STRUCTURAL AND THERMODYNAMIC CHARACTERISTICS OF LaNi$_5$Sn- and NdNi$_5$Sn- BASED INTERMETALLIC HYDRIDES

Masashi Sato, Marit Stange and Volodymyr Yartys[*]

Institute for Energy Technology, Instituttveien 18, P.O.Box 40, Kjeller, N-2007, Norway

INTRODUCTION

The ternary intermetallic LaNi$_5$Sn is a constituent of the pseudobinary LaNi$_{5-x}$Sn$_x$ (x = 0–0.4) compounds, which are applied in the Ni-MH batteries [1]. The aim of this work was to characterise the LaNi$_5$Sn-H and related NdNi$_5$Sn-H systems by structural and thermodynamic studies.

EXPERIMENTAL PROCEDURES

The RNi$_5$Sn (R = La, Nd) samples were prepared by Ar arc melting using high purity constituent elements. The alloys were annealed at 773K for 4 weeks. The hexagonal CeNi$_5$Sn type structures were confirmed by Powder XRD (Siemens D5000, Cu Kα_1 radiation). The lattice parameters agree well with the reference data [2].

High resolution synchrotron X-ray powder diffraction pattern data for LaNi$_5$Sn and its hydride were collected with a wavelength of λ = 0.7250(2) Å at ESRF, Grenoble, France using a hydrogenation setup for the *in situ* studies of the absorption-desorption processes in hydrogen gas. Neutron scattering experiments were carried out at ILL, Grenoble, France. Powder diffraction patterns were recorded under D$_2$ gas with p = 3.1 MPa at 298 K, using a wavelength of λ = 2.524 Å. P-C isotherms for H$_2$ absorption-desorption were determined volumetrically, using Sieverts' type apparatus. The measurements were made at temperatures 258–423 K, and at pressures in the range from 10^{-3} to 2.5 MPa.

RESULTS AND DISCUSSIONS

Clear plateaux pressure could be reproducibly measured between approximately [H]/[LaNi$_5$Sn] = 0.3 and 1.4, indicating the coexistence of the solid solution and hydride phase as shown in Fig.1. The H solubility limit is drastically decreased by a transition from AB$_5$ to AB$_5$X type compounds.

Earlier Luo et al. observed that the hysteresis in LaNi$_{5-x}$Sn$_x$ is reduced from ~308 J/mol H in LaNi$_5$ to ~199 J/mol H in LaNi$_{4.8}$Sn$_{0.2}$ at room temperature [3,4]. Calculated hysteresis in the LaNi$_5$Sn-H system, 112 J/mol H at 298 K, is significantly smaller than for the LaNi$_{5-x}$Sn$_x$-H systems. A similar reduction of hysteresis was also observed in the Nd-based intermetallic hydrides; from 568 J/mol H for NdNi$_5$-H [8] to 198 J/mol H for NdNi$_5$Sn-H. This may indicate that a partial substitution of Ni by Sn reduces markedly the hysteresis effects and shows an intrinsic role of Sn additions. The effect of Sn is very specific since in a similar system LaNi$_5$In-H the hysteresis is much higher (770 J/mol H at 292 K, according to data presented in [6]) and even exceeds the value for the LaNi$_5$-H system.

The changes of the partial molar enthalpy and entropy during the decomposition of hydrides are calculated from the van't Hoff plot and are equal to −18.5 kJ/mol H and −53.7 J/(K mol H) for LaNi$_5$Sn-H, and −18.5 kJ/mol H and −51 J/(K mol H) for the NdNi$_5$Sn-H systems, respectively.

The obtained thermodynamics data and reference data are summarised in Table 1. With increasing Sn contents in LaNi$_{5-x}$Sn$_x$ compounds, the enthalpy decreases. On a transition to LaNi$_5$Sn, the stability of the hydride decreases. Entropy changes for LaNi$_5$Sn are similar to the values observed for the LaNi$_{5-x}$Sn$_x$ compounds. Decrease of the stability of the LaNi$_5$Sn-based hydride may be related to the absence of La$_2$Ni$_2$ interstitial sites in the structure (the most attractive for hydrogen in the AB$_5$-based hydrides), in contrast to the LaNi$_5$ and LaNi$_{5-x}$Sn$_x$ intermetallics. On the other hand, the situation for the Nd-containing compounds is quite different. Here the enthalpy changes in case of the NdNi$_5$Sn-H system are much higher compared to the NdNi$_5$ and NdNi$_{5-x}$Sn$_x$ compounds indicating a big increase in the stability of the NdNi$_5$Sn-based hydride.

The lattice parameters were measured under D$_2$ pressure of 3.1 MPa at 298 K, allowing to achieve a D/LaNi$_5$Sn ratio of 3.0. The lattice expansion due to D$_2$ absorption in LaNi$_5$Sn is rather small: $\Delta a/a$ = 0.69%, $\Delta c/c$ = 0.60% and $\Delta V/V$ = 1.99% where a

---

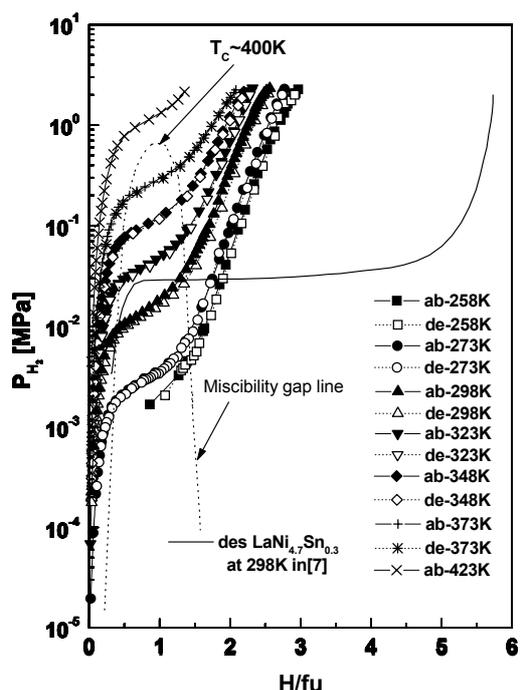and c are lattice parameters and V is the volume of the unit cell.

Fig.1. P-C-T dependences in the LaNi$_5$Sn-H system. A simple lattice gas model calculation yields that LaNi$_5$Sn hydride is stable up to around 400K.

Table.1 Thermodynamics data of H$_2$ absorption in LaNi$_{5-x}$Sn$_x$ (x = 0–0.4), LaNi$_5$Sn and NdNi$_5$Sn

Alloy	ΔH_H [kJ/mol H]	ΔS_H [J/(K mol H)]	Ref.
LaNi$_5$	-15.9	-54.0	[5]
LaNi$_{4.8}$Sn$_{0.2}$	-17.0	-54.0	[4]
LaNi$_{4.7}$S$_{0.3}$	-18.3	-56.3	[3]
LaNi$_{4.6}$Sn$_{0.4}$	-19.0	-54.3	[4]
LaNi$_5$Sn	-18.5	-53.7	This work
LaNi$_5$In	-18.0*		[6]
NdNi$_5$	-14.0	-58.9	[8]
NdNi$_{4.8}$Sn$_{0.2}$	-12.9	-51.3	[8]
NdNi$_{4.6}$Sn$_{0.4}$	-13.2	-49.7	[8]
NdNi$_5$Sn	-18.5	-51.9	This work

 *Estimated from ref.[6]

CONCLUSIONS

The great benefit of the Sn-containing compounds is in reducing the hysteresis effects during H absorption and desorption. The differences in the thermodynamic behaviour of LaNi$_5$Sn-based hydrides seem to be caused by the crystal structure changes on a transition from AB$_5$ to AB$_5$X compounds. The volume change by H uptake in LaNi$_5$Sn is rather small and is in agreement with a reduced H storage capacity of LaNi$_5$Sn in comparison with the LaNi$_{5-x}$Sn$_x$ intermetallics.

REFERENCES

1. J.M.Joubertet et al., J.Alloys and Comp., 293-295 (1999) 124.

2. R.V.Skolozdra, ed.by K.A.Gschneidner,Jr. and L.Eyring, Hand book on the Physics and Chemistry of Rare Earths, Vol.24, 1997,p 436, Chapter 164.

3. S.Luo et al., J.Alloys and Comp., 267 (1998) 171.

4. S.Luo et al., J.Alloys and Comp., 330-332 (2002) 531.

5. H.H.van Mal et al., J.Less-Common Met.,35 (1974) 65.

6. I.I.Bulyk, Int.J.Hydrogen Energy, 24 (1999) 927.

7. O.Yu.Khyzhum et al., J.Alloys and Comp., in press.

8. Y.Takaguchi and K.Tanaka, J.Alloys and Comp., 297 (2000) 7.