Thermodynamic modelling of ortho-equilibrium and para-equilibrium in the $LaNi_{5-x}Al_x$-H system

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For hydrogen storage purposes, a deep understanding of thermodynamic properties for the investigated material is required. Despite the general lack of reliable experimental data, the assessment of metal-hydrogen systems according to the Calphad approach can provide a consistent thermodynamic description, able to reproduce and predict the overall temperature-pressure-composition behaviour [1].

In this work, the $LaNi_{5-x}Al_x$-H system was investigated, and an extensive experimental and theoretical analysis was performed. Samples with different Al contents (x=0, 0.2, 0.4, 0.6 and 0.8) have been prepared by arc melting. PCI (Pressure Composition Isotherm) at 25, 40, 60, 80 and 100 °C have been measured on as-prepared and well annealed samples. Following the assessment of the La-Ni-H system [2], a three sublattices model $(La)(Ni,Al)_5(H,Va)_7$ was selected for the hydride phase. First principles calculations have been performed to estimate the formation energies of metastable end-members ($LaAl_5$ and $LaAl_5H_7$). Experimental and theoretical information, together with available literature data, was used as an input for a thermodynamic assessment performed by Thermocalc.

Calculations have been performed considering both ortho-equilibrium and para-equilibrium conditions [3]. The observed slope in experimental PCI plateaux for as-prepared samples is not predicted for para-equilibrium conditions, but it is due to compositional inhomogeneities. The comparison of calculated PCI with experimental results obtained for annealed samples confirms that, due to the different diffusivity of metals and hydrogen, para-equilibrium conditions are present.

References

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