The Al-Li-Si System (Aluminum-Lithium-Silicon)

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Introduction

The Al-rich corner of the Al-Li-Si ternary system was studied by [84Han], [76Kad], [76Dri], [49Boo1], and [49Boo2]. [76Kad] and [76Dri] constructed the liquidus surface and an isotherm at 550 °C for the Al-rich corner, using high-purity Al, Li, and Si and using thermal and microstructural analysis. However, their diagrams are inconsistent with those accepted for constituent binaries. For example, they assumed the Li concentration in the Al-Li eutectic to be between 8.4 and 9.9 wt.% Li, contrary to the 7.5 wt.% Li reported by [82Mca] in their evaluation of the Al-Li system. The study of [84Han], which was more recent, assumed the Al-Li binary eutectic to be at 10 wt.% Li.

This evaluation is intended to correlate the existing data for the Al-Li-Si ternary system and to resolve inconsistencies among the ternary data and the accepted binary data.

Binary Systems

The constituent binary phase diagrams for the Li-Si and Al-Si systems are well established, as assessed by [Shunk] and [84Mur],

respectively, and are adopted in this evaluation. The Al-Li system has been established with reasonable certainty [80Sch, 81Sch, 82Mca] with the evaluation of [80Sch, 81Sch] as reported by [90Goe] used here. Important phases and reactions (with their compositions) of the Al-Li system are summarized in "The Al-Li-Mn (Aluminum-Lithium-Manganese System," in this issue.

The Al-Li eutectic reaction at a composition of 7.5 wt.% Li and 600 ± 5 °C was established by [82Mca], contrary to the eutectic composition between 8.4 and 9.9 wt.% Li reported by [76Kad] and the 10 wt.% Li assumed by [84Han]. [82Mca] tabulated a value of 8.29 wt.% (26 at.%) Li for the Al-Li eutectic, but the diagrams show 7.5 wt.% (24 at.%), which is assumed to be correct in this evaluation.

In the Li-Si system, Li₄Si and Li₂Si are known to form by a peritectic reaction at 635 °C and a eutectic reaction at 650 °C, respectively [Shunk]:

$$p_1$$
: L (47.46 wt.% Si) + Li₂Si (66.84 wt.% Si)
↔ Li₄Si (49 to 50.5 wt.% Si) at 635 °C



and



e₁: L (72.0 wt.% Si) ↔ Li₂Si (66.84 wt.% Si) + (Si) at 650 °C

However, [76Kad] assumed the Li-Si eutectic to occur at 635 °C.

[84Mur] reported that the Al-Si eutectic occurs at 12.6 wt.% Si and 577 °C, in agreement with [84Han], but contrary to the eutectic composition of 11.7 wt.% Si reported by [76Kad]. The Al-Si eutectic reaction of [84Mur] is adopted in this evaluation:

e₂: L (12.6 wt.% Si) ↔ (Al) (1.56 wt.% Si) + (Si) (100 wt.% Si) at 577 °C

The Al-Li-Si ternary diagram has therefore been altered in the present evaluation to correspond to the most recent binary diagrams.

Ternary Diagrams

From a study of the solidification of several Al-Li-Si alloys, [49Boo1] and [49Boo2] showed that invariant transformations take place at a temperature approximately 8 °C lower than that of the Al-Si eutectic (577 °C). He also reported the presence of a ternary compound, as an extension of AlLi up to the formula Al2Li3Si2 (11.2 wt.% Li and 45.2 wt.% Si). [76Kad] and [76Dri] studied the phase equilibria and phase relationships at the Al-rich corner of the Al-Li-Si system, using high-purity alloys with up to 12 wt.% Li and Si and employing thermal analysis (under controlled heating and cooling conditions) and microscopy. From polythermal sections with constant contents of 2.0, 5.0, 7.0, and 11.5 wt.% Si; 3.0 and 5.0 wt.% Li; 92 wt.% Al and sections with a Si-to-Li ratio of 2.7 (some of which are shown in Fig. 1 to 4), [76Kad] constructed the liquidus projection, which is shown as dashed lines in Fig. 5. From their microstructural examination and thermal analysis results for the polythermal sections, they established the eutectic reactions:



Fig. 3 Al-Li-Si polythermal section with constant content of 5 wt.% Si. From [76Kad].



E₁: L (11.5 wt.% Si and 0.5 wt.% Li) ↔ (Al) + (Si) + T at 565 ± 3 °C

and

E₂: L(2.0 wt.% Si and 9.2 wt.% Li) ↔ (Al) + AlLi + T at 595 ± 2 °C

where T is the ternary compound with the approximate chemical formula $Al_2Li_3Si_2$. Later work by [63Boo] indicated that the ter-





nary phase is AlLiSi and this agrees with other, more recent studies.

[76Kad] also found a quasibinary region between (Al) and the ternary compound; it is a simple eutectic system (Fig. 6), with limited solubility in the solid state. The temperature of the eutectic equilibrium is about 635 °C, and the concentrations at the eutectic point of Li and Si are 1.5 and 3.8 wt.%, respectively.

A liquidus projection from a more recent study by [84Han] on 40 Al-Li-Si ternary alloys with up to 14 wt.% Li and 25 wt.% Si is also shown in Fig. 5 (shown as solid lines) for comparison with the results of [76Kad]. [84Han] reported (as is also clear from Fig. 5) that the Al-AlLi binary eutectic is depressed by Si to the ternary eutectic point E.1, and the Al-Si binary eutectic is also depressed by Li to the ternary eutectic point E.2:

E.1: L(1.1 wt.% Si + 10.6 wt.% Li) ↔ (Al) + AlLi + X at 592 °C

where X is a faceted phase that appears to be a ternary compound approximating AlLiSi and

E.2: L (13.8 wt.% Si + 1.4 wt.% Li) ↔ (Al) + (Si) + Al-LiSi at 575 °C

Whereas the temperature of the eutectic E_2 of [76Kad] is similar to that of the eutectic E.1 of [84Han], the compositions are quite different. Both the temperature and composition for the other ternary eutectic were reported differently by the two investigators. The composition of the maxima in the monovariant valley at ~630 °C and 4.0 wt.% Li and 5.0 wt.% Si of [84Han] was also different from that of [76Kad], who reported the same to occur at 1.4 wt.% Li and 3.4 wt.% Si and 635 °C.

The inconsistency in the Si-rich ternary eutectic is due to the difference in the composition of the binary eutectic assumed by [76Kad] and [84Han]. In view of the correct composition of Al-Si eutectic assumed by [84Han], their ternary eutectic E.2, in place





of the ternary eutectic E_1 of [76Kad], is accepted in this evaluation.

The disagreement regarding the ternary eutectic E_2 of [76Kad] and E.1 of [84Han] is due primarily to a wide divergence in the position of the Al-Li binary eutectic. Because the work of [84Han] is more recent, their liquidus projection with the Al-Li binary eutectic shown at 7.5 wt.% Li tentatively is assumed to be correct in this evaluation and is shown separately in Fig. 7, with the liquidus surface isotherms included.

Isothermal Sections

[76Dri] determined isothermal sections for the Al-rich corner of the Al-Li-Si ternary system from microscopic examination of alloys deformed and annealed at 550, 500, and 200 °C. The only isothermal section (at 550 °C) available from their published work is shown in Fig. 8. Using the results of their polythermal sections and forcing agreement with the accepted binary diagrams, we have been unable to construct isothermal sections at temperatures above 600 °C that are consistent with the data. For example, for the Al-2 wt.% Si section (Fig. 1) in the range 8 to 12 wt.% Li at 610 °C, the phase field sequence L, L+AlLi, L+(Al) + AlLi does not seem possible. Further, the section for 5 wt.% Si in Fig. 3 shows the composition Al-5 wt.% Si-11 wt.% Li to be liquid at temperatures above 600 °C, whereas the liquidus temperature for this composition is over 700 °C (Fig. 7).

However, the data presented by [76Kad] at Li concentrations below about 8 wt.% are consistent, and an isotherm at 600 $^{\circ}$ C drawn from the data of [76Kad] (Fig. 1 to 4) is shown in Fig. 9.

Regions of Primary Crystallization and Ternary Compounds

The phases reported [84Han, 76Kad, 76Dri] to be in equilibrium with the (Al) solid solution are: (1) the (Si) solid solution; (2) a solid solution based on AlLi; and (3) the ternary compound AlLi-Si, reported by [Pearson2] to occur at about equimolar proportions of Al:Li:Si and to have cubic structure (space group Fd3m; 16 atoms per unit cell; lattice parameter ranging from 0.594 nm at AlLiSi as 216- $F\overline{4}3m$ (cF12) with a = 0.593 nm. These regions of primary solidification are shown clearly marked in Fig. 8 and 9.

The solubilities of Si and Li in Al binary alloys at different temperatures are well established [82Mca, 84Mur]. Additions of Si and Li mutually lower the solubility of each other in Al. From a close look at the isothermal sections, the general conclusion of [76Kad] and [76Dri] (as discussed below) are accepted as such in this evaluation: The boundaries of the two-phase regions (Al) + (Si) and (Al) + AlLi are very close to those of the binary systems, indicating little or no homogeneity ranges based on (Si) and AlLi in the ternary system. The (Al) + AlLiSi two-phase range is considerable, suggesting a significant homogeneity range based on the ternary compound. The three-phase regions (Al) + (Si) + AlLiSi and (Al) + AlLi + AlLiSi are fairly wide. With decreasing temperature, the single- and two-phase regions become much smaller, whereas the three-phase regions become broad.

Conclusions

From the limited experimental data of [84Han], [76Kad], [76Dri], [49Boo1], and [49Boo2], the following general con-



clusions can be drawn concerning the phase relationships at the Al corner of the Al-Li-Si system:

- (Si), AlLi, and the ternary phase = AlLiSi are in equilibrium with the (Al) solid solution.
- The ternary compound has the approximate formula AlLiSi, instead of Al₂Li₃Si₂.
- There are two ternary invariant eutectic reactions, with a maxima in the monovariant valley.
- Additions of Si and Li mutually lower the solubilities of each other in (Al).
- With decreasing temperature, the extent of single- and twophase regions decrease appreciably, whereas those of threephase regions widen.
- These exists a large area of homogeneity, based on the ternary compound, that decreases appreciably with increasing temperature.

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