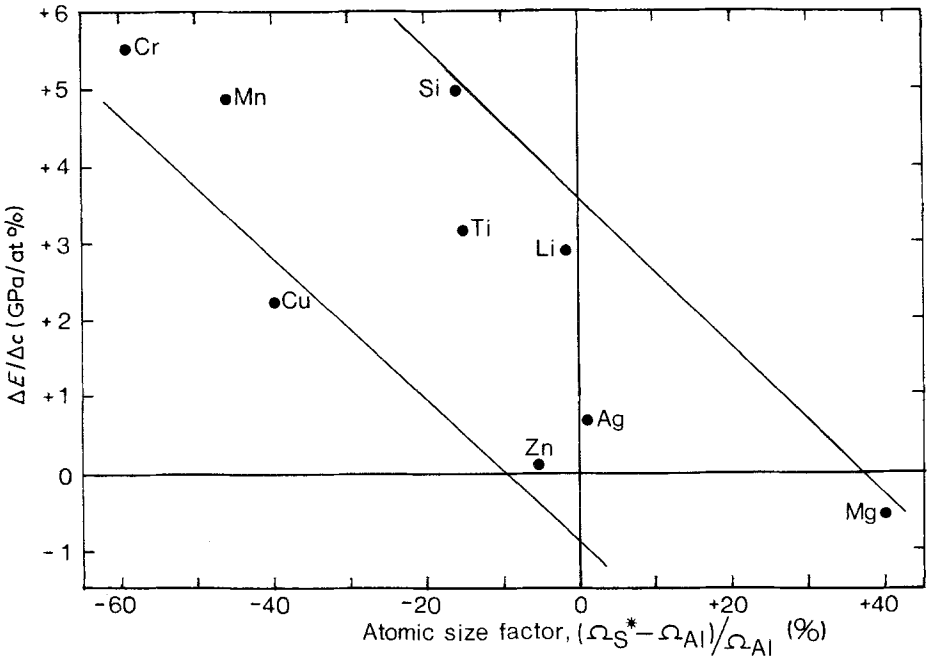


Figure 8 Change in modulus of solid-solution alloys plotted as a function of atomic size factor.

tween modulus and strain energy of the solid solution. For example, lithium, zinc and silver additions all have volume size factors close to zero and yet lithium has a much greater effect on modulus than does silver or zinc. This lack of correlation is perhaps not surprising since it is well established in copper-based alloys that modulus decreases with increasing strain energy [12, 13], i.e. the reverse of the trend being observed in the aluminium-based alloys.

If now the change in modulus is plotted against the parameter,

$$(\Omega_S^* - \Omega_S)/\Omega_S$$

where Ω_S is the true atomic volume of the solute atom [11], then a much better correlation is obtained (Fig. 9). This parameter is a direct measure of the deviation from Vegard's Law which predicts a linear dependence of atomic volume on concentration between the values for pure solvent and pure solute. Deviation from the law in a metallic solid solution reflects the changing electronic environment around the atoms and this of course will influence the bonding properties, and hence the elastic modulus.

Examination of Figs 8 and 9 shows that magnesium has a very large volume size factor (+40%) but shows only a small deviation from Vegard's Law. The change in modulus caused by magnesium additions is also very small, indicating the importance of electronic effects on modulus rather than strain energy effects. Similarly, in the case of Al–Li, where the volume size factor is very small (−2%), the deviation from Vegard's Law is high, and this is reflected in a large value of the elastic modulus. The modulus of a solid-solution alloy is probably dependent on a complex combination of

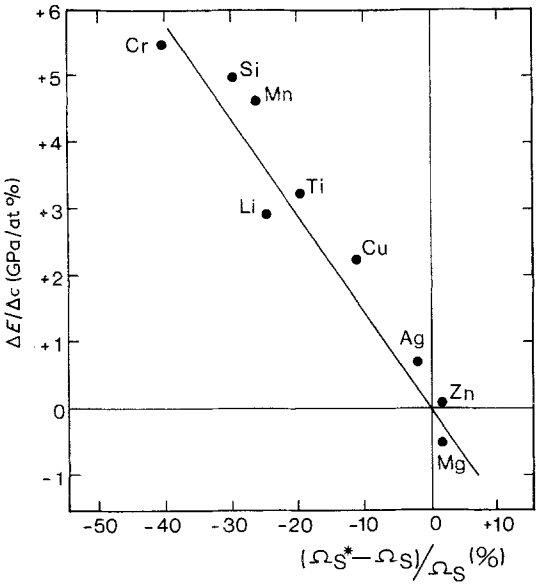


Figure 9 Change in modulus of solid-solution alloys as a function of deviation from Vegard's Law.

several factors including atomic size differences and electronic structure. However for the Al–Li alloys under study it appears that the modulus is being largely controlled by the electronic structure of the solid solution.

The data in Fig. 9 indicate that the effectiveness of elements in solid solution in aluminium for improving the elastic modulus increases in the order of Mg, Zn, Ag, Cu, Li, Si and Cr. Of the elements at the higher end of this ranking only lithium dissolves in aluminium to any appreciable extent. It is this high solid solubility of lithium that enables the high elastic modulus to be achieved in the Al–Li system.

5. Conclusions

(a) Up to 14 at % lithium (4 wt %) can be dissolved in aluminium and after suitable heat treatment a Young's modulus of up to 86 GPa can be achieved (increase of 30% relative to pure aluminium).

(b) The major contribution to the modulus arises from lithium in solid solution, its effect being to modify the electronic structure of the alloy. Short-range ordering or strain-energy effects do no make a significant contribution to the modulus.

(c) The elastic modulus of the intermetallic compound Al_3Li is approximately 96 GPa, and that of AlLi is 105 GPa.

(d) Alloys of commercial interest contain 7 and 11 at % (2 and 3 wt %) lithium. In the former alloy the relative contribution to the modulus is 86/14 from the solid solution/δ', and in the latter alloy 70/30.

(e) In alloys containing 7 and 11 at % (2 and 3 wt %) lithium the specific modulus is increased by 28% and 34% respectively, relative to pure aluminium.

(f) Magnesium additions to Al–Li alloys lower the elastic modulus by approximately 0.5 GPa per atomic per cent. However, the specific modulus of the alloy is not adversely affected.

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