SPP 2315 EnAM
Engineered Artificial Minerals

DFG

A01: Thermodynamic database development for the Li_2O-Al_2O_3-SiO_2-MnO_x system: application for Li recycling

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Overview

The importance to recycle and recover valuable transition metals (such Co, Ni) and Li increased in the recent years [1]. Several metallurgical methods have been investigated to obtain transition metals from their respective oxides after reduction slag separation and crystallization processes. In this process Li_2O reacts with slag forming $LiAlO_2$ or spinel solid solution. In this context, the development of thermodynamic database for the Li_2O-MnO_x-SiO_2-Al_2O_3 is an important step to create a tool to optimize conditions, at which maximal separation of Li_2O can be obtained. Thus, investigations of pseudo-ternary and pseudo-binary systems among these oxides are necessary to provide some data and contribute to improve the processing conditions.

Methods

Experimental procedures

Samples will be prepared using solid state reaction methods and sol-gel technique. For solid state reaction Li_2CO_3, Al_2O_3 (corundum), SiO_2 (amorphous), MnO/$MnCO_2$ will be used. In case of applying sol-gel method tetraethoxysilan, $LiNO_3$, $Mn(NO_3)_2$, $Al(NO_3)_3$ will be used following experimental procedure of Sycheva et al. [2]. The Li-acetate and Mn-acetate will be used in case of synthesis in the Li_2O-MnO_x system, according to route of Cupid et al. [3]. Binary and ternary compounds will be synthesized for heat capacity measurements. The samples will be characterized using XRD and scanning electron microscopy (SEM/EDX). Also, the temperatures of some invariant reactions will be experimentally determined using DTA.

Thermodynamic modeling

The thermodynamic parameters of the Li_2O-MnO_x-SiO_2-Al_2O_3 system will be critically optimized based on the Compounds Energy and Formalism (CEF). This formalism allows an adequate description of the thermodynamic properties of each phase, taking the crystal structure into account. The two-sublattice partially ionic liquid model will be adopted for the liquid description. Optimization of model parameters will be performed using PARROT module, while the phase diagrams will be calculated using the POLY-3 of the Thermo-Calc software.

Preliminary results

Phase diagrams of Li_2O-Al_2O_3 system (Figure 1a) and Li_2O-SiO_2 system (Figure 1b) have been thermodynamically optimized by our research group to provide consistent data for the future assessment of the Li_2O-Al_2O_3-SiO_2 system. Phase diagrams of MnO-Al_2O_3-O_2 system were calculated based on thermodynamic description reported by Ilatovskaia and Fabrichnaya [4] at $P(O_2) = 1 \cdot 10^{-5}$ bar (Figure 1c) and $P(O_2) = 0.21$ bar. Considering the literature data, the

preliminary thermodynamic description of the MnO-SiO_2 system was derived and the phase diagram was calculated (Figure 1d).

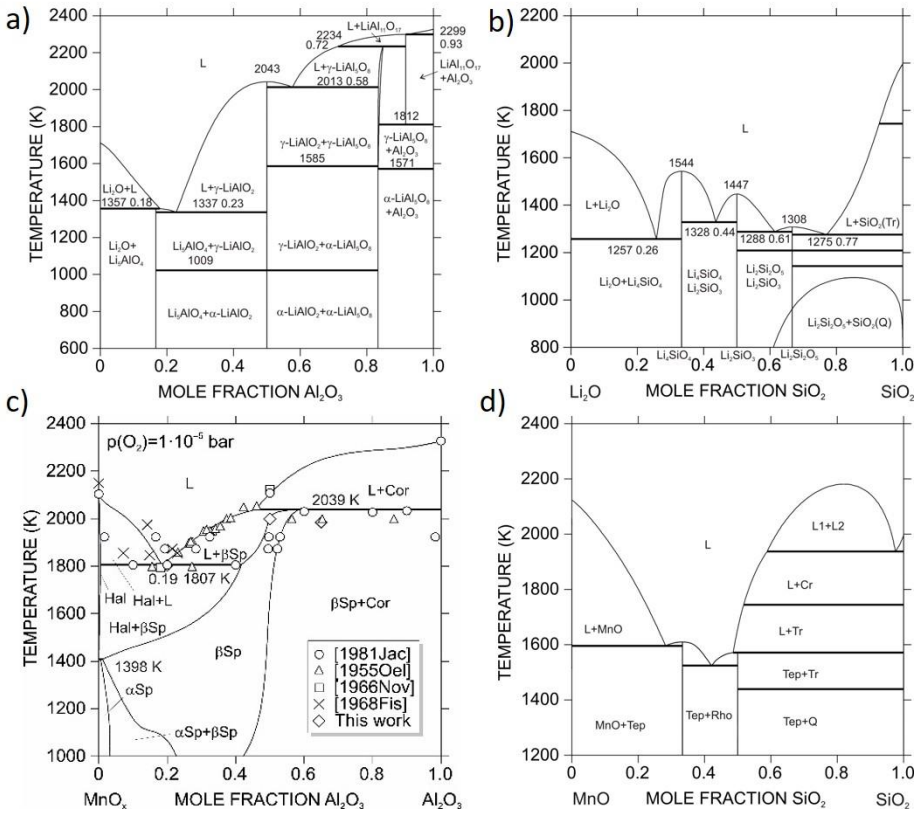

Figure 1: Calculated phase diagrams of the: (a) Li_2O-Al_2O_3 system, (b) Li_2O-SiO_2 system, (c) MnO_x-Al_2O_3 system and (d) MnO-SiO_2 system.

References

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[2] D.M. Cupid, T. Lehmann, T. Bergfeldt, H. Berndt, H.J. Seifert, Investigation of the lithium rich boundary of the Li1+xMn2-xO4 cubic spinel phase in air. J. Mater. Sci. 48 (2013) 3395-3403.

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