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High-pressure phase diagram of an aluminium-rich Al–Li alloy at a pressure of 5.4 GPa

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The high-pressure phase diagram of an aluminium-rich Al–Li alloy at a 5.4 GPa pressure was investigated. To determine the equilibrium state under high-pressure and high-temperature conditions, the quenching method was applied and a phase analysis of the sample was performed using X-ray diffraction and microscopic observations. The experimental results were then compared with a thermodynamic theoretical calculation and good agreement was found. The resultant solid solubility of lithium in aluminium was subsequently increased up to 20 at % and the eutectic temperature increased up to 800 °C.

1. Introduction

Al–Li alloys are well known for their high strength, low density, and high elastic modulus characteristics [1]. Although these materials possess many structural advantages for aerospace applications, a few technical difficulties have limited their practical use, e.g. explosions can occur during the casting process due to liquid lithium having an extremely high reactivity in air. Furthermore, the addition of lithium to aluminium achieves higher strength but reduces ductility. As a result of these problems, powder metallurgy (P/M) using hot isostatic pressing (HIP) has been introduced as an effective technique to improve material strength by allowing the use of a rapidly cooled powder having both very fine-grain and homogeneous particle sizes [2]. The solubility and eutectic temperatures at high pressure, are generally different from those under atmospheric pressure; however, the high-pressure phase diagram of an Al–Li binary system has not yet been reported.

This led to the present study which utilized the quenching process to determine the high-pressure phase diagram of an aluminium-rich Al–Li system at 5.4 GPa. In addition, the subsequent lithium solubility under high pressure was compared with results from a thermodynamic-based theoretical calculation.

2. Experimental procedure

Samples containing up to 30 at % lithium were prepared from 99.99% pure aluminium and an Al–Li alloy comprised of 18.5 wt % lithium, 0.10 wt % iron, 0.04 wt % silicon, 0.003 wt % nickel, and the balance of aluminium. They were melted together in alumina crucibles in an electric furnace with LiCl flux directed on to the sample surface, and then cast into a cylindrical iron mould, with both processes being done under atmospheric conditions. Alloy compositions were 5, 10, 12.5, 15, 17.5, 20, 22.5 and 30 at % lithium. The samples were cut into 6 mm diameter cylinders having a 6 mm length, and density was measured by Archimedes' method. All samples were then homogenized at 400 °C for 5 h at 1×10^{-5} torr and cooled in the furnace to room temperature.

The specimens were placed in a cylindrical capsule in which boron nitride (BN) was used as an insulator and graphite as the heater element (Fig. 1). The capsule was then embedded in a cubic-shaped pressure-transmitting medium made of pyrophyllite. Temperature was measured by a chromel–alumel thermocouple and pressure dependence of thermo-electromotive force was corrected as detailed by Bundy [3]. Six anvils made of tungsten carbide, each having a 15 mm × 15 mm pressure application area, were used to subject the pyrophyllite cubic apparatus to large hydrostatic pressures on all sides. The system was designed to convert the uniaxial force generated by a 12 MN press machine into six equal components. The pressure scale was calibrated using standard pressures, i.e. bismuth (I–II) at 2.55 GPa, bismuth (II–III) at 5.67 GPa, tantalum (II–III) at 3.67 GPa, and barium (I–II) at 5.50 GPa. Here, a 5.4 GPa pressure was generated with a 8 MN force.

A high-pressure solid-solutioning technique was applied to the sample as follows. The sample was compressed at 5.4 GPa while being heated at the specific temperatures. In order to obtain sufficient phase-equilibrium, the high-pressure and high-temperature

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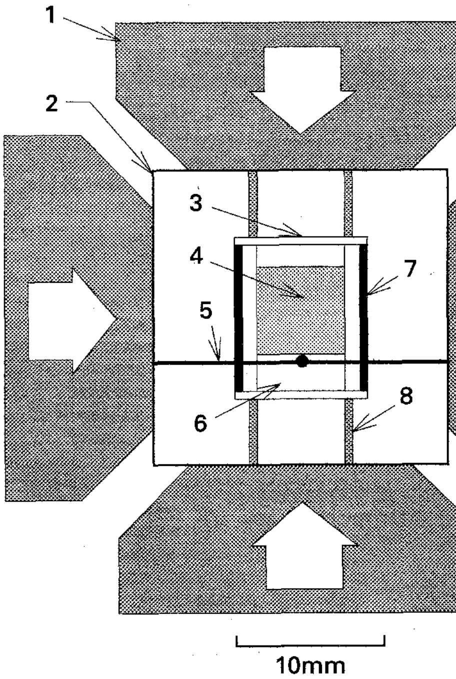


Figure 1 Cross-sectional diagram of the high-pressure and high-temperature sample treatment apparatus. 1, Anvil; 2, pyrophyllite gasket; 3, steel disc; 4, specimen; 5, thermocouple; 6, BN insulation; 7, graphite heater; 8, copper ring.

conditions were maintained for 10 h. Following this, the samples were quenched to room temperature by de-energizing the heaters (cool down rate 150 K s^{-1}). Pressure was then lowered to atmospheric pressure, with the microstructure of the sample being immediately analysed using X-ray diffraction (XRD) with CuK_α radiation. After being metallographically polished, the resultant microstructures were further examined using conventional optical microscopy. The dendrite structure was particularly important because it indicates whether the sample actually melted.

3. Results and discussion

Fig. 2 shows resultant XRD patterns from the Al–15 at % Li alloy. The spectrum in Fig. 2a was obtained before the high-pressure solid-solutioning process, whereas Fig. 2b and c are resultant spectra after the process was carried out at 690 and 790 °C, respectively. The X-ray diffraction pattern lines identify the α-phase and also the δ-phase (AlLi) which does not contain the δ′-phase (Al_3Li). The δ′-phase precipitates when a sample containing more than 5 at % is quenched from the homogeneous α-phase region [1]. However, the precipitation of δ′-phase is difficult to confirm using X-ray diffraction because the grains are so fine. Nonetheless, it is clearly evident that the diffraction lines of the δ-phase for the sample treated at 690 °C (Fig. 2b) are less than those before the treatment (Fig. 2a), and that they disappear in the 790 °C sample (Fig. 2c). These results indicate that the δ-phase completely dissolves in the aluminium solution at a treatment temperature of 790 °C, thereby obtaining a single α-phase solid solution which was formed between 790 and 690 °C. The solubility limits for other lithium (at %) compositions were similarly estimated.

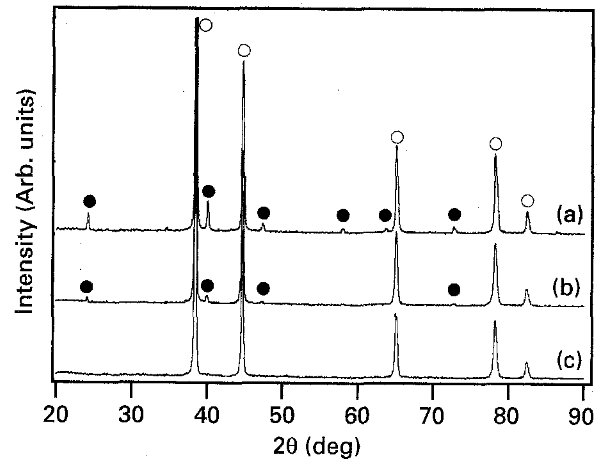


Figure 2 X-ray diffraction patterns of Al–15 at % Li alloys (a) annealed under atmospheric pressure, and quenched from (b) 690 °C and (c) 790 °C under a pressure of 5.4 GPa. (○) α-phase (Al), (●) δ-phase (AlLi).

Fig. 3a–c show the optical microstructure of an Al–22.5 at % Li alloy treated under 5.4 GPa at the respective temperatures of 750, 850, and 950 °C. In Fig. 3a, many particles are uniformly precipitated in the α-phase, being identified by XRD to be the δ-phase. Because the microstructures in Fig. 3b and c show the typical structure of dendrite, evidence of melting during the high-pressure heat treatment is confirmed, thus enabling the eutectic temperature to be estimated to occur between 750 and 850 °C.

These experiments led to the establishment of a well-defined solidus and the solid-solubility line of an aluminium-rich Al–Li system under a pressure of 5.4 GPa. Fig. 4 shows the experimentally determined high-pressure phase diagram, the theoretical solid-solubility line calculated at a pressure of 5.4 GPa, and the conventional phase diagram [4] at 0.1 MPa. In addition, the estimated liquidus–solidus line and eutectic composition are shown, although they are not based on actual data. It should be noted that the solid-solubility line at 5.4 GPa is very similar to that at 0.1 MPa, although a lower lithium concentration occurs from 200–600 °C. The maximum solubility of the α-phase and the eutectic temperature at 5.4 GPa were, respectively, determined as 20 at % Li and 800 °C. The higher pressure increased the maximum solubility by 5 at % and the eutectic temperature by 200 °C.

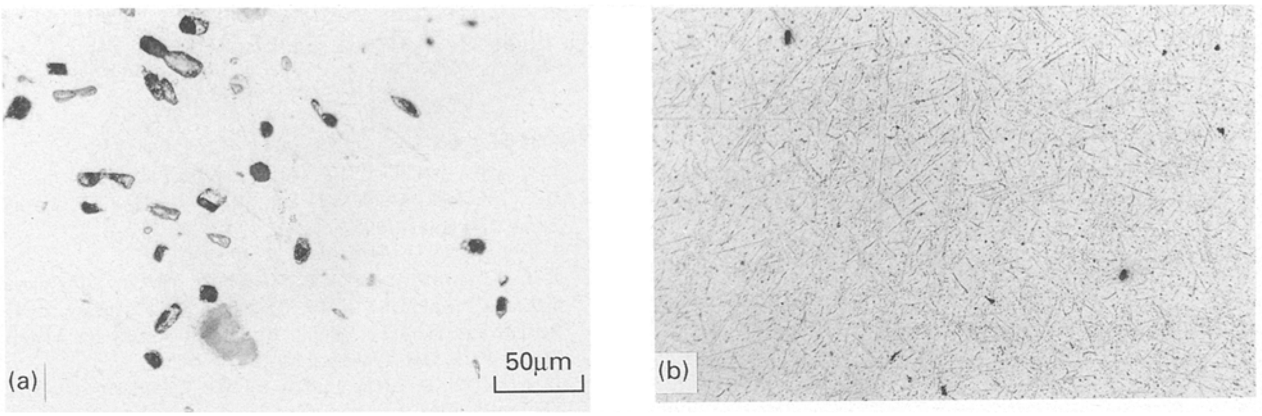
The solid solubility at temperature, T, and pressure, P, is expressed as

$$C(P,T) = C(P_0,T)\exp\frac{-\Delta V(P-P_0)}{kT} \qquad (1)$$

where $C(P_0,T)$ is the solid solubility at 0.1 MPa, k is the Boltzmann constant, and ΔV is the volume difference between the solid solution and the δ phases. This difference is given by

$$\Delta V = \left(V_\varepsilon - \frac{V_p - 1}{C_p}\right)\Omega \qquad (2)$$

where V_ε is the internal lattice strain, V_p is the ratio of the volume of a precipitation atom to that of an



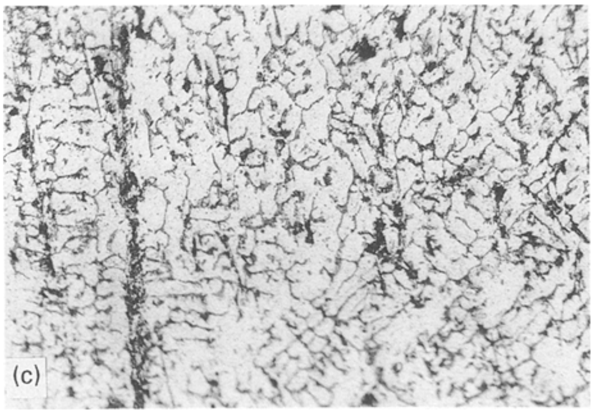


Figure 3 Optical microstructure of Al–22.5 at % Li after high-pressure solid solutioning under 5.4 GPa pressure at (a) 750 °C, (b) 850 °C, and (c) 950 °C.

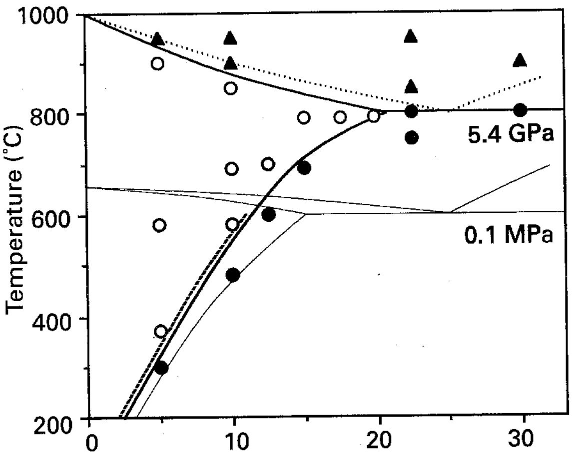


Figure 4 Phase diagram of the aluminium-rich Al–Li alloy under a 5.4 GPa pressure. The single α-phase (○) and (α + δ)-phases (●) of quenched samples are shown, as are samples in which dendrite was observed in the microstructure; an indication the sample had melted (▲). Using these data, the solidus and solid-solubility line was determined as shown. Although no reliable information on the liquidus–solidus line and eutectic composition was obtained, they were estimated (···) as shown. Also indicated (– – –) is the theoretical thermodynamic solubility line calculated from Equation 1.

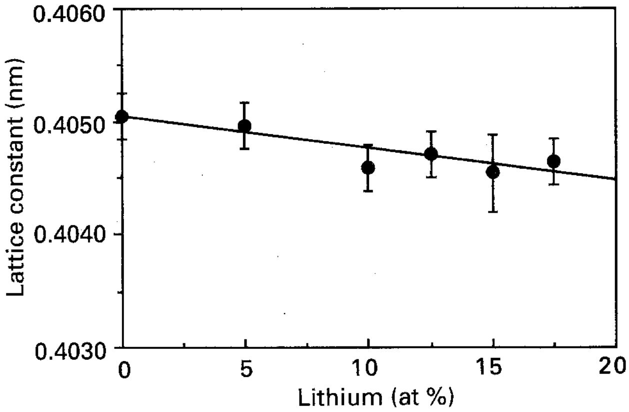


Figure 5 Variation of aluminium matrix lattice constant with respect to lithium atomic concentration.

aluminium atom, C_p is the stoichiometric ratio of the solute lithium atom, and Ω is the mean atomic volume of an aluminium atom. The actual value of ΔV can be represented by the difference between the internal lattice strain which results from solutioning, V_ε, and that which results from precipitation, V_p. The value of V_ε can be estimated as follows from the lattice constant a

$$V_\varepsilon = \left(\frac{1}{a_0}\frac{da}{dc}\right)^3 \tag{3}$$

where a_0 is the lattice constant of aluminium and c is the solute concentration. The variation of the lattice constant (Fig. 5) allowed V_ε to be estimated as -0.01, being in relatively good agreement with that reported by Axon *et al.* [5]. A $\Delta V = 0.61$ is subsequently found; hence shifting the solid-solubility line at 5.4 GPa to a lower lithium (at %) concentration than that at 0.1 MPa (Fig. 5). It is of great interest that the experimental solid-solubility line is in excellent agreement with the theoretical line, with this strongly suggesting that the increase in the eutectic temperature at 5.4 GPa is the primary reason that the maximum solid solubility increases up to 20 at % Li.

This attractive increase in the maximum solid solubility is expected to improve significantly the physical and mechanical properties of Al–Li alloys. Investigations are now underway to quantify the material's elastic properties.

4. Conclusion

The solid-solubility line and the eutectic temperature of Al–Li alloys quenched at a pressure of 5.4 GPa were determined, with resultant phase analysis being carried out by X-ray diffraction and optical microscopic observations. The solid-solution line shifted to a lower concentration, although the eutectic temperature increased from 600 °C to 800 °C in comparison with the phase diagram at 0.1 MPa. The maximum solid solubility also correspondingly increased from 15 at % to 20 at % due to the increase in the eutectic temperature. The experimental solid-solubility line was found to be in good agreement with thermodynamic, theoretically calculated results.

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