ASSESSMENT OF THERMODYNAMIC PROPERTIES OF HYDRIDES

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Hydrides are studied for various applications, including hydrogen storage, electrochemical energy storage, heat storage and, more recently, CO_2 capture/conversion [1]. A full picture of the thermodynamic properties of a system can be obtained by the CALPHAD approach [2]. The goal is to obtain a description of the dependence of the free energy of all phases on temperature, pressure and composition. The optimized parameters can be obtained with a least square procedure, starting from experimental values of existing phase diagrams and thermodynamic data. In absence of experimental information, the output of quantum mechanical models can be used. In several cases, it is observed that stable phases cannot be obtained experimentally during phase transformations, so that metastable phase diagrams have to be considered.

Examples will be given for Mg-based alloys, including MgH_2, $LaMg_2Ni$ and Mg-Al compounds. Paraequilibrium conditions will be shown for $LaNi_{5-x}Al_x$-H system ($0 \leq x \leq 1$) [3]. Assessed phase diagrams will be shown for pure borohydrides (i.e. $NaBH_4$, $LiBH_4$, $Mg(BH_4)_2$ and $Ca(BH_4)_2$) [4,5]. From available database, the effect of anion and cation substitution in borohydrides has been considered and an estimation of interaction parameters has been obtained. Examples will be provided for $LiBH_4$-LiCl [6] and $Mg(BH_4)_2$-$Zn(BH_4)_2$ [7] systems. The description of thermodynamic properties of the liquid phase in hydride systems remains a big challenge, because of lacking of experimental data. Examples of calculated phase diagrams will be provided for eutectic mixtures (e.g $LiBH_4$-$NaBH_4$). A description of thermodynamic properties will be also shown for $Li_4(NH_2)_3(BH_4)$ and $Li_2(NH_2)(BH_4)$ compounds, allowing the assessment of the $LiBH_4$-$LiNH_2$ phase diagram [8]. Developed assessments underlined inconsistencies among experimental results, driving the selection of the most reliable data.

References

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