J. Min. Metall. Sect. B-Metall. 53 (3) B (2017) 203 - 208

Journal of Mining and Metallurgy,
Section B: Metallurgy

CALORIMETRIC MEASUREMENTS OF THE Ca-Li LIQUID ALLOYS

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(Received 08 May 2017; accepted 30 June 2017)

Abstract

An isothermal high-temperature mixing calorimeter was used for the determination of the enthalpy of mixing $\Delta_{mix}H$ *for liquid Ca-Li solutions, for 63 alloys of different compositions at the four following temperatures: 588 K, 648 K, 820 K and 1159 K. The studies were performed by way of dropping solid metal samples at ambient temperature into liquid alloys, starting from pure elements. In three series, calcium was dropped into liquid lithium, whereas solid Li samples were added into liquid Ca in the fourth series. Because of the high reactivity of the alloy components, all the steps of the experiment were conducted in a high purity argon atmosphere. It was found that the Ca-Li system is characterized by small negative* $\Delta_{mix}H$ *values and its minimal value is lower than -1.5 kJ/mol. Additionally, the differential thermal analysis was used to determine the phase transformation temperature for 11 Ca-Li alloys.*
Finally, the Calphad method was used to assess the phase diagram, applying the data of these studies as well as all the experimental results available in the literature.

Keywords: *Molar mixing enthalpy; Ca-Li system; calorimetry; DTA; Calphad method; thermochemistry.*

1. Introduction

The Ca-Li alloys have a great importance in metallurgy and materials engineering. However, these alloys are one of the few two-component systems whose thermodynamic properties have not been thoroughly investigated in the world literature.

The limited of thermodynamic data is most probably the result of experimental difficulties, due to high reactivity of the alloy components with O_2, H_2, N_2 and the moisture. However, calcium-lithium alloys play an important role in the aluminum and magnesium industries and can be applied for safe and ecological hydrogen storage in the power and automobile industry. The thermodynamic properties of solid and liquid alloys have not been investigated, except for the formation enthalpy of the intermetallic $CaLi_2$ compound [1]. The studies in this field, undertaken by a number of research centers and car companies, are not only caused by the search for new energy sources, but also the need to drastically reduce the CO_2 emissions in individual countries of the EU.

A review of the available literature data concerning the Ca-Li phase relations was presented in [2] on the formation enthalpy measurements of the $CaLi_2$ compound and the heat of solution of the components. The main goal of this work was to measure calorimetrically the change of the enthalpy of mixing $\Delta_{mix}H$ of the liquid phase, as well as to assess the determination of the phase transformations temperature, and finally to calculate the phase diagram based on all the available thermodynamic results.

2. Material and methods

2.1 Calorimetric measurements

An isothermal high-temperature mixing calorimeter, originally constructed at the Max-Planck-Institute (Stuttgart, Germany) and copied with some modifications at the Institute of Metallurgy and Materials Science, Polish Academy of Sciences in Krakow, was used to perform the experiments at four temperatures: 588 K, 648 K, 820 K and 1159 K. The construction of the calorimeter was described in our previous works [2-4]. The measurements were performed by way of dropping solid samples of metals at ambient temperature into liquid alloys, starting from pure liquid Li, in three series, whereas in the forth one, Li was added into liquid Ca. The experiments were performed in a high purity Ar atmosphere. The calibrations were made by way of adding solid samples of the bath metal (Ca, Li) before the measurements began. The changes in the

Dedicated to the memory of Professor Dragana Živković

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DOI:10.2298/JMMB170508018D

calibration coefficient with the increasing amount of melt were considered in the calculations. The voltage signal from the thermopile was registered in a digital form and next the heat effects and the enthalpies were calculated according to the procedure presented in [5].

Because of the high reactivity of the alloy components, all the steps of the experiment preparation were made inside the glove box MBraun in a high purity argon atmosphere with trace amounts of moisture and O_2, which were continuously removed from the argon to the level lower than 1 ppm by a molecular sieve and catalytic Cu. The nitrogen was removed from Ar by means of a reaction with a Ti sponge kept at 1223 K. Its concentration in the argon was not monitored.

In the experiments, high purity metals were used: Ca 99.98 mass. % and Li 99.9 mass. %. (Alfa Aesar). Small pieces of the added metals were weighed and next closed in a calorimetric antechamber inside the glove-box. Then, the antechamber was removed from the glove box and connected to the calorimeter. Before the Li or Ca pieces were dropped into the calorimetric bath (Ca or Li), the apparatus was three times evacuated and flashed by high purity argon of the same quality as that in the glove box.

2.2 Differential Thermal Analysis (DTA)

Phase transformations and liquidus temperature measurements of the Ca-Li alloys were conducted by means of the DTA technique with the use of the Q-1500 (Paulik-Paulik-Erdey) derivatograph. The samples were prepared in a glove box filled with high purity argon, similarly to the calorimetric measurements. The alloys were prepared by way of melting the metals in Ti crucibles, which were sealed with the use of a hydraulic press. The Ti crucibles were preliminary heated in air to 1073 K to avoid the energy effects of the reaction of Ti with $N_2$and/or O_2 in the course of DTA measurements. Afterwards, DTA measurements were performed in air with the temperature rate of 5 K/min.

2.3 CALPHAD Optimization and Assessment

The Gibbs energy function $G_i^{\Phi}(T) = {}^{0}G_i^{\Phi}(T) - H_i^{\mathrm{SER}}(T)$ $(298.15K)$ for the pure element i (i=Ca, Li) in the given phase Φ (Φ=Liquid, solid solution: fcc or bcc) is expressed as follows:

$$G_i^{\Phi}(T) = a + b\cdot T + c\cdot T\cdot \ln T + d\cdot T^2 + e\cdot T^{-1} + \\ + f\cdot T^3 + g\cdot T^7 + h\cdot T^{-9} \tag{1}$$

where: ${}^{0}G_i^{\Phi}(T)$ is the absolute Gibbs free energy of the element i; H_i^{SER} is the molar enthalpy of the element i at 298.15 K and 1 atm. in its standard element reference state (SER), T is the absolute temperature and a-h are the adjustable coefficients of the model. The parameters of the Gibbs energy functions for Ca and Li above 298.15 K (a to h, parameters) were taken from the SGTE (Scientific Group Thermodata Europe) pure elements database compilation by Dinsdale [6].

The liquid and the disordered solid solutions of the bcc and fcc phases were described with the use of a substitutional solution model, the Gibbs free energy being defined by the following expression:

$$G_m^{\Phi}(T) = x_{Ca}\cdot G_{Ca}^{\Phi}(T) + x_{Li}\cdot G_{LI}^{\Phi}(T) + \\ + RT(x_{Ca}\cdot \ln x_{Ca} + x_{Li}\cdot \ln x_{Li}) + {}^{ex}G_m^{\Phi} \tag{2}$$

where R is the gas constant and x_{Ca}, and x_{Li} are the mole fractions of Ca and Li, respectively.

${}^{ex}G_m^{\Phi}$ is the excess Gibbs energy term, expressed by the Redlich-Kister polynomial [7]

$${}^{ex}G_m^{\Phi} = x_{Ca}\cdot x_{Li}\cdot \sum_{v=0}^{n} L^{v}\cdot\left(x_{Ca} - x_{Li}\right)^{v} \tag{3}$$

The $CaLi_2$ compound is described as a stoichiometric phase: (Ca)(Li)2. Because no heat capacity data are available, the Kopp–Neumann relation is used and the Gibbs energy functions of these (Ca)(Li)2 compounds are given as follows:

$$G_{Ca:Li}^{CaLi_2} = \mathrm{a} + \mathrm{b}{*}\mathrm{T} + x_{\mathrm{Ca}}\cdot G_{Ca}^{0,fcc} + x_{\mathrm{Li}}\cdot G_{Li}^{0,bcc} \tag{4}$$

3. Results and Discussion

3.1. Calorimetric and DTA results

The measurements of the enthalpy of mixing $\Delta_{mix}H$ were performed by way of transporting the samples from the calorimetric antechamber kept at ambient temperatures into the calorimeter, held at the desired high temperature. The mixing enthalpies were calculated with the aid of the two following equations:

$$H_{DISS-X} = \left(\Delta H_{Signal}\cdot K\right) - \left(H_X^{T_D\to T_M}\cdot n_X\right) \tag{5}$$

$$\Delta_{mix}H = \frac{\sum H_{DISS-X}}{n_{Ca} + n_{Li}} \tag{6}$$

where ΔH_{Signal} is the heat effect for each drop of metal (Ca or Li) into the liquid Ca-Li alloys, which equals the added drop enthalpy, K is the calibration constant and T_D and T_M are the drop and calorimeter absolute temperatures, respectively. $H_X^{T_D\to T_M}$ is the enthalpy change of pure metals (Ca or Li) between the T_D and T_M temperatures, calculated from the Dinsdale [6] and n_{Ca} and n_{Li} are the numbers of moles of calcium and lithium, respectively. $H_{\mathrm{DISS-X}}$ is the enthalpy of dissolution of pure calcium or lithium. The errors in the calorimetric measurement were less than 1.0 kJ/mol.

The enthalpy of the pure metals, the numbers of moles, the mole fraction of pure calcium, the drop enthalpy and the integral molar enthalpy of mixing of the liquid Ca-Li alloys obtained in the four separate series at four temperatures between 588 K and 1159 K are given in Table 1.

Table 1. *Integral enthalpies of mixing of liquid Ca-Li alloys.*

Enthalpy of the pure metals	Number of moles	Mole fraction	Drop enthalpy	Integral enthalpy
	n_i	x_{Ca}	$\Delta_{Signal}H$	$\Delta_{mix}H$
[kJ/mol]	[mol]		[kJ]	[kJ/mol]
H_{Ca} = 17.4908	Series 1: T=588 K, starting amount: n_{Li}= 0.074053, K=-0.00008016kJ/μVs.			
H_{Li} = 11.1948	n_{Ca}			
	0.003668	0.0472	-0.024	-0.313
	0.004242	0.0965	0.006	-0.224
	0.004366	0.1422	0.004	-0.169
	0.003468	0.1753	-0.017	-0.352
	0.003318	0.2047	-0.012	-0.465
	0.003618	0.2345	-0.006	-0.512
	0.004266	0.2668	-0.007	-0.562
	0.005215	0.3028	-0.009	-0.618
	0.004716	0.3324	-0.006	-0.641
	0.00484	0.3603	-0.02	-0.785
	0.005539	0.3895	-0.027	-0.969
	0.005439	0.4157	-0.021	-1.096
	0.005339	0.4394	-0.027	-1.255
	0.00504	0.46	-0.017	-1.336
H_{Ca} = 19.3352	Series 2: T=648 K, starting amount: n_{Li}=0.0742, K=-0.000095 kJ/μVs.			
H_{Li} = 12.9954	n_{Ca}			
	0.003	0.0388	-0.001	-0.012
	0.0027	0.0709	-0.001	-0.027
	0.003	0.1042	-0.026	-0.343
	0.0032	0.1372	0.011	-0.208
	0.0026	0.1625	-0.022	-0.454
	0.0037	0.1964	0.008	-0.345
	0.0028	0.22	-0.024	-0.59
	0.0042	0.2531	-0.031	-0.872
	0.0044	0.2851	-0.037	-1.191
	0.0044	0.3144	-0.014	-1.275
H_{Ca}= 24.9382	Series 3: T=820 K, starting amount: n_{Li}= 0.0785, K=-0.000095 kJ/μVs.			
H_{Li} = 18.0128	n_{Ca}			
	0.0025	0.0308	-0.009	-0.11
	0.0027	0.062	-0.012	-0.249
	0.0021	0.0846	-0.009	-0.353
	0.0029	0.1148	0.004	-0.291
	0.003	0.1437	0.007	-0.206
	0.0031	0.1718	-0.001	-0.21
	0.0038	0.2035	0.001	-0.189
	0.0035	0.2309	0.003	-0.158
	0.0039	0.2595	-0.007	-0.22
	0.0042	0.2878	-0.054	-0.701
	0.0045	0.3155	-0.036	-0.986
	0.0043	0.3402	-0.014	-1.067
	0.0039	0.3611	-0.024	-1.225

Table 1 is continued on the next page.

Table 1 continues from the previous page

	0.0042	0.3821	-0.024	-1.375
	0.004	0.401	-0.006	-1.375
	0.0038	0.4179	0.001	-1.329
	0.0037	0.4335	-0.012	-1.378
	0.0035	0.4474	0.098	-0.654
	0.0029	0.4585	-0.032	-0.864
	0.0041	0.4733	-0.049	-1.17
	0.0045	0.4887	0.007	-1.088
	0.0043	0.5025	-0.02	-1.188
	0.0041	0.5151	-0.034	-1.367
	0.0077	0.5371	0.046	-1.035
	0.0071	0.5557	0.052	-0.698
	0.0079	0.5746	-0.012	-0.734
	0.0075	0.5912	0.015	-0.63
	0.0102	0.6119	-0.063	-0.911
H_{Ca} = 37.9450	Series 4: T=1159 K, starting amount: n_{Ca}= 0.0504, K=-0.000162 kJ/μVs.			
H_{Li} = 27.7866	n_{Li}			
	0.005	0.909	-0.024	-0.435
	0.0069	0.8081	0	-0.385
	0.0089	0.7068	-0.005	-0.41
	0.0098	0.6214	-0.011	-0.501
	0.0095	0.5562	-0.007	-0.521
	0.0092	0.5048	-0.034	-0.817
	0.0079	0.4676	0.002	-0.737
	0.0118	0.4214	-0.004	-0.7
	0.0134	0.3789	-0.003	-0.654
	0.0184	0.3328	-0.035	-0.802
	0.021	0.2922	-0.05	-0.994

All the experimental data of mixing enthalpies presented in Fig. 1 were compared with the available literature data [1, 8] and the data calculated with the use of the Miedema model [9, 10].

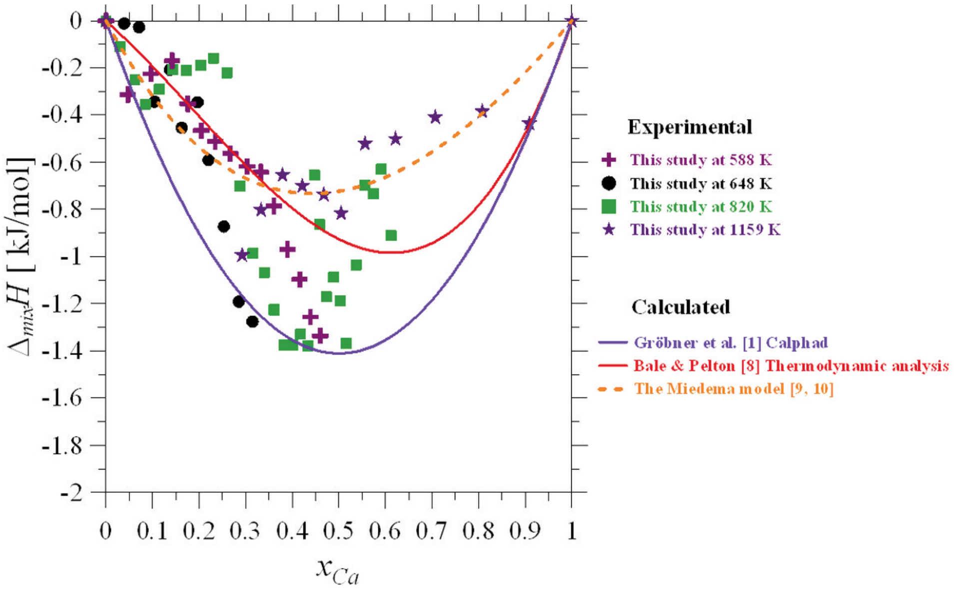

***Figure 1**. Enthalpy of mixing of Ca-Li liquid solutions.*

The measurements of the phase transformations were conducted with the use of DTA measurements for 11 alloys, which were prepared earlier in a glove-box. The obtained results are shown in Table 2 and in Fig. 2, together with the literature data.

Table 2. *Differential Thermal Analysis data for Ca-Li alloys.*

No. of alloy	Alloy composition	Transitions temperatures		
	x_{Li}	K		
1	0.1	503	643	1010
2	0.12	503	643	992
3	0.2	503	643	902
4	0.3	503	643	791
5	0.4	503	643	681
6	0.5	503		580
7	0.67	418		512
8	0.7	418		509
9	0.8	418		490
10	0.9	418		436
11	0.96	418		434

3.2. The CALculation of the PHAse Diagram (CALPHAD)

The thermodynamic model parameters for the binary Ca–Li system were evaluated on the basis of the experimental data of this work with the use of the least-squares optimization module PanOptimizer of the Pandat software [11]. First, the mixing parameters of the liquid phase and then those of the $CaLi_2$ compound were assessed to fit the thermodynamics data [1, 2, and this work] and the invariant reaction liquid↔$CaLi_2$. Next, the mixing parameter of fcc, bcc was evaluated to fit the liquidus lines, followed by the evaluation of the invariant reactions bcc↔fcc+liquid, liquid↔fcc+$CaLi_2$ and liquid↔$CaLi_2$+bcc. At the final stage, the thermodynamic parameters were obtained by simultaneous optimizations of all the mixing parameters. Finally, we verified that no high-T artifact was calculated with our thermodynamic optimized parameters. The problem of limitation of the linear model was described by Kaptay [15]. All the calculated invariant reactions of the Ca–Li binary system are shown in Table 3. The results are presented in Table 4. The Ca–Li phase diagram computed with the use of the current set of thermodynamic parameters is shown in Fig. 2, together with some experimental data. The enthalpies of mixing at 1073 K (from liquid standard states) calculated with the use of the optimized parameters for the Ca–Li liquid phase are shown in Fig. 3, in a comparison with the experimental data from this study. The calculated enthalpy of formation of $CaLi_2$ phase in comparison with experimental data [1, 5] is shown in table 5.

Table 4. *Thermodynamic parameters for phases of the Ca-Li system in J/mol of at.*

Liquid	$L^{(0,Liquid)}_{(Ca,Li)} = -7212.22 + 0.0546 * T$
bcc	$L^{(0,bcc)}_{(Ca,Li)} = 6026.51 - 0.1949$
fcc	$L^{(0,fcc)}_{(Ca,Li)} = 6387.42 - 0.1551$
$CaLi_2$	$G^{(CaLi_2)}_{(Ca,Li)} = -2900 + 0.3935 \cdot T +$ $+0.333333 \cdot G_{Ca}{}^{(0,fcc)} + 0.666667 \cdot G_{Li}{}^{(0,bcc)}$

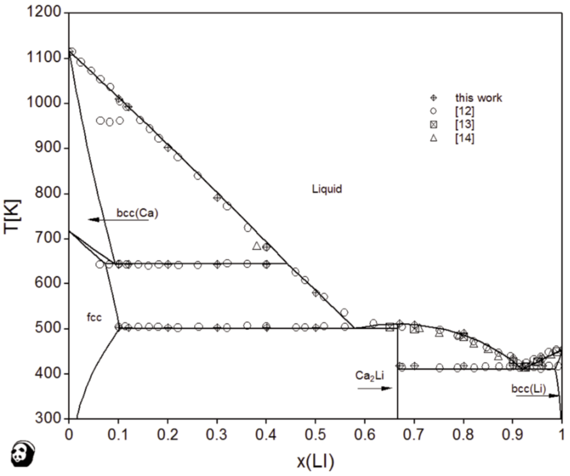

Figure 2. *Calculated phase diagram of the Ca–Li system in the present study along with the experimental data [12-14].*

The experimental data of the phase transformations temperature measured in this study show an excellent agreement with those from the earlier studies, and the observed differences are not

Table 3. *Calculated invariant reactions in the Ca–Li binary system.*

Reaction	Reaction type	Temperature K	x_{Li}		
bcc(Ca) -> fcc + Liquid	Catatectic	644	0.073	0.093	0.442
Liquid -> fcc + $CaLi_2$	Eutectic	501	0.579	0.103	0.667
Liquid -> $CaLi_2$ +bcc(Li)	Eutectic	410	0.92	0.667	0.985
Liquid -> $CaLi_2$	Congruent	510		0.667	

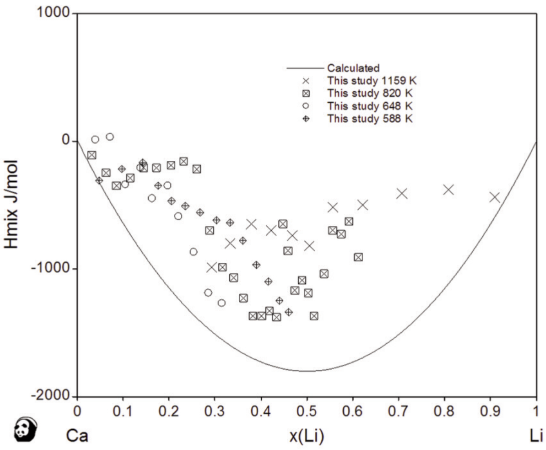

Figure 3. *Calculated enthalpy of mixing of the Ca–Li liquid phase at 973 K with the experimental data obtained in this study.*

Table 5. *Calculated formation enthalpy of the* $CaLi_2$ *phase compared with the experimental data [1, 5].*

Phase	Temperature K	Experimental		This work
		[kJ/g-atom]		[kJ/g-atom]
$CaLi_2$	979	-4.5±1.5	[1]	-2.9
	1020	-2.7±0.6	[5]	
	1126	-2.9±0.9	[5]	

higher than 5 K. Also, the agreement of the phase diagram calculated with the experimental data is satisfactory and the observed maximal deviations between the experimental and the calculated data are a bit lower than 10 K, especially for the alloys of the Li concentration higher than that in the $CaLi_2$ compound (except for 3 points for Ca-rich solutions between the liquidus and the solidus).

Measurements of the activity of metals should be undertaken in the future to update the thermodynamic properties of the Ca-Li liquid and solid solutions elaborated in this study based on the DTA data and only the calorimetric data.

4. Summary

The studies of the mixing enthalpy change showed that it characterizes in negative deviations from the ideal solutions. The observed maximal values are lower than -1.5 kJ/mol for the alloy concentration near the $CaLi_2$ intermetallic phase and the maximal differences between the experimental data are lower than 1 kJ/mol for the alloys in the central composition range.

The calculated values of the mixing enthalpy change of this work (Eq. 7) are more exothermic in comparison to those by Groebner at al. and are comparable to those by Bale and Pelton, which are, however, asymmetric, with the minimum located almost for x_{Ca} =~ 0.62.

The values of $\Delta_{mix}H$ calculated by the Miedema model are more exothermic in comparison with the data of Groebner at al., this study (except for the alloys with a high concentration of Li) and those proposed by Bale and Pelton (except for the solutions of x_{Li} higher than 0.5).

Acknowledgements

Research supported by the Polish Ministry of Science and High Education (Project No. N N508 379235).

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