ELSEVIER

Journal of Alloys and Compounds 253–254 (1997) 295–297

Journal of
ALLOYS
AND COMPOUNDS

In situ neutron diffraction study of solid gas desorption of non-stoichiometric AB_5 type hydrides

M. Latroche[a,*], P.H.L. Notten[b], A. Percheron-Guégan[a]

[a]LCMSTR-UPR209-CNRS, 1 Pl. A. Briand, 92195 Meudon CEDEX, France
[b]Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

Abstract

In situ neutron diffraction studies during in beam solid gas desorption have been carried out on both stoichiometric $LaNi_4CuD_y$ and non-stoichiometric $LaNi_5CuD_y$ deuterides. The first compound exhibits a two phase behaviour typical of the β to α transformation in agreement with the plateau pressure observed in the pressure composition isotherm curve. The second one shows only one phase typical of a solid solution. The continuous cell volume variation observed for the non-stoichiometric $LaNi_5Cu$ deuteride is assumed to be the origin of its better cycle life when used as negative electrode material in NiMH batteries.

Keywords: In situ neutron diffraction; $LaNi_4CuD_y$; AB_5-type hydrides

1. Introduction

AB_5-type hydrides have attracted serious interest in the last few years due to their widespread application in rechargeable nickel metal hydride (NiMH) batteries. The breakthrough of this new battery type was accomplished by the discovery that the electrochemical long-term cycling stability of $LaNi_5$ could be substantially improved by replacing part of B-type atoms (Ni) by other transition metals within the AB_5 stoichiometry [1]. Recently, it was shown that the electrochemical cycling stability can also be improved by employing non-stoichiometric AB_{5+x} compounds [2–6]. It has been shown by in situ XRD measurements under hydrogen that incorporation of copper alters the hydride-formation mechanism and, in this way, positively influences the long-term cycling stability [4,5]. As it is already known that this replacement induces an increase of the equilibrium pressure with a modification of the shape of pressure–capacity curve [5,7], such a substitution must be carefully investigated to check its influence on the material performance. The aim of this neutron diffraction study was to perform an in situ experiment to get detailed information about the dynamics of the transformation during deuterium desorption. Crystallographic information obtained from the refined patterns have been associated with the thermodynamic ones obtained from the solid–gas desorption experiments. We will compare in this paper the crystallographic and thermodynamic behaviours of stoichiometric $LaNi_4Cu$ deuteride versus non-stoichiometric $LaNi_5Cu$.

2. Experimental details

The samples were prepared as described in Ref. [4]. Stoichiometry and homogeneity were controlled by X-ray diffraction, metallographic examination and microprobe analysis. The XRD patterns were indexed in the $CaCu_5$ hexagonal cell. Results are summarized in Table 1.

As neutron diffraction experiments necessitate the use of deuterium instead of hydrogen which induces large incoherent scattering, Pressure–Composition–Temperature (PCT) diagrams were characterised with deuterium gas in

Table 1
Characterisation of alloys

Compounds	Microprobe analysis	Cell parameters	
		a	*c* (Å)
$LaNi_4Cu$	$La_{1.00(1)}Ni_{4.01(2)}Cu_{0.99(1)}$	5.038(1)	4.008(1)
$LaNi_5Cu$	$La_{1.00(1)}Ni_{4.8\ 4(1)}Cu_{0.95(2)}$	4.988(1)	4.033(1)
	+ traces of $Ni_{79}Cu_{21}$	3.545(1)	

---

[*] Corresponding author. LCMSTR-UPR209-CNRS, 1 Pl. A. Briand, 92195 Meudon Cedex, France.

PII S0925-8388(96)02899-X

order to detect any isotopic effects. About 0.5 g of samples were ground mechanically under controlled atmosphere and activated five times. Then the absorption isotherm curves were determined from these powders by pressure variation measurements using calibrated and thermalised volumes. Neutron diffraction (ND) measurements were performed on the position sensitive detector (PSD) diffractometer D1B at Institut Laue-Langevin. The 400 PSD cells cover the range $28° < 2\theta < 108°$ in 2θ and the high flux reactor allows to record a powder diffraction patterns each 10 min. The wavelength was set to 2.52 Å and about 10 g of sample, contained in a silica tube were placed into the neutron beam. This sample holder was connected to a volumetric device equipped with pressure gauges that allows to measure the amount of deuterium removed from the sample. Desorption process was obtained by an incremental method. The position, intensity and width of the diffraction lines of each phase were obtained by a fitting procedure using the program FULLPROF [8].

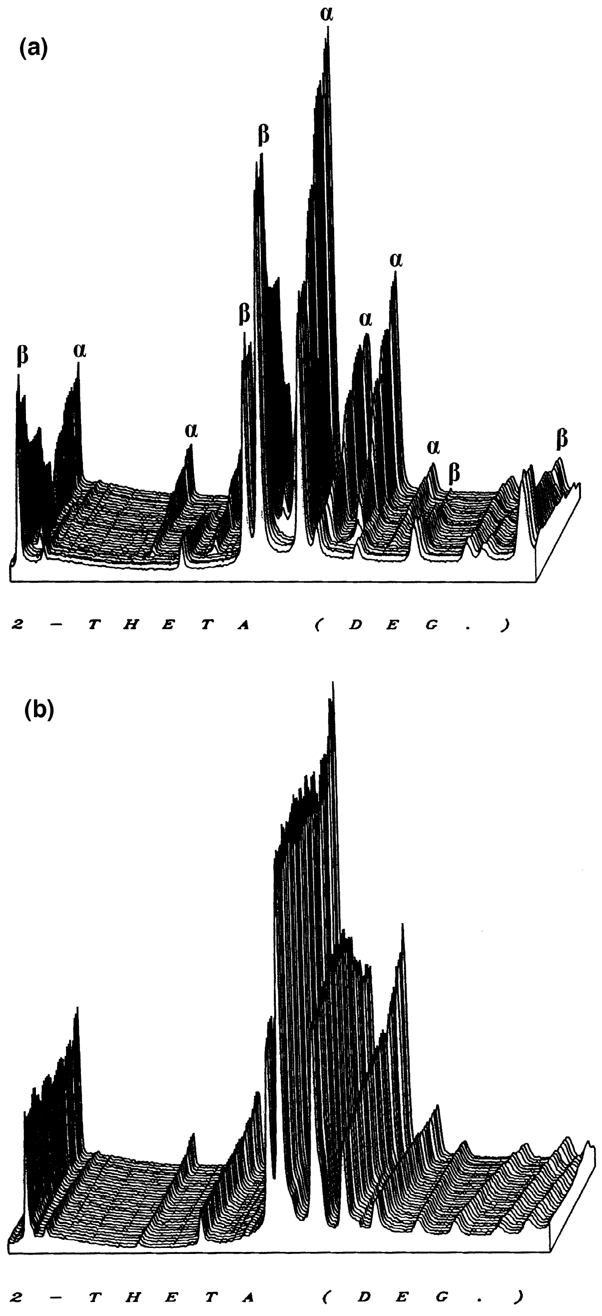

Fig. 1. Three dimensional ND patterns of $LaNi_4CuD_x$ (a) and $LaNi_5CuD_x$ (b) during solid–gas desorption.

3. Results

As can be seen from the 3D neutron diffraction pattern plots in Fig. 1, different processes occur during desorption depending on the stoichiometry. For the $LaNi_4Cu$ compound, the presence of two phases is observed, for which line positions are nearly constant but intensities vary in opposite. This two phase behaviour is typical of the equilibrium between the α and β phases as can be recognised on the pressure plateau in the P–C isotherm (Fig. 2). For the non-stoichiometric $LaNi_5Cu$ compound,

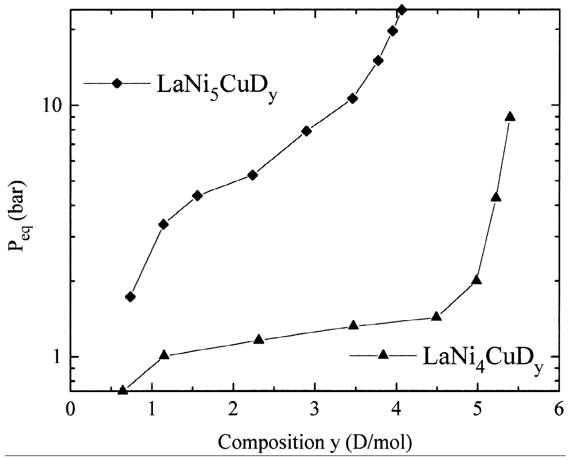

Fig. 2. Pressure–composition–isotherm curves at 25 °C for $LaNi_4Cu$ (▲) and $LaNi_5Cu$ (♦).

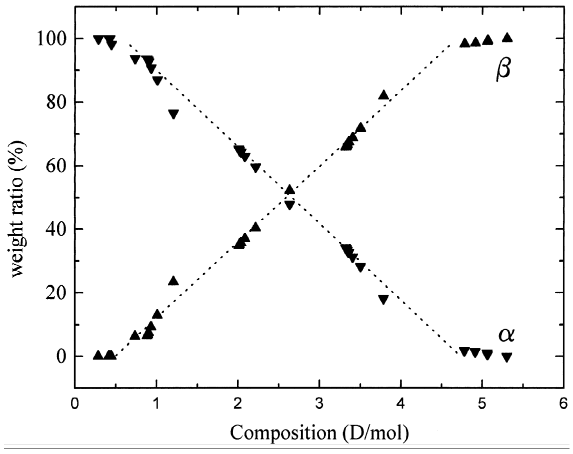

Fig. 3. Relative weight ratio between the α and β phases for $LaNi_4CuD_y$ as a function of deuterium content.

only one phase is observed with a continuous variation of the line positions but constant intensities. This behaviour is related to a solid solution process without phase transformation, which is in agreement with the sloping plateau found in the P–C isotherm of Fig. 2.

As pressure measurements allow to calculate the quantity of deuterium remaining in the metallic compounds, it is possible to plot for $LaNi_4Cu$ (Fig. 3) the weight ratio between the α and β phases as a function of deuterium content. Such a plot shows that the desorption process starts in the β branch from 5.3 down to 4.8 D/mol. Then the gradual β→α transformation occurs down to 0.4 D/mol. Below this value only the α phase is observed.

Such a plot cannot be drawn for the $LaNi_5Cu$ compound since there is only one phase involved in the desorption process. However the cell volume variations for both compounds are plotted as a function of D content in Figs. 4 and 5. It emphasizes the difference between the two processes: the non-stoichiometric compound continuously decreases its volume during desorption, whereas the phase transformation in the stoichiometric compounds induces a cell volume variation of 16%. It has been shown that this so-called discrete lattice expansion is responsible for the poor mechanical stability and, consequently, for the poor electrochemical cycling stability of this stoichiometric compound in commercial batteries [4,6]. Therefore the improved electrochemical stability observed for the non-stoichiometric compound is clearly related to the absence of such phase transformation.

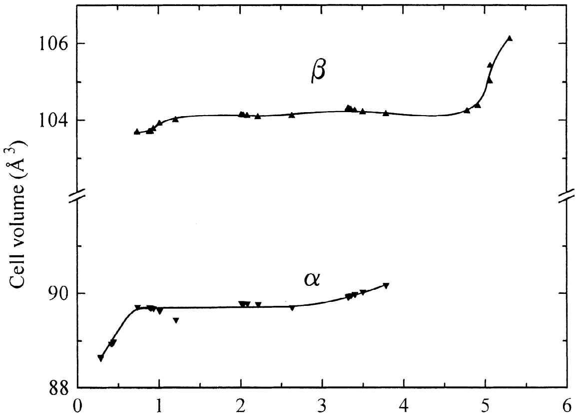

Fig. 4. Evolution of cell volumes for the α and β phases as a function of deuterium content for $LaNi_4CuD_y$.

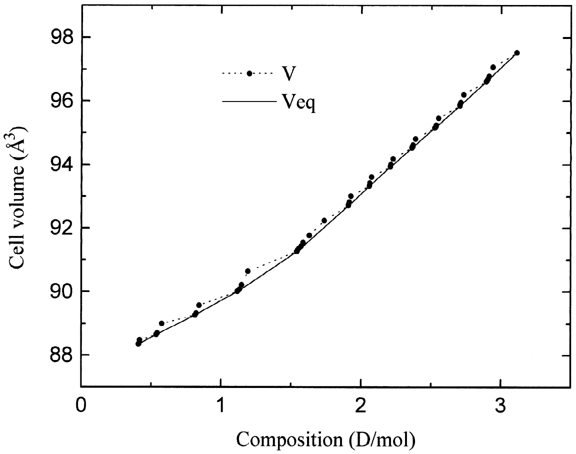

Fig. 5. Evolution of the cell volume for the $LaNi_5CuD_y$ solid solution as a function of deuterium content. (V_{eq} is the volume obtained under equilibrated pressure).

References

[1] J.J.G. Willems, *Philips J. Res. Suppl., 39* (1984) 1.

[2] P.H.L. Notten, J.L.C. Daams and R.E.F. Einerhand, *Ber. Buns. Phys. Chem., 96* (1992) 656.

[3] P.H.L. Notten, R.E.F. Einerhand and J.L.C. Daams, *Zeitschrift Phys. Chem., 183* (1994) 267.

[4] P.H.L. Notten, R.E.F. Einerhand and J.L.C. Daams, *J. Alloys Comp., 210* (1994) 221.

[5] P.H.L. Notten, J.L.C. Daams and R.E.F. Einerhand, *J. Alloys Comp., 210* (1994) 233.

[6] P.H.L. Notten, R.E.F. Einerhand and J.L.C. Daams, *J. Alloys Comp., 231* (1995) 604.

[7] S. Luo, T.B. Flanagan and P.H.L. Notten, *J. Alloys Comp., 239* (1996) 214.

[8] J. Rodríguez-Carvajal, *Abstracts of Satellite Meeting on Powder Diffraction*, Congr. Int. Union of Crystallography, Toulouse, France, 1990, p. 127.