Ca – Li (Calcium – Lithium)

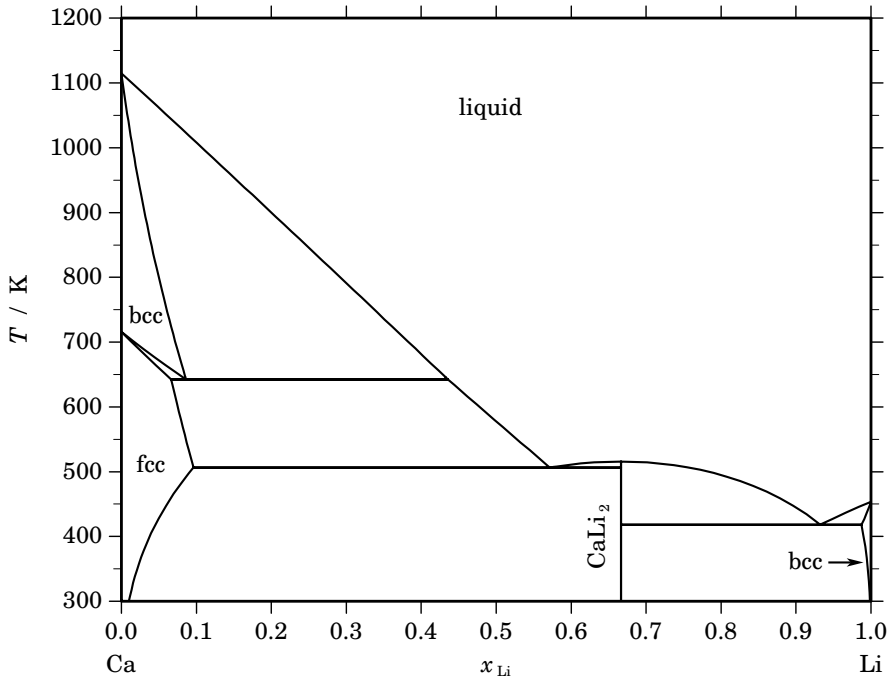

Fig. 1. Calculated phase diagram for the system Ca-Li.

Calcium and lithium are both important alloying elements for magnesium. Calcium acts as a grain refiner and it improves the creep resistance while Li decreases the density of the alloys. The literature on the Ca-Li system has been reviewed in [1987Bal, 2002Grö] and a thermodynamic assessment has been given in [2002Grö]. The phase diagram has been thoroughly investigated by [1966Car]. The enthalpy of formation of $CaLi_2$ has been measured by drop solution calorimetry [2002Grö]. Based on these data, the critical recommendations for the phase diagram and the invariants given in [1987Bal] and using the SGTE element data the thermodynamic description for Ca-Li has been optimised.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Ca,Li)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Ca,Li)_1$
$CaLi_2$	$C14$	$MgZn_2$	$hP12$	$P6_3/mmc$	CALI2	Ca_1Li_2
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Ca,Li)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Ca,Li)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Li}			$\Delta_r H$ / (J/mol)
bcc $\rightleftharpoons$ fcc + liquid	metatectic	642.5	0.086	0.066	0.435	−708
liquid $\rightleftharpoons$ $CaLi_2$	congruent	515.5	0.667	0.667		−8244
liquid $\rightleftharpoons$ fcc + $CaLi_2$	eutectic	506.5	0.572	0.096	0.667	−8117
liquid $\rightleftharpoons$ $CaLi_2$ + bcc	eutectic	418.1	0.932	0.667	0.987	−3723

Table IIIa. Integral quantities for the liquid phase at 1200 K.

x_{Li}	ΔG_{m} [J/mol]	ΔH_{m} [J/mol]	ΔS_{m} [J/(mol·K)]	$G_{\mathrm{m}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{m}}^{\mathrm{E}}$ [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−4098	−508	2.991	−854	0.289	0.000
0.200	−6511	−903	4.674	−1518	0.513	0.000
0.300	−8088	−1185	5.752	−1993	0.673	0.000
0.400	−8992	−1354	6.365	−2277	0.770	0.000
0.500	−9288	−1410	6.565	−2372	0.802	0.000
0.600	−8992	−1354	6.365	−2277	0.770	0.000
0.700	−8088	−1185	5.752	−1993	0.673	0.000
0.800	−6511	−903	4.674	−1518	0.513	0.000
0.900	−4098	−508	2.991	−854	0.289	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: Ca(liquid), Li(liquid)

Table IIIb. Partial quantities for Ca in the liquid phase at 1200 K.

x_{Ca}	ΔG_{Ca} [J/mol]	ΔH_{Ca} [J/mol]	ΔS_{Ca} [J/(mol·K)]	$G_{\mathrm{Ca}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Ca}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Ca}	γ_{Ca}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−1146	−56	0.908	−95	0.032	0.891	0.991
0.800	−2606	−226	1.984	−380	0.128	0.770	0.963
0.700	−4413	−508	3.254	−854	0.289	0.643	0.918
0.600	−6615	−903	4.760	−1518	0.513	0.515	0.859
0.500	−9288	−1410	6.565	−2372	0.802	0.394	0.788
0.400	−12558	−2031	8.773	−3416	1.154	0.284	0.710
0.300	−16662	−2764	11.582	−4650	1.571	0.188	0.627
0.200	−22131	−3610	15.434	−6073	2.052	0.109	0.544
0.100	−30660	−4569	21.742	−7686	2.597	0.046	0.463
0.000	$-\infty$	−5641	∞	−9489	3.207	0.000	0.386

Reference state: Ca(liquid)

Table IIIc. Partial quantities for Li in the liquid phase at 1200 K.

x_{Li}	ΔG_{Li} [J/mol]	ΔH_{Li} [J/mol]	ΔS_{Li} [J/(mol·K)]	$G_{\mathrm{Li}}^{\mathrm{E}}$ [J/mol]	$S_{\mathrm{Li}}^{\mathrm{E}}$ [J/(mol·K)]	a_{Li}	γ_{Li}
0.000	$-\infty$	−5641	∞	−9489	3.207	0.000	0.386
0.100	−30660	−4569	21.742	−7686	2.597	0.046	0.463
0.200	−22131	−3610	15.434	−6073	2.052	0.109	0.544
0.300	−16662	−2764	11.582	−4650	1.571	0.188	0.627
0.400	−12558	−2031	8.773	−3416	1.154	0.284	0.710
0.500	−9288	−1410	6.565	−2372	0.802	0.394	0.788
0.600	−6615	−903	4.760	−1518	0.513	0.515	0.859
0.700	−4413	−508	3.254	−854	0.289	0.643	0.918
0.800	−2606	−226	1.984	−380	0.128	0.770	0.963
0.900	−1146	−56	0.908	−95	0.032	0.891	0.991
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Li(liquid)

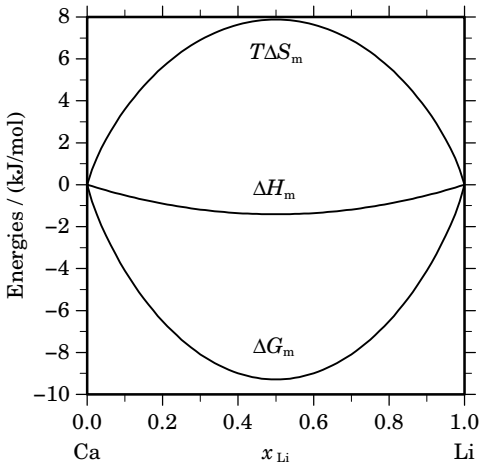

Fig. 2. Integral quantities of the liquid phase at T=1200 K.

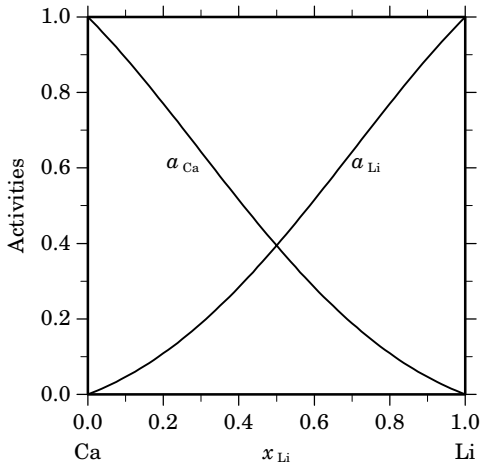

Fig. 3. Activities in the liquid phase at T=1200 K.

Table IV. Standard reaction quantities at 298.15 K for the compounds per mole of atoms.

Compound	x_{Li}	$\Delta_f G^\circ$ / (J/mol)	$\Delta_f H^\circ$ / (J/mol)	$\Delta_f S^\circ$ / (J/(mol·K))	$\Delta_f C_P^\circ$ / (J/(mol·K))
Ca_1Li_2	0.667	−3258	−3894	−2.132	0.000

References

[1966Car] D.G. Carfagno, Ph.D. Thesis, Syracuse Univ., Syracuse, NY, 1966.
[1987Bal] C.W. Bale, A.D. Pelton: Bull. Alloy Phase Diagrams **8** (1987) 125–127.
[2002Grö] J. Gröbner, R. Schmid-Fetzer, A. Pisch, C. Colinet, V.V. Pavlyuk, G.S. Dmytriv, D.G. Kevorkov, O.I. Bodak: Thermochim. Acta **389** (2002) 85–94.