Low-temperature calorimetric evaluation of aluminum–lithium alloys

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Low temperature calorimetric measurements have been made on a series of binary aluminum alloys containing 1–10 at. % lithium. The heat capacity data are analyzed in terms of an electronic and a lattice contribution. Accordingly, the low level of lithium addition yields appreciable changes in the electronic density-of-states at Fermi level and the characteristic Debye temperature of lattice. These results reflect certain degrees of electron localization between aluminum and lithium atoms, providing a fundamental basis for solid solution strengthening in the lightweight materials with great potential in aerospace applications. © *2003 American Institute of Physics.*
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There have been continuous efforts in developing lighter and stronger alloys of aluminum to complement titanium alloys and composite materials for advanced structures in the aerospace industry. One particular system of current interest is based on the addition of lithium, which is the lightest metal with a density (0.536 g/cm^3) only one-fifth of that of aluminum (2.702 g/cm^3). Binary alloy phase diagram[1] indicates a solubility limit of ~ 14 at. % or 4 wt % Li at the 600 °C eutectic. An increase in Li concentration increases the Young's modulus (6% with each 1 wt % Li added), but plasticity decreases sharply.[2] The optimal combination of strength and ductility is provided with 2.0–2.5 wt % Li. Several commercial alloys containing this level of Li and small amounts of other elements such as copper, magnesium and carbon begin to find their way into components applications. Their development has followed typical alloy design approaches, which rely mostly on mechanical testing data and microstructural analysis. In this work the emphasis is placed on a better understanding of the lattice and electronic behavior of binary aluminum–lithium alloys. Such information as derived from low temperature calorimetric studies should provide some insight for elucidating the fundamental aspects of solid solution strengthening. A certain level of interaction between aluminum and lithium, which have electronegativities of 1.47 and 0.97, respectively, is evident by the fact that a relative stable intermetallic compound AlLi has a melting point near 700 °C, which extrudes into the liquidus. It also has high hardness and brittleness characteristic to directional bonding. While this compound as an excellent electrode material has been the subject of several articles,[3] very little basic research has been reported on α-phase alloys with low lithium content.

To cover the α-phase field, four 0.5 in.×4 in.-cylindrical samples with nominal compositions of 1, 3, 5, and 10 at. %

Li, respectively, were prepared by pyrosynthesis. Each mixture of Al (99.999% pure) and Li (99.9% pure), in a carefully measured ratio to yield the required composition, was contained in a graphite crucible inside a bell jar evacuated and refilled with argon. After being melted above 750 °C, the molten charge was poured into a 0.5 in.-diameter steel mold. The product was then homogenized by annealing at 500 °C, followed by ice-brine quenching. Using a Philips X'pert MPD diffractometer with Cu $K\alpha_1$ radiation ($\lambda = 1.540\,46$ Å), x-ray diffraction patterns in Fig. 1 confirm the fcc-phase purity. By fitting to the well defined peaks, the lattice constant for each sample is obtained as shown in Fig. 2. It decreases monotonically with increasing Li content from ~ 4.052 Å for pure aluminum, which agrees with the literature value, to 4.030 Å at 10 at. % Li.
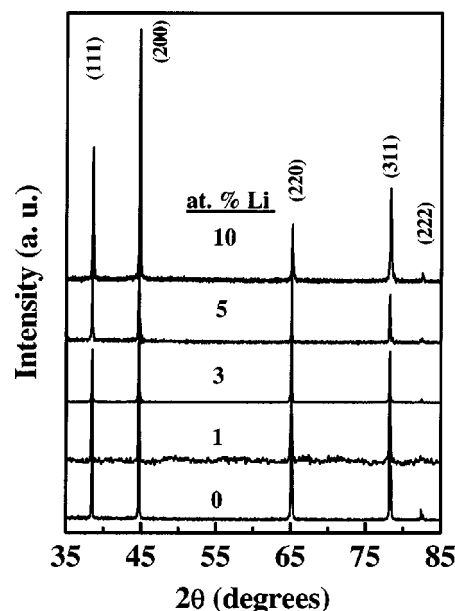

FIG. 1. X-ray diffraction patterns confirm the fcc-phase purity in all samples.

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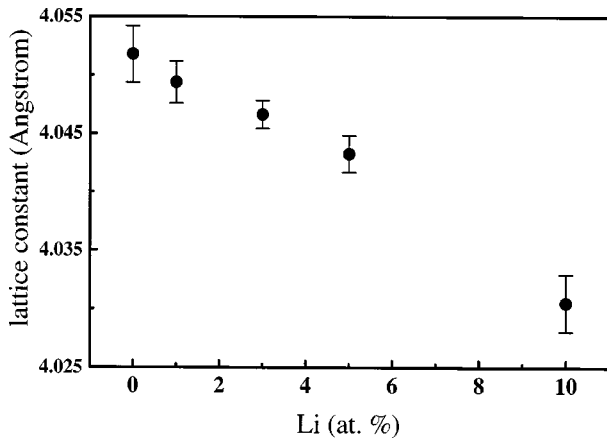[b]Author to whom correspondence should be addressed; electronic mail: james.ho@wichita.edu

J. Appl. Phys., Vol. 94, No. 12, 15 December 2003

Wang *et al.* 7939

FIG. 2. Decreasing lattice constant with increasing Li content.

TABLE I. Low-temperature calorimetrically determined parameters of Al–Li alloys.

at. % Li	γ (mJ/mol K^2)	θ_D (mJ/mol K^4)
0	1.34	435
1	1.30	442
3	1.23	444
5	1.20	456
10	1.16	468

Heat capacity (C) measurements between 2 and 10 K were made on a 1 in. section of each alloy sample as well as the pure aluminum. The standard adiabatic calorimeter in a liquid helium cryostat employed a precalibrated germanium thermometer and a noninductively wound manganin wire for pulsed Joule heating. The thermometer-heater assembly was separately measured for addenda correction.

For metallic solids at low enough temperatures the heat capacity can be typically expressed as the sum of an electronic and a lattice term:

$$C = \gamma T + \beta T^3. \tag{1}$$

With its s/p bonding, aluminum is a nearly free-electron metal. Following the free-electron approximation, therefore, the electronic heat-capacity coefficient γ can be related to the total density-of-states at Fermi level $N(E_F)$:
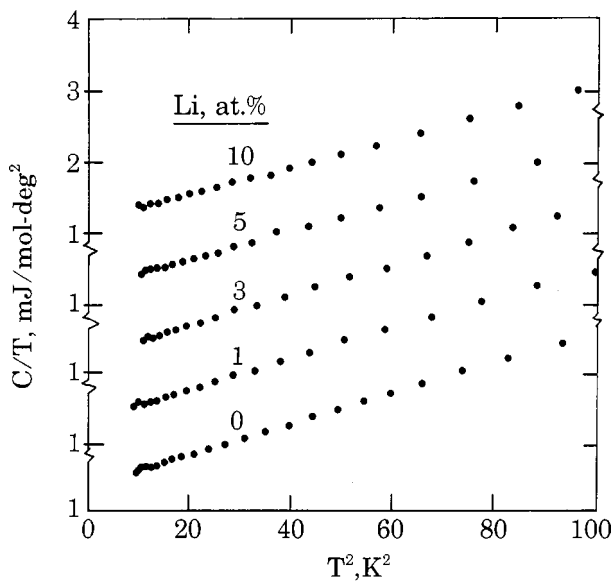
$$\gamma = (1/3)\pi^2 k^2 N(E_F), \tag{2}$$

with k being Boltzmann's constant. The lattice heat-capacity coefficient β corresponds to the characteristic Debye temperature θ_D:

$$\beta = (12/5)\pi^4 N_A k (\theta_D)^{-3}, \tag{3}$$

where N_A is Avogadro's number. Equation (1) is often rewritten as

$$C/T = \gamma + \beta T^2 \tag{4}$$

to indicate a linear dependence of C/T on T^2. Indeed, each set of data in Fig. 3 can be fitted accordingly. The resulting parameters are summarized in Table I. For pure Al, they are in good agreement with literature values.[4] As graphically displayed in Fig. 4, γ decreases and θ_D increases with increasing Li content. The trend in γ is somewhat expected, considering that Li has only one conduction electron per atom as compared to three for aluminum. According to Eq. (2), the γ value is directly proportional to the density-of-states at Fermi level, which is in turn proportional to the cubic-root of electron density. Meanwhile, a higher Debye temperature should prevail due to a higher phonon frequency, which is inversely proportional to the squared root of atomic mass. However, these factors appear to be responsible only partly for the observed changes. From 0 to 10 at. % Li, the average number of conduction electrons per atom drops by 7%. This electron

FIG. 3. Heat capacity data in the format of C/T vs T^2 (note the consecutive 1 mJ/mol K^2 scale shift in C/T).
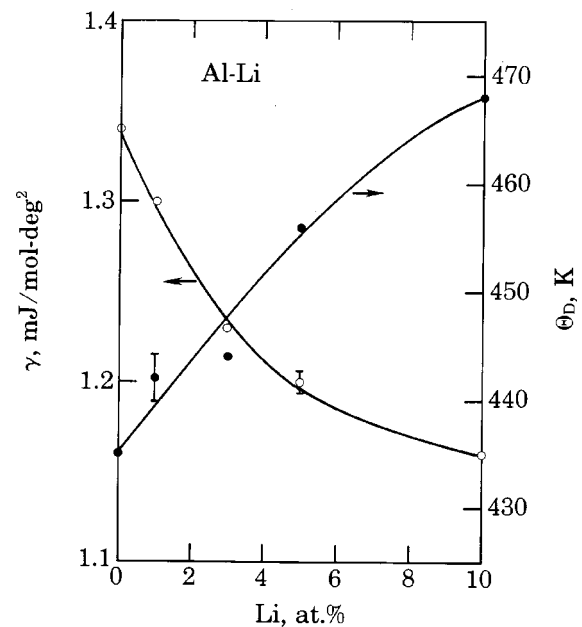

FIG. 4. Li-content dependence of the electronic heat capacity coefficient and the Debye temperature.

density change would lower the γ value by less than 3%, which is much smaller than the actually observed 14% drop in γ. Similarly, the squared root of average mass decreases by 4%, while θ_D increases by 7%. The additional effect is believed to arise from the interaction between aluminum and lithium atoms, which manifests in electron localization. The latter leads to a reduced number of free electrons, and consequently to the lower density-of-states at Fermi level. Realizing that the ionic radius is larger for lithium (0.68 Å) than aluminum (0.51 Å), the reduction of lattice constant with increasing Li content in Fig. 2 may reflect the same cause. Meanwhile, the directional nature of the electron localization could stiffen the lattice and thus raise the Debye temperature, but lowers the ductility. Similar solid solution strengthening has been suggested to occur in titanium with various alloying elements including aluminum, tin, and gallium.[5] It also explains the brittleness of the intermetallic compound Ti_3Al.[6] In fact, the formation of intermetallic compounds with relatively high melting points may be considered as a clue to interatomic bonding even in dilute alloys. More recently, the electron localization effect has been observed also in high-strength, ternary compounds Ti_3SiC_2, $Ti_3Si_{1.1}C_{1.8}$, and Ti_4AlN_3.[7,8]

In conclusion, low temperature calorimetric parameters thus obtained revealed the fundamental basis, in terms of solid solution strengthening through electron localization, for the benefit of lithium additions to aluminum. The binary alloys can be then further developed into practical materials with additional alloying elements to meet such designed purposes as microstructural modification and specific mechanical property enhancement.

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