Experimental and Theoretical Contributions to the Al-Li-Si System

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ABSTRACT

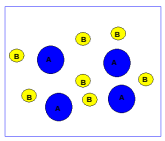
As a part of a on-going work on modeling the hydrogen solubility in aluminium alloys, the parameters of the thermodynamic model used to describe the energetic behaviour of the different phases present in the Al-Li-Si system were reassessed. The modified quasichemical model is used for the liquid solution in order to better fit the partial heat of mixing and the activity of the different solution components. Short-range order observed in the liquid binary Li-Si subsystem justifies the necessity to reassess the thermodynamic model, as presented in this work. The lack of some thermodynamic experimental data for the solid ternary compounds of the Al-Li-Si system is partially resolved by drop calorimetry measurements and ab initio calculations: data that were used with other reported experimental data to obtain the thermodynamic description of the Al-Li-Si system presented in this work.

THERMODYNAMIC MODELING (BINARY SYSTEMS)

The Gibbs energy of all phases present in the Al-Li-Si systems has to be describe by an appropriate thermodynamic model. Short-range order (***SRO**) observed in the liquid solution has an important impact on the entropic contribution to the Gibbs energy of the solution. This is taken into account by the Modified Quasichemical model for ordered liquid phases.

All available thermodynamic data (heat of mixing, emf, partial pressure, liquidus, etc.), including calorimetric and ***ab initio*** calculations performed in this work, were used to obtain the best set of thermodynamic parameters for the different phases.

*SRO



For a liquid phase made of A and B atoms, the Quasichemical first nearest neighbour pair reaction is :

[A-A] +[B-B]↔ 2 [A-B]

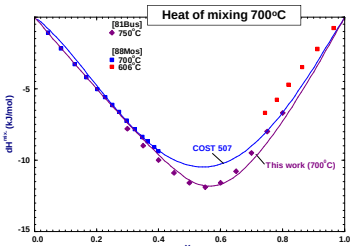
If $\Delta g_{A-B} << 0$ → SRO

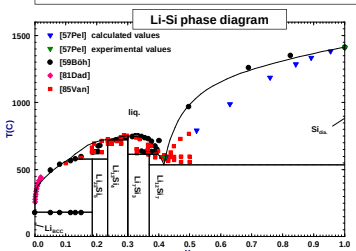
Modified Quasichemical model (liquid alloy)

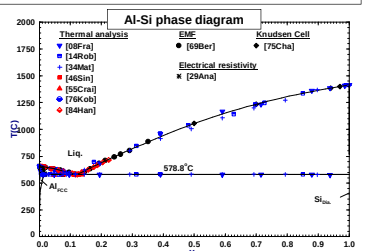
$$G = \left(n_A g^o{}_A + n_B g^o{}_B\right) - T\Delta S^{config} + \frac{n_{A-B}}{2}\Delta g_{A-B}$$

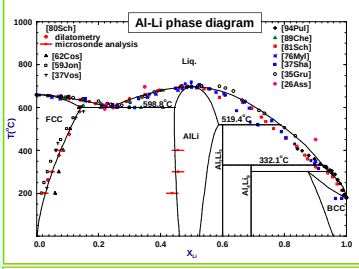
$$\Delta S^{config} = -R\left[n_A \ln(X_A) + n_B \ln(X_B)\right] - R\left[n_{AA}\ln\left(\frac{X_{AA}}{X_A^2}\right) + n_{BB}\ln\left(\frac{X_{BB}}{X_B^2}\right) + n_{AB}\ln\left(\frac{X_{AB}}{2X_A X_B}\right)\right]$$

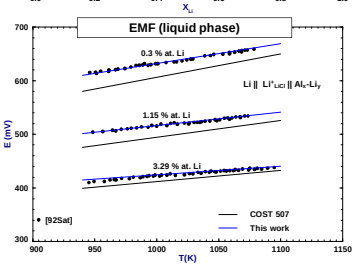
$$\Delta g_{A-B} = \Delta g^0_{A-B} + \sum_{j\geq 1} g^{i0}_{A-B} X^{\,i}_{A-A} + \sum_{j\geq 1} g^{0j}_{A-B} X^{\,j}_{B-B}$$

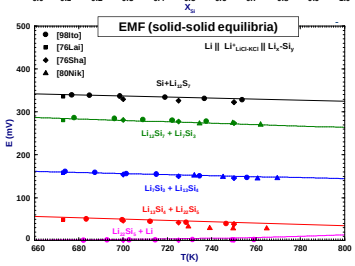


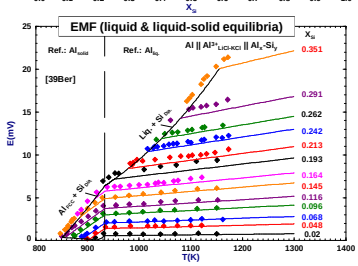








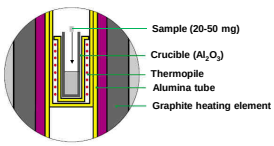




INVESTIGATION OF TERNARY INTERMETALLIC COMPOUNDS

Kevorkov [2001] investigated phase equilibria in the Al-Li-Si system by DTA and XRD analysis. In the present work, calorimetric measurements and ***ab initio*** calculations involving ternary Al-Li-Si compounds have been performed to complement the results of Kevorkov [2001].

ISOTHERMAL DROP CALORIMETRY (720ºC)



LEGEND		
f(t)	= thermopile signal	[=] mV
m	= sample mass	[=] mg
(t_1-t_0)	= dissolution duration	[=] sec
M	= sample molar weight	[=] mg/mol

The heat of formation of ternary intermetallic compounds are essential thermodynamic data needed for the modeling of Al-Li-Si system. Isothermal drop calorimetry is a first approach to obtain this thermodynamic property.

Step 1: Calibration (pur Al^{298K}_{solid} in Al^{993K}_{liquid})

$$Al^{298K}_{solid} \rightarrow Al^{993K}_{liquid}$$

$$K^{calibration} = \frac{1}{\int_{t_0}^{t_1} \frac{f(t)dt}{m}} * \Delta\underline{h}^{transformation} [=] \frac{J}{mV*\sec}$$

$$\Delta\underline{h}^{transformation} = \int_{298K}^{T^{fusion}_{Al}} C_p^{Al,solid} dT + \Delta h^{fusion}_{Al} + \int_{T^{fusion}_{Al}}^{993K} C_p^{Al,liquid} dT [=] \frac{J}{mg}$$

Step 2: Dissolution of the sample

$$Sample^{298K}_{solid} \rightarrow Sample^{993K}_{in\ Al}$$

$$Q^{dissolution} = \int_{t_0}^{t_1} \frac{f(t)dt}{m} * K^{calibration} * M [=] \frac{J}{mol}$$

Step 3: Heat of formation calculation

$$-\Delta h^0_{formation} = \Delta h^0_{decomposition} = Q^{dissolution}_{Al_xLi_ySi_z} - xQ^{dissolution}_{Al\ in\ Al} - yQ^{dissolution}_{Li\ in\ Al} - zQ^{dissolution}_{Si\ in\ Al} [=] \frac{J}{mol}$$

AB INITIO CALCULATIONS

Since experimental investigations are difficult to realize for the Al-Li-Si system due to:

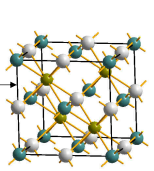
- ❑ *Volatilization of Li during the intermetallic synthesis*
- ❑ *High reactivity of Li with O_2*
- ❑ *Difficulty to obtain low PO_2 in the drop calorimeter*
- ❑ *Difficulty to dissolve the intermetallics (low density compared to Al)*

Ab initio calculations are a powerful tool to determine the heat of formation of ternary compounds. By assuming a negligible contribution of the heat capacity from 0K to 298K to the heat of formation, we can calculate this property as followed:

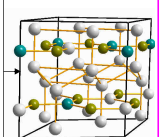
$$\Delta h^0_{formation} = \frac{E_{Al_xLi_ySi_z} - xE_{Al^{FCC}} - yE_{Li^{BCC}} - zE_{Si^{Dia}}}{x+y+z} [=] \frac{eV}{atom}$$

$E_{Al(FCC)}$	= -3.69 eV/atom
$E_{Li(BCC)}$	= -1.89 eV/atom
$E_{Si(Dia)}$	= -5.42 eV/atom

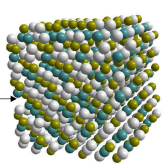
AlLiSi
Space group: F-43m
Number of atoms per cell: 12
Heat of formation: -0.2488 eV/atom
-72kJ/mol AlLiSi
Vs
-80kJ/mol AlLiSi (calorimetry)



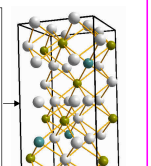
$Al_3Li_{15}Si_6$
Space group: $P6_3/m$
Number of atoms per cell: 24
Heat of formation: -0.2817 eV/atom
-652kJ/mol $Al_3Li_{15}Si_6$



$Al_3Li_7Si_4$
Space group: F-43m
Number of atoms per cell: 112
Heat of formation: -0.2546 eV/atom
-344kJ/mol $Al_3Li_7Si_4$

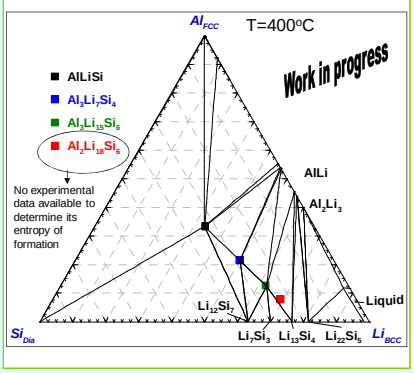


$Al_2Li_{18}Si_6$
Space group: $I4_1/amd$
Number of atoms per cell: 26
Heat of formation: -0.1790 eV/atom
-449kJ/mol $Al_2Li_{18}Si_6$



THERMODYNAMIC MODELING

The next step of the thermodynamic optimization of the Al-Li-Si system is to interpolate the binary thermodynamic parameters of the liquid, FCC and BCC phases in the ternary system by appropriate techniques. Small ternary interactions parameters can be added if necessary.



CONCLUSION

The Modified Quasichemical model was used to describe the energetic thermodynamic behaviour of the liquid phase.

Calorimetric measurements were made to obtain the heat of formation of AlLiSi intermetallics.

The heat of formation of all ternary intermallic compounds present in the Al-Li-Si system were obtained by ***Ab initio*** calcultations.

DTA analysis in the ternary field of composition of the Al-Li-Si system are minimaly required to complete the thermodynamic modelling of this system. Integration of the binary interactions in the liquid phase between hydrogen and the three elements is straightforward. Few hydrogen solubility measurements in liquid Al-Li-Si will be required to test and adjust the thermodynamic model of the liquid phase.

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