An Investigation on the Elastic Modulus and Density of Vacuum Casted Aluminum Alloy 2024 Containing Lithium Additions

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The elastic modulus and density of (2024 + LiX) alloys are investigated. To the alloy of 2024, the weight percentages of lithium added are 2, 3, and 4. Melting is carried out in an induction furnace under argon gas protection; casting is done under vacuum. To obtain the maximum strength and hardness, the specimens are solution heat treated under 495 C and quenched in water at room temperature. Then, they are aged naturally and artificially. For the purposes of comparing, some of the specimens are melted under argon gas, but casting is done without vacuum. All the specimens are subjected to tension tests.

As a result of this work, the alloys of aluminum that are difficult to manufacture by the known methods are manufactured safely by the vacuum casting method. For 1% of lithium added to the alloy, an increase of 6% in the elastic modulus and 3% decrease in the density are obtained. The specific elastic modulus, E/ρ , ratio increases by about 10% for each 1% addition of lithium.

Keywords 2024 (AlCu4Mg1), Al-Li alloys, elastic modulus, density, vacuum casting, and specific elastic modulus.

1. Introduction

Alloy 2024 is an aluminum alloy containing copper, magnesium, manganese, and some minor alloying elements. Hot extrusion and hot rolling mainly fabricate it. The cast structure consists of cored dendrites of an aluminum solid solution with a variety of constituents in the interdentritic region.^[1,2]

Lithium is one of the eight elements that have more than 1 at.% solubility in aluminum. Only three other elements (copper, magnesium, and zinc) have as high solubility in aluminum as lithium. Lithium is the lightest metallic element and the only one (except beryllium) that when alloyed with aluminum increases the elastic modulus and decreases the density (magnesium decreases the elastic modulus). For every weight percent lithium added to aluminum, the density is reduced 3% and the elastic modulus (up to lithium content of about 4%) is increased about 6%.^[1,3–8] Decreasing density while increasing elastic modulus increases the specific elastic modulus, E/ρ .^[9] Furthermore, there is considerable hardening from the δ' (Al₃Li) phase.^[1,10–12] It is this characteristic that has aroused interest in Al-Li alloys for aerospace applications.^[13,14]

Solute hydrogen, which is typically present in very small concentrations of 0.1 to 0.5 N cm³/100 g, is a most troublesome impurity in melts of aluminum and its alloys. Rejection of this gas from solution in the metal is not only a cause of harmful porosity in castings but also of blistering of annealed aluminum.^[15]

To avoid such defects, it is often essential to degas aluminum melts before casting. The level to which the hydrogen concentration in the melts should be reduced to avoid porosity in final cast-

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ing depends both on the composition and solidification mode of the metal or alloy, $^{[4,15,16]}$ but consideration of these earlier works shows that a reduction to 0.1 N cm³/100 g will normally be sufficient.

The most widely used degassing methods employ flushing of the melt with a carrier gas, typically chlorine or chlorinenitrogen mixture.^[15] The use of toxic gas, chlorine, presents serious practical difficulties,^[17,18] and vacuum degassing has been tried as an alternative degassing method.

It has been shown that holding an aluminum melt in a vacuum results in improved soundness of the casting. It has also been suggested that passing an aluminum melt as a stream through a vacuum would be an efficient degassing method, and preliminary work on the stream degassing of aluminum appears to support this hypothesis.^[15]

As written above, aluminum-lithium alloys have two advantages over conventional aluminum alloys: first, they show an increased elastic modulus and, second, they have a lower density. Their commercial applications have been slowed by difficulties in production sound castings and by the low toughness of the alloys.^[1,2,19,20] The casting problems can be overcome at some additional cost by the use of a vacuum process.

The present work is concerned with the determination of elastic modulus and density of (2024 + LiX) aluminum alloys.

2. Alloys, Equipment, and Processing

The 2024 aluminum alloy was supplied by Etibank (Turkey). Its chemical composition is given in Table 1.

The 2024 + LiX aluminum alloys were prepared as a special alloy including lithium in the laboratory induction furnace under argon atmosphere. Metallic lithium used for alloying is Merck (Merck Co., Germany) 805660 (SAE J 993) and 99.9% pure. The chemical composition of the materials used in the experiments after alloying is shown in Table 2. Unless otherwise stated, all alloy compositions in this paper are expressed in weight percentages.

Table 1Chemical composition of 2024 aluminum alloy(wt.%)

Fe	Si	Cu	Mn	Mg	Zn	Ti	Cr	Al
0.50	0.50	4.45	0.71	1.36	0.20	0.15	0.10	balance

Table 2The real and nominal chemical composition of theexperimental materials (wt.%)

	Real analysis					
Materials	Li	Cu	Mg	Mn	Fe	Al
2024 (a)	0.00	4.23	1.69	0.65	0.53	balance
2024 (b)	0.00	4.42	1.36	0.71	0.53	balance
2024 + %2 Li (a)	2.01	3.95	1.65	0.86	0.49	balance
2024 + %2 Li (b)	1.86	4.09	1.40	0.75	0.58	balance
2024 + %3 Li (a)	2.95	3.84	1.51	0.66	0.51	balance
2024 + %3 Li (b)	2.74	4.16	1.41	0.61	0.46	balance
2024 + %4 Li (a)	3.98	4.07	1.53	0.67	0.75	balance
2024 + %4 Li (b)	3.82	4.16	1.28	0.48	0.46	balance
(a) Under vacuum						

(b) Without vacuum

For melting and casting, an Inresa S 600 type induction furnace capable of casting under vacuum was used. The graphite crucible consists of a 55 mm high \times 50 mm diameter \times 5 mm thick cylinder with a heat resistant ceramic cone. The 2024 and metallic lithium were proportioned and put into the crucible. Inserting argon gas by some intervals exhausted the air in the crucible. The argon gas was fed at a constant volume flow rate of 3 dm 3/minute.

When the temperature in the crucible reached 750 °C and the metal was completely melted, the ingot, which is heated up to 500 °C in another furnace, was placed into the casting chamber. The chamber was closed, and the casting cycle started and was performed under vacuum. The temperature of the molten aluminum during melting and casting is measured using the cromel-alumel thermocouple. The accuracy of temperature measurement was ± 5 °C. The vacuum pump stopped automatically. The pressure in the chamber increased and solidification occurred under atmospheric pressure. The vacuum chamber was 18 cm high and 15 cm in diameter. The vacuum system consists simply of a root pump and vacuum gauges (0 to 20 Torr) mounted at the vacuum off-take port. Elastomer O-rings were used for vacuum sealing. The vacuum in the chamber during casting was normally 1 Torr, *i.e.*, ± 0.5 Torr.

The melting process was performed completely with argon gas and, for comparison, vacuum was not applied to some casts. The specimens were 35 mm in diameter and several lengths. The cast material was hot extruded to produce tension test rod. The diameter was reduced from 35 to 5 mm in one step. The extrusion ratio was 49/1 (A_1/A_2). During this process, the die temperature was 400 °C and material temperature was 450 °C. All over the extrusion work the process velocity was constant. After extrusion, the diameter of the rods was produced 5 mm. The tensile testing specimens were machined on lathes according to ASTM-E8 dimension specifications. They were 4 mm in diameter and 40 mm in length.

Before heat treatment, all the specimens were annealed in a furnace at 415 ± 3 °C for 3 h, to eliminate aging present initially or caused later by extrusion. Solution heat treatment was performed in a furnace at 495 ± 3 °C. Specimens were kept in the furnace for 1 h and protected against direct thermal radiation. After a few seconds, the specimens were quenched in water at room temperature. Artificial aging was applied to some specimens in a furnace under several temperatures (120, 160, 190, and 200 °C) and for several intervals (T6). Others were naturally aged at room temperature for 1 week (T4).

The tensile tests of the specimens were performed on an Instron (Instron Co., England) 1114 hydraulic machine. Some of the analyses were performed at the Engineering Faculty of Selcuk University by a Varian Techtron AA-175 atomic absorption spectrometer and others in Etibank-Seydisehir Aluminum Company's Research Laboratory.

3. Discussion of the Experimental Results

3.1 Modulus of Elasticity

Modulus measurements were made statically using strain gauges attached to each side of the specimen. Particular attention was paid too axially of loading in the tensile machine, and it is estimated that errors in the modulus value due to nonaxially of loading did not exceed 0.5%.

The increases in elastic modulus obtained in alloys T4 and T6 are similar and are, respectively, due to the presence of lithium in solution and due to the precipitation of a small volume of A'. Vacuum application did not change the modulus of elasticity either. A1% increase in added lithium increased the modulus of elasticity by 6%. The experimental results shown in Table 3 are shown in Fig. 1.

Using the least-squares method (LSM) as follows, the equation giving the dependence of modulus of elasticity on the amount of lithium can be derived:

$$E = 73.5 + 4.446 \times (\text{Li \%})$$
 [GPa]

The modulus of elasticity depends on many parameters such as electronic structure, atomic size differences, and interatomic bonds.^[7,21] Determination of δ and δ' solvus lines in Al-Li alloys and the high solubility of lithium in solid solution in room temperature show that the solid solution effects the increase in elastic modulus. However, the mechanism that increases the modulus of elasticity in Al-Li alloys is not yet perfectly understood.^[3]

The percentages in modulus of elasticity are calculated by the formula $[(E2-E1)/E1] \times 100$. The percentage increases in the modulus of elasticity are shown graphically in Fig. 2. From the obtained results, using the LSM again, the following equation is derived:

% Increase in modulus of elasticity = $6.030 \times (\text{Li \%}) + 0.188$

The slope of the equation is 6.030. In other words, for a 1% increase in lithium, there is a 6.03% increase in modulus of elasticity. This result is consistent with those in the literature.^[3,7,21,22,23]

Materials	Under Vacuum E (GPa)	Without Vacuum E (GPa)
2024 + 0%Li	73.50	73.50
2024 + 2%Li	82.23	82.15
2024 + 3%Li	87.02	86.97
2024 + 4%Li	91.31	91.04

Table 3 Elastic modulus of 2024 + LiX



Fig. 1 Variation of elastic modulus with increasing lithium concentration



Fig. 2 Change of elastic modulus percent with increasing lithium concentration

3.2 Effect of Protective Atmosphere and Vacuum

It is an important advantage to reach melting temperatures quickly by induction heating. During melting, the alloy is well mixed by a magnetic field to obtain a homogenous solution. The protective atmosphere isolates the alloy from hydrogen, oxygen, and moisture of the air and prevents diffusion of hydrogen through the melting metal. The melted alloy is poured from the bottom of the crucible, and since the inclusions and impurities float on the surface of the melted metal, the cast will be clean. The only soluble gas is hydrogen in melted aluminum. A protective atmosphere prevents hydrogen from diffusing into the melting metal and vacuum will cause other gases in the metal to leave. In this way, the mechanical properties are increased. The principal solution to hydrogen contamination during casting involves using efficient degassing procedures and maintaining a continuous, protective atmosphere of argon gas.

Applying or not applying vacuum did not cause any significant change in the modulus of elasticity. For this reason, the above equations are derived without making any distinction between the two cases.

3.3 Effect of Lithium

For lithium contents up to 1.35%, the increase in the elastic modulus has been attributed to a solid solution effect. The basis for this conclusion is that at room temperatures the solubility of lithium is high, that is, the δ solvus and δ' solvus lines are close.

The addition of lithium produces an age hardenable alloy with the precipitation sequence

Supersaturated solid solution $\rightarrow \delta'$ (Al₃Li) $\rightarrow \delta$ (AlLi)

After suitable heat treatment, the transition phase δ' forms as spherical particles, which have an ordered L1₂, structure and this results in considerable strengthening. Additional strengthening can be achieved by the presence of further elements, *e.g.*, magnesium produces solid solution strengthening.^[3,12,24]

The general strengthening of Al-Li alloys results from the presence of a large volume fraction of the coherent δ' phase, but the case of the high modulus is not known. It has been suggested that the δ' phase may have a high intrinsic modulus due to its ordered nature and that this produces the high values of elastic modulus observed in the alloys, but no systematic study appears to have been carried out.^[3,10,25,26]

Furthermore, discrepancies exist in reported elastic modulus data beyond the region of 1.35% lithium; *i.e.*, in the range of the age hardening δ' phase. It has been reported in one study that the influence of lithium on the elastic modulus is independent of whether the lithium is in the form of or in supersaturated solid solution, whereas in two other investigations, there was a change in elastic modulus with aging. However, these last two investigations reported opposite trends with aging. In one case, it was observed that the elastic modulus was greatest in the as-quenched condition, remaining relatively constant up to peak, and decreasing slightly with overaging, whereas in the other work, the elastic modulus was significantly lower in the as-quenched condition compared to the peak-aged condition.^[27]

While discussing the effect of lithium additions on the elastic properties of aluminum alloys, it should be noted that the influence of alloying elements depends on whether these are in solution or are present in a second phase. If the alloying elements are in solution, the magnitude of the elastic constants is determined by the nature of the atomic interactions and the interatomic potentials; if the alloying elements are present in a second phase, the magnitude of the elastic constants is determined by the volume fraction and the intrinsic modulus of the second phase. Even then the elastic constants of aluminum solid solutions (except for those in which lithium or magnesium is the solute), calculated as the weighted sum of the elastic constants of the respective solute and aluminum, agree well with the measured value.^[3,21] The effect of lithium is anomalous in that it substantially increases the values of the elastic constants of Al-Li solid solutions, although the values of its own constants are lower than those of aluminum. In alloys containing a high modulus second phase, in addition to the volume fraction and the intrinsic modulus of the second phase, the nature of occurrence of the second phase is important; with second phases that are not coherent with the matrix, *e.g.*, oxide particles in mechanically mixed oxide-dispersed alloys, the overall modulus is lower than that predicted by the rule of mixtures.^[2]

3.4 Solid Solution Alloys

The limit of solid solubility of lithium in aluminum is 4.2 wt.% (14.4 at.%) at 600 °C. These alloys containing 0, 2, 3, and 4wt.% lithium have been produced in the single-phase α state by rapid quenching from above the δ solvus temperature. Noble and his friends showed by electron microscopy that a very small quantity of fine δ' is produced during the quenching of the more concentrated alloys, and later proved that this did not have a large effect on the measured modulus values.^[3]

The results of the elastic modulus determinations are shown in Fig. 3, 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 percent addition, but thereafter, the rate of increase falls. Alloys for commercial interest contain between 2 and 3 wt.% (7 to 11 at.%) lithium, and for these alloys, the lithium in solid solution has increased the modulus from 74 to 91 GPa, *i.e.*, a 23% improvement.

3.5 Alloys Aged to Produce δ' and δ Phase

The alloys containing 0, 2, 3, and 4 wt.% lithium were aged at 120, 160, 190, and 200 °C. The δ' solvus occurs at approximately 2% lithium for this aging temperature, so those alloys containing 2 to 4% lithium contained increasing amounts of the δ' phase. Noble and his friends showed by electron microscopy that the size and volume fraction of δ' varied between 20 and 30 nm and 0.01 and 0.30, respectively. No δ phase was detected in any of the alloys containing less than 4% lithium.^[3]

The effect of aging on the modulus values of the alloys is shown in Fig. 3. No change occurred in alloys containing less



Fig. 3 Variation of elastic modulus with lithium in aged alloys^[3]

than 2% lithium, but in those alloys containing the δ' phase, a small increase in modulus occurred relative to the solutiontreated value. The value of the modulus in alloys containing δ' increased in a linear manner with lithium concentration, from a value of 82 GPa at 2% lithium to 91 GPa at 4% lithium. Modulus determinations were also made on alloys that had been aged at 200 °C, and the values found to be the same as those aged at 120, 160, and 190 δ C thus indicated that the equilibrium fraction of δ' has been closely approached at the lower aging temperature.

Alloys with more than 4.5% lithium contain the δ phase formed directly from the melt.

3.6 Effect of Magnesium

In the solution-treated and aged conditions, the effect of magnesium is to reduce the modulus, the extent of the reductions being approximately 0.5% per at.% magnesium. From a modulus point of view, therefore, magnesium additions are not at first sight a desirable addition. However, at some 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.^[3,4,28]

This result is expected since there is a slight degradation in the elastic modulus in the binary aluminum magnesium system with increasing magnesium content. In summary, it can be said that lithium additions lead to an increase in the elastic modulus of the aluminum alloys; however, the exact physical description for the increase is still in question.^[27]

3.7 Effect of Copper

In Al-Li alloys with copper, several precipitation sequences occur, which are partly related to the binary Al-Cu system and partly to the Al-Li system:

The stable T_1 (Al₂CuLi) phase is hexagonal and partly coherent. Which of the various phases precipitates depends upon the Cu/Li ratio. For low Cu/Li ratios (*e.g.*, 2.5% Cu, 2% Li), the T_1 phase occurs at all aging temperatures along with the δ' phase. For medium Cu/Li ratios (*e.g.*, 1.3% Cu, 1.5% Li), the T_1 phase forms at temperatures above 170 δ C in homogeneous distributions. Parallel to T_1 , the δ' and ϑ' phases are also always present. With higher Cu/Li ratios, with the alloy 2020 as an example (4.5% Cu, 1.3% Li), the precipitation sequence of the binary Al-Cu system dominates. Like magnesium, copper decreases the solubility of lithium in aluminum.^[3,5]

Commercial aluminum-lithium alloys contain magnesium as well as copper. The phase diagram of the quaternary system Al-Li-Cu-Mg has not been determined. However, what has been observed is the age hardening phase δ' (Al₃Li), S' (Al₂CuMg), and T_1 (Al₂CuLi) in the matrix, and primarily on the grain boundaries, the equilibrium δ (AlLi) and S (Al₂CuMg) phases can occur. The ratios and amounts of the various phases depend on composition and aging conditions.^[3,29]

3.8 Density

The density of the alloys was determined by the liquid (acetonitrile) displacement method and is given in Table 4. Density measurements were carried out on all the specimens. The density values obtained for various lithium amounts are shown graphically in Fig. 4. It is seen that the density of casts made under vacuum are higher than that of casts made without vacuum. This is because during casts made under vacuum, the gases in the melted metal are carried away and the material become denser.

The equations of lines are calculated for both cases by the method of the LSM as follows:

Density = $-88 \times (\text{Li \%}) + 2789$	[Kg/m ³] (under vacuum)
Density = $-83 \times (Li \%) + 2726$	[Kg/m ³] (without vacuum)

The slopes of both equations are approximately the same. That is, these two lines are parallel. The offset between the two is 72 kg/m^3 .

The lithium added into 2024 alloy produces lithium phases such as $\delta'(Al_3Li)$, $\delta(AlLi)$, $S(Al_2MgLi)$, and $T_1(Al_2CuLi)$ in the alloy, while copper produces copper phases such as δ and δ' . The densities of all phases are different. The densities of multiphase alloys are calculated by adding the values obtained by multiplying the densities of each phase by the volume ratio of that phase.

For each 1% lithium added into the 2024 alloy, density decreases by about 3%. This decrease is the same as that obtained in Al-Li alloys when compared with pure aluminum and is consistent with those in previous studies.^[2,6,13,28,30] It is obvious that lithium having a density of about half of that of water (543 kg/m³) would decrease the density of 2024 alloy. There is also 1.2 to

Table 4 Density of 2024 + LiX

Materials	Under Vacuum ρ(kg/m³)	Without vacuum ρ(kg/m³)
2024 + 0%Li	2801	2734
2024 + 2%Li	2617	2569
2024 + 3%Li	2531	2474
2024 + 4%Li	2452	2428



Fig. 4 Variation of density with increasing lithium concentration

1.8% magnesium in the specimens. For each 1% magnesium added into the aluminum alloy, the density of the alloy decreases by 0.47%.^[2]

3.9 Specific Modulus of Elasticity

In aluminum-lithium alloys, it is known that the modulus of elasticity increases and density decreases with increasing percentage of lithium. A specific modulus of elasticity is found by dividing the modulus of elasticity of the material by its density. A specific modulus of elasticity computed depending on various lithium percentages is shown in Fig. 5. The increase is linear.

The E/ρ ratio increases by about 10% for each 1% addition of lithium. This value is produced by the splat-quenched method; the E/ρ ratio obtained from 2024 alloy, which contains lithium, is reached.^[2]

Therefore, aluminum-lithium alloys reduce mass when used as structural materials. The reduction in density of any one component has the most potential for reducing aircraft mass. With the drastic increase in fuel costs in the early 1970s, the development of aluminum alloys containing lithium for aircraft structures was promoted in different research laboratories in the world. It is Anticipated that improved aluminum-lithium alloys will be competitive with the modern fiber-reinforced resins.^[1,13,14]

4. Conclusions

- For 1% increase in added lithium, the modulus of elasticity increased 6%.
- For 1% increases in added lithium, a 3% decrease in the density of alloy was observed.
- The specific elasticity modulus *E/ρ* was increased 10% for 1% increases in added lithium.
- By this method, Al-Li alloys were manufactured safer than all other conventional methods.
- Although these alloys are two or three times more expensive than the currently used aluminum alloys, they may be preferred as aircraft materials for their high specific modulus of elasticity.



Fig. 5 Change in specific modulus of elasticity with increasing lithium concentration

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