Thermodynamic Modeling of the Mg-Li-Al-Si System

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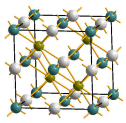
ABSTRACT

Mg alloys are promising materials for the automotive industry. The two-phase region of the Mg-Li system is of particular interest since the presence of both HCP and BCC phases exhibit better formability than the HCP phase alone. Al-Li alloys are of great interest for aeronautic applications because of their low specific weight, high stiffness and high strength. The chemical reactivity of lithium in the fabrication of the alloys influences the production techniques and the cost of the final product. Another concern is the thermal stability of certain phases when subjected to a temperature gradient induced upon heating or cooling during use of these products. Thermodynamic models describing the Gibbs free energy of the different phases of the Mg-Al-Li-Si are crucial for a better understanding of the various chemical phenomena observed in Mg-Al-Li-Si alloy production, shaping and application.

THERMODYNAMIC MODELING

Phases

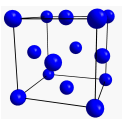
Stoichiometric Compounds



Ex.: AlLiSi (F-43m)

Binary Compounds	Ternary Compounds
Li_7Si_3	$Al_{53}Mg_{14}Li_{33}$
$Li_{13}Si_4$	Li_2MgSi
$Li_{22}Si_5$	$Li_{12}Mg_3Si_4$
$Li_{12}Si_7$	Li_8MgSi_6
Al_2Li_3	$Li_7Al_2Si_4$
Al_4Li_9	$Li_{18}Al_2Si_6$
$Al_{30}Mg_{23}$	$Li_{15}Al_3Si_6$
$Al_{140}Mg_{89}$	

Solid Solutions



Ex.: Al-FCC (Fm-3m)

- Mg-HCP
- Li-BCC
- Al-FCC
- Si-Diamond
- Mg_2Si dissolving Li
- γ phase ($Al_{12}Mg_{17}$)
- AlLi

Crystallographic data

Model

Stoichiometric Compound Model

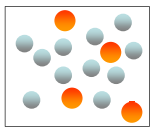
$$G^{o}(T) = \Delta H^{o}_{298.15K} - TS^{o}_{298.15K} + \int_{298.15K}^{T} C_p dT - T\int_{298.15K}^{T} \frac{C_p}{T} dT$$

Compound Energy Formalism

$$Ex.: \ (A,B,....)^{I}_{a}(X,Y,....)^{II}_{b}$$

$$G = \sum_m \sum_n y^{I}_m y^{II}_n G^{o}_{mn} + aRT\left(\sum_m y^{I}_m \ln\left(y^{I}_m\right)\right) + bRT\left(\sum_n y^{II}_n \ln\left(y^{II}_n\right)\right) + \sum_{i,j,k} y^{I}_i y^{I}_j y^{II}_k \sum_q L^{(q)}_{i:j:k}\left(y^{I}_i - y^{I}_j\right)^q + \sum_{i,j,k} y^{I}_i y^{II}_j y^{II}_k \sum_q L^{(q)}_{i:j:k}\left(y^{II}_j - y^{II}_k\right)^q$$

Liquid Solution



In multicomponent liquid metallic solutions, some nearest-neighbor interactions can be strong enough to modify the configuration of the liquid (short-range-ordering).

The thermodynamic model must take this effect into account in the configurational entropy expression of the liquid phase.

Modified Quasichemical Model – Pair Approximation

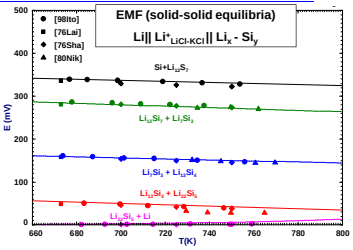
$$G = \left(n_A g^{o}_A + n_B g^{o}_B\right) - T\Delta S^{config} + \frac{n_{A-B}}{2}\Delta g_{A-B}$$

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

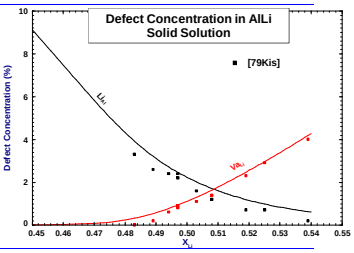
$$\Delta g_{A-B} = \Delta g^{0}_{A-B} + \sum_{i\geq 1} g^{i0}_{A-B} X^{i}_{A-A} + \sum_{j\geq 1} g^{0j}_{A-B} X^{j}_{B-B}$$

Thermodynamic data

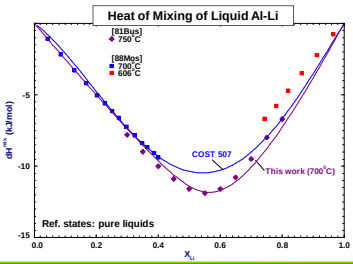
- Heat of formation
- Heat capacity
- EMF
- ab initio calculations
- Phase diagram data (liquidus, eutectic, XRD)



- Heat of mixing
- EMF
- Defect concentrations
- XRD analysis
- Microprobe analysis
- Phase diagram data
- Vapor pressure

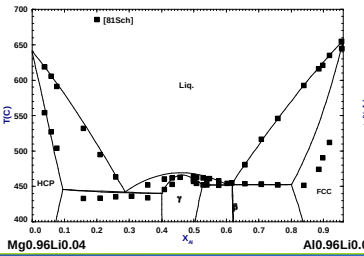


- Heat of mixing
- EMF
- Phase diagram data
- Vapor pressures
- DTA

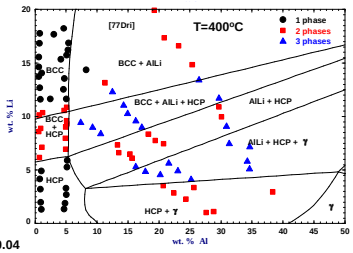


VALIDATION OF THE TERNARY MODEL

Mg-Li-Al

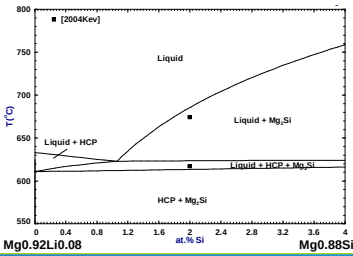


Mg0.96Li0.04

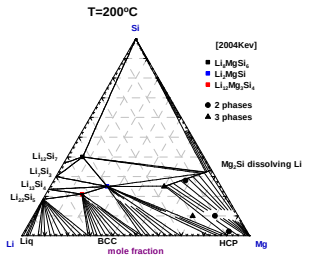


Al0.96Li0.04

Mg-Li-Si



Mg0.92Li0.08

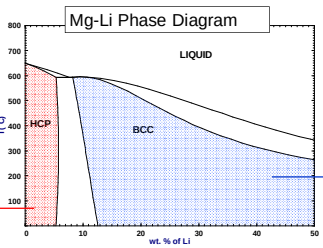


Mg0.88Si0.04Li0.08

APPLICATION OF THE DATABASE

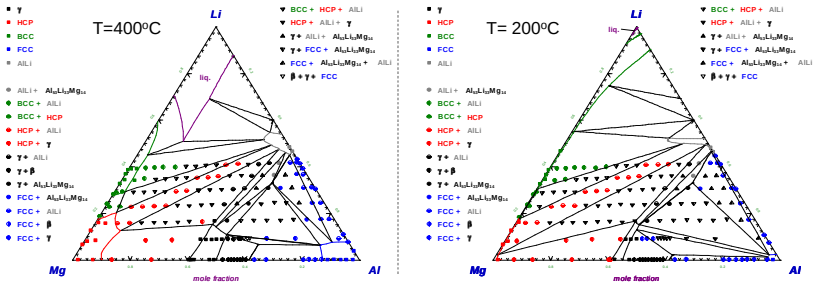
I) Mg-Li Alloy Design

Moderate strength
Low formability
Good creep resistance



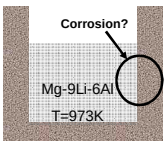
Good ductility
Low strength
Low creep resistance

Effect of Al Additions in Mg-Li alloys

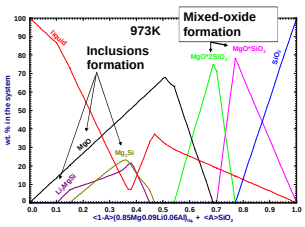


II) Mg-Li-Al Alloy Elaboration

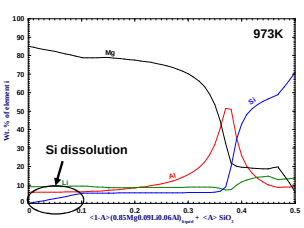
Casting of Mg-Li-Al alloys in sand molds (SiO_2)



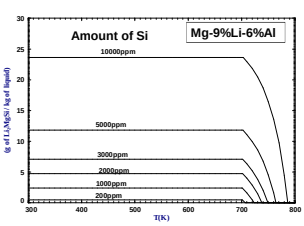
Reaction between the liquid and SiO_2



Evolution of the Composition of the Liquid Alloy



Effect of Si in Mg-Li-Al Alloys during Equilibrium Cooling



Scheil Cooling of a Mg-Li-Al Alloy