Aluminium – Calcium – Lithium

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Literature Data

The first investigations in the ternary Al-Ca-Li system was published by [1986Lee] who calculated vapor pressures over ternary melts on the basis of thermodynamic data of binary Al and Li liquid alloys. [1990Mil] reported, in the form of an abstract, that the equilibria between the binary Laves phases $CaAl_2$ (Cu_2Mg structure type) and Li_2Ca ($MgZn_2$ structure type) does not occur on the 33.33 at.% Ca section. A ternary Laves phase of the Ni_2Mg structure type occurs on this section and enters into equilibrium with $CaAl_2$ and Li_2Ca. No further details were given. [1992Mil] reported crystal structure determination of a ternary phase "$Li_xCa_{8-x}Al_3$". This phase is part of ternary solubility of the later reported binary phase Ca_8Al_3 [2001Kev]. [1993Nes] synthesized series of compounds Li_xCaAl_{2-x} in Mo crucibles and structurally characterized them afterwards. They confirmed the ternary $MgNi_2$ type Laves phase between $0.80 \le x \le 1.0$ and a second one of $MgZn_2$ type between $0.80 \le x \le 1.0$. A schematic ternary phase diagram is shown. Small ternary solubilities of the binary Laves phases $CaAl_2$ and Li_2Ca were indicated. In this isothermal section two additional ternary phases were included. The phase $Li_{11}Ca_6Al_{12}$ is reported later in detail by [1996Hae]. For the further phase with the composition $Li_xCa_8Al_{7-x}$ no information is given in the text.
Phase equilibria in the Al-Ca-Li system were studied by [1988Gan, 1999Gan, 2000Gan] using X-ray phase and differential thermal analyses. A partial isothermal section up to 33 at.% Ca at 150°C is given by [1999Gan]. [2000Gan] show additionally six vertical sections and a constructed partial liquidus surface. In these investigations neither the existence of a large solubility range of the Laves phase, nor the earlier reported ternary phases was considered. In contrast recent experimental work in this system [2003Jan] confirmed clearly the stability of the ternary Laves phase of the Ni_2Mg structure and the phase $Li_{11}Ca_6Al_{12}$. The phase $Li_2Ca_6Al_2$ reported by [1993Nes] was not confirmed in this work.

Binary Systems

For Al-Li [2002Gro] and Al-Ca [2002Ted] the evaluation in MSIT Binary Evaluation Program already assessed binary diagrams were used. The binary system Ca-Li was taken from [Mas2].

Solid Phases

No complete solid solution between the two binary Laves phases Li_2Ca and $CaAl_2$ was observed. [1993Nes] found a two-phase field between Li_2Ca and "LiCaAl". Towards $CaAl_2$ a continuous series $Ca(Li_xAl_{2-x})$ of two phases, τ_1 crystallizing in the $MgZn_2$ ($0.80 \le x \le 1.0$) structure type and τ_2 in the $MgNi_2$ ($0.25 \le x \le 0.75$) structure type were found. Additional two ternary phases were reported by [1993Nes]. [1996Hae] determined the crystal structure of τ_3, $Li_{11}Ca_6Al_{12}$, one of these phases. The second phase, τ_4, $Li_xCa_8Al_{7-x}$, was found to be metastable by [2003Jan]. All phases together with the crystallographic data are given in Table 1.

Liquidus Surface

A partial liquidus surface constructed from thermoanalytic results is shown by [2000Gan]. It is questionable since it is in contradiction with all other authors and therefore is not reproduced here.

Isothermal Sections

The only isothermal section is given by [1999Gan, 2000Gan] at 150°C. It is partial up to 33 at.% Ca and disregard the already earlier known ternary phases. Figure 1 shows the isothermal sections at room temperature concerning the investigations of [1993Nes] and [2003Jan].

Temperature – Composition Sections

Six vertical sections from $CaAl_2$ to Li_2Ca, $CaAl_2$ to Li, $CaAl_2$ to Li_9Al_4, $CaAl_4$ to LiAl, $CaAl_2$ to LiAl and $CaAl_2$ to Li_3Al_2 are given by [2000Gan]. They are classified to be tentative because they are in substantial contradiction with the established ternary phases.

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(αAl) < 660.452	*cF*4 $Fm\bar{3}m$ Cu	*a* = 404.96	at 25°C [Mas2]
(βCa) 842-443	*cI*2 $Im\bar{3}m$ W	*a* = 448.0	[Mas2]
(αCa) < 443	*cF*4 $Fm\bar{3}m$ Cu	*a* = 558.84	at 25°C [Mas2]
(Li) < 180.6	*cI*2 $Im\bar{3}m$ W	*a* = 351.0	pure Li at 25°C [V-C2]
Li_2Ca	*hP*12 $P6_3/mmc$ $MgZn_2$	*a* = 631.3 *c* = 1028	[Mas2]
Li_9Al_4 (δ) 347-275	*mC*26 *C*2/*m*	*a* = 1915.51 *b* = 542.88 *c* = 449.88 β = 107.671°	[1982McA]
Li_9Al_4 (δ`) < 275	?	?	
Li_3Al_2 (γ) < 520	*hR*15 *Rm*	*a* = 450.8 *c* = 1426	[1982McA] 60 to 61at.% Li [Mas2]
LiAl (β) < 704	*cF*16 $Fd\bar{3}m$ NaTl	*a* = 637	at 50 at.% Li [1982McA] 45 to 61 at.% Li [Mas2]
$CaAl_4$ (h) 700-170	*tI*10 Al_4Ba	*a* = 435.3 *b* = 1107	[V-C2]
$CaAl_4$ (l) < 170	*mC*10	*a* = 615.26 ± 0.15 *b* = 617.30 ± 0.13 *c* = 632.90 ± 0.14 β = 118.026 ± 0.016°	[1993Mil]
$CaAl_2$ < 1086	*cF*24 $Fd\bar{3}m$ Cu_2Mg	*a* = 804.0	[V-C2] Powder X-ray diffraction
$Ca_{13}Al_{14}$ < 633	*mC*54	*a* = 1555.1 ± 0.4 *b* = 987.3 ± 0.2 *c* = 972.6 ± 0.2 β = 108.09 ± 0.02°	[1998Hua] Single-crystal X-ray diffraction

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Ca_8Al_3 < 578	*aP*22 Ca_8In_3	*a* = 948.4 ± 0.3 *b* = 959.2 ± 0.3 *c* = 967.1 ± 0.3 α = 99.02 ± 0.03° β = 101.13 ± 0.03°	[1998Hua] Single-crystal X-ray diffraction
		a = 947.0 ± 0.2 *b* = 960.2 ± 0.2 *c* = 964.6 ± 0.2 α = 99.17 ± 0.02° β = 101.08 ± 0.02°	[1992Mil] at 0.13 at.% dissolved Li
*τ_1, Li_xCaAl_{2-x}	*hP*12 $P6_3/mmc$ $MgZn_2$	*a* = 582.0 to 626.8 *c* = 936.6 to 1021.9	0.80 ≤ *x* ≤ 1.0 [1993Nes]
*τ_2, Li_xCaAl_{2-x}	*hP*24 Ni_2Mg	*a* = 573.0 to 579.6 *c* = 1856.4 to 1875.4	0.25 ≤ *x* ≤ 0.75 [1993Nes]
*τ_3, $Li_{11}Ca_6Al_{12}$	*cF*116 $Fm\bar{3}m$ Th_6Mn_{23}	*a* = 1343.0	[1996Hae]
*τ_4, $Li_xCa_8Al_{7-x}$	?	?	[1993Nes] metastable [2003Jan]

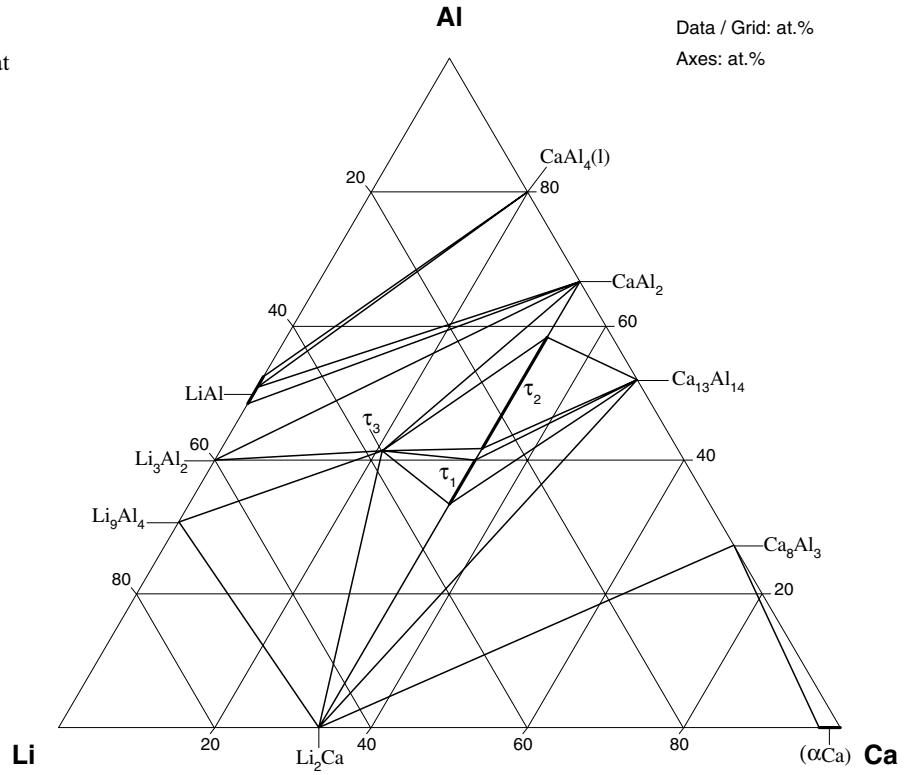

Fig. 1: Al-Ca-Li. Isothermal section at room temperature