



ELSEVIER

Journal of Alloys and Compounds 311 (2000) 248–251

Journal of  
ALLOYS  
AND COMPOUNDS

www.elsevier.com/locate/jallcom

# Study of the $\text{ZrCr}_{0.7}\text{Ni}_{1.3}$ multiphased system under hydrogen pressure by in-situ neutron diffraction

M. Bououdina\*, J.L. Soubeyroux, D. Fruchart

*Laboratoire de Cristallographie, CNRS Grenoble, BP 166, 38042 Grenoble cedex 9, France*

Received 7 February 2000; accepted 16 May 2000

## Abstract

Both X-ray and neutron diffraction Rietveld analyses show that the as-cast  $\text{ZrCr}_{0.7}\text{Ni}_{1.3}$  alloy crystallises with the C15-type Laves phase type structure, with the presence of  $>30$  wt.%  $\text{Zr}_7\text{Ni}_{10}$  and a few weight percent chromium. After annealing at 1373 K, we observed the disappearance of chromium metal and a reduction by more than half of  $\text{Zr}_7\text{Ni}_{10}$ .  $P$ - $C$ - $T$  measurements performed on the as-cast material show an absorption capacity of about 0.9 H/AB<sub>2</sub> at 323 K and under  $P = 10$  bar. In-situ neutron diffraction experiments performed at 323 K under deuterium gas pressure reveal that, after full hydrogenation of the sample, the  $\text{Zr}_7\text{Ni}_{10}$  phase transforms into an amorphous phase, but recrystallises under vacuum when the temperature is raised above 373 K. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Hydrogen storage materials; Energy storage materials; Crystal structure; Neutron diffraction; X-ray diffraction

## 1. Introduction

Zr-based Laves phase multicomponent alloys have attracted much attention in the last few years. Such Ni-rich alloys crystallize either in the hexagonal C14- or in the cubic C15-type Laves phase, even in both types, with the presence of secondary phases, mainly Zr–Ni-related phases [1–3]. Moreover, in the presence of large amounts of vanadium [4], bcc type solid solutions are observed.

Hydrogenation/dehydrogenation processing of multiphased alloys via pressure–composition–temperature measurements reveals faster kinetics in comparison with single Laves phase alloys [5], low hystereses and usually sloppy plateau pressure. The reaction kinetics are enhanced by the presence of secondary phases, the grain boundaries playing the role of active pathways for hydrogen diffusion [3].

However, to our knowledge, no in-situ absorption/desorption studies related to a multiphased alloy have yet been undertaken. Neutron diffraction experiments under various hydrogen gas pressures at different temperatures have been carried out in order to obtain more information

on both the hydrogen diffusion and the hydriding/dehydriding processes occurring in a multiphased Zr–Ni-based alloy.

## 2. Experimental

Ingots of  $\text{ZrCr}_{0.7}\text{Ni}_{1.3}$  alloy were prepared from starting elements of 3N purity using the HF induction melting technique. The samples were melted several times to ensure good homogeneity. Half of the as-cast samples were heat-treated at 1373 K for 3 days in a sealed silica tube under argon atmosphere and then quenched in cold water.

Powder X-ray diffraction measurements were performed using a D5000 Siemens diffractometer with Cu K $\alpha$  radiation.

$P$ - $C$ - $T$  diagrams were constructed using a thermogravimetric device described elsewhere [6].

For the in-situ neutron diffraction experiments, the sample was activated under the conditions described above followed by complete dehydrogenation at 523 K under vacuum. The data were recorded at  $\lambda = 2.52$  Å using a D1B powder diffractometer (ILL, Grenoble, France) which is equipped with a 400 cell PSD. The sample was placed in a silica tube and connected to a pressure/vacuum device

\*Corresponding author. Department of Materials, Queen Mary and Westfield College, University of London, Mile End Road, London E1 4NS, UK.

comprising a D<sub>2</sub> gas cylinder, manometers and a turbo pump. The hydrogen pressure was maintained stable for 40 to 60 min (depending on the record) and then increased or decreased. When after 5 to 10 min of rest time, no pressure variation was detected, the data acquisition was launched and every 5 min a diffraction pattern was recorded.

### 3. Results and discussion

The as-cast ZrCr<sub>0.7</sub>Ni<sub>1.3</sub> material crystallises as a multiphased alloy containing large amounts of a C15 Laves phase in equilibrium with the Zr<sub>7</sub>Ni<sub>10</sub> phase (SG: *Aba2*,  $a = 9.211 \text{ \AA}$ ,  $b = 9.156 \text{ \AA}$ ,  $c = 12.386 \text{ \AA}$ ,  $\alpha = \gamma = \beta = 90^\circ$ ) and traces of elemental chromium. After annealing at  $T = 1373 \text{ K}$  for 3 days, the phase composition was drastically modified with the complete disappearance of the free chromium and a reduction by more than 50% of the Zr<sub>7</sub>Ni<sub>10</sub> [7].

The results of the EDX mapping analysis carried out on both the as-cast and heat-treated alloys were found to be in good agreement with X-ray and neutron diffraction Rietveld analyses [7,8]. The relative phase abundance measured before and after annealing corresponds to a local chemical composition redistribution. The chemical composition of the main phase is effectively modified from ZrCr<sub>0.97</sub>Ni<sub>1.27</sub> before to ZrCr<sub>0.80</sub>Ni<sub>1.42</sub> after annealing. Accordingly, a slight change in the lattice parameters of both phases is observed.

From  $P$ – $C$ – $T$  experiments performed on the as-cast alloy, a maximum hydrogen capacity of  $C_{\text{max}} = 2.9 \text{ H/f.u.}$  is obtained at 323 K. However, the reversible hydrogen amount measured in the pressure range 10 to 100 kPa is only about 2 H/f.u.

Electrochemical measurements performed on both the as-cast and the annealed alloys show a much higher discharge capacity for the as-cast than for the annealed alloy:  $c_{\text{as-cast}} = 306$  and  $c_{\text{annealed}} = 156 \text{ mAh g}^{-1}$ , respectively [7].

The discharge capacity of the as-cast alloy ( $c_{\text{as-cast}} = 306 \text{ mAh g}^{-1}$ ) was measured at 40 mA for a temperature of 313 K. The theoretical discharge capacity ( $C_{\text{th}} = (96\,487 \times [\text{H}/\text{M}]) / (3.6 \times M_{\text{av}})$ , where  $[\text{H}/\text{M}]$  is the hydrogen capacity and  $M_{\text{av}}$  is the average atomic weight of the alloy) estimated from the  $P$ – $C$ – $T$  diagram is

$$C_{\text{th}}(T = 298 \text{ and } [\text{H}/\text{M}] = 3.1) = 407.4 \text{ mAh g}^{-1}$$

$$C_{\text{th}}(T = 323 \text{ and } [\text{H}/\text{M}] = 2.7) = 354.9 \text{ mAh g}^{-1}$$

and if we assume that the hydrogen capacity varies linearly with temperature, then

$$C_{\text{th}}(T = 313 \text{ and } [\text{H}/\text{M}] = 2.7) = (354.9 + 407.4) / 2 = 381.2 \text{ mAh g}^{-1}$$

The reversible hydrogen capacity observed from the  $P$ – $C$ – $T$  diagram is about 2 H/f.u. and corresponds to a discharge capacity of  $C_{\text{th}}^* = 262.9 \text{ mAh g}^{-1}$ .

From the above calculations and according to the experimental values, we can state that the multiphased alloy releases more than 80% of its capacity during electrochemical discharge. However, during the solid–gas reaction, only 67% of its total capacity can be desorbed. The large hydrogen release from electrochemical reactions is related to the presence of the Zr<sub>7</sub>Ni<sub>10</sub> phase, which has already been reported to possess good electrochemical properties [9].

The absorption/desorption kinetics of the multiphased ZrCr<sub>0.7</sub>Ni<sub>1.3</sub> alloy were found to be faster than for a single Laves phase system, both from solid–gas and electrochemical reactions [5]. The marked improvement in terms of reaction kinetics can be explained not only by the presence of Zr<sub>7</sub>Ni<sub>10</sub> as a secondary phase [3,5], but also by the presence of elemental chromium which acts as a catalyst for H<sub>2</sub> molecule dissociation.

During the absorption cycle performed along with the in-situ neutron diffraction experiment, we observed that, during the first hydrogen insertion process, the Bragg peaks of the Zr<sub>7</sub>Ni<sub>10</sub> phase (indicated by asterisks in Fig. 1) become broader and broader. Simultaneously, the intensity of these peaks decreases while no peak belonging to the C15 hydrided phase is observed. However, after a few minutes, the main peaks of a C15 hydride appear and grow rapidly. The intensity of the Bragg peaks of both the Zr<sub>7</sub>Ni<sub>10</sub> phase and the C15 compound decrease continuously. For the maximum hydrogen pressure applied under the experimental conditions ( $P = 0.8 \text{ MPa}$ ), the diffraction pattern reveals the presence of both the C15 alloy and its hydride. The complete disappearance of the diffraction peaks of the Zr<sub>7</sub>Ni<sub>10</sub> phase during the hydrogenation process can be attributed to a phase transformation, upon which this phase becomes amorphous [8].

During the desorption process initiated by a decrease of the applied gas pressure, we can see clearly from Fig. 2 that, after only three recorded patterns (i.e. 15 min), the total amount of  $\beta$ -hydride is transformed into alloy (or at least into the  $\alpha$  solid solution). The release of hydrogen from the cubic C15 compound occurs with very fast kinetics. However, after a complete desorption cycle, no diffraction peaks related to the orthorhombic Zr<sub>7</sub>Ni<sub>10</sub> phase is observed.

At the end of the desorption cycle, heat treatment under vacuum was applied (Fig. 3). We observed a gradual recrystallisation process with the recovery of the diffraction peaks related to Zr<sub>7</sub>Ni<sub>10</sub>. This is achieved at 373 K for about 140 min.

From our experiments, findings and thermodynamics considerations, a mechanism for the hydrogenation of the studied multiphase system can be proposed [8]. However, this does not explain the amount of non-reversible hydrogen. This could be due to the Zr<sub>7</sub>Ni<sub>10</sub> phase present in

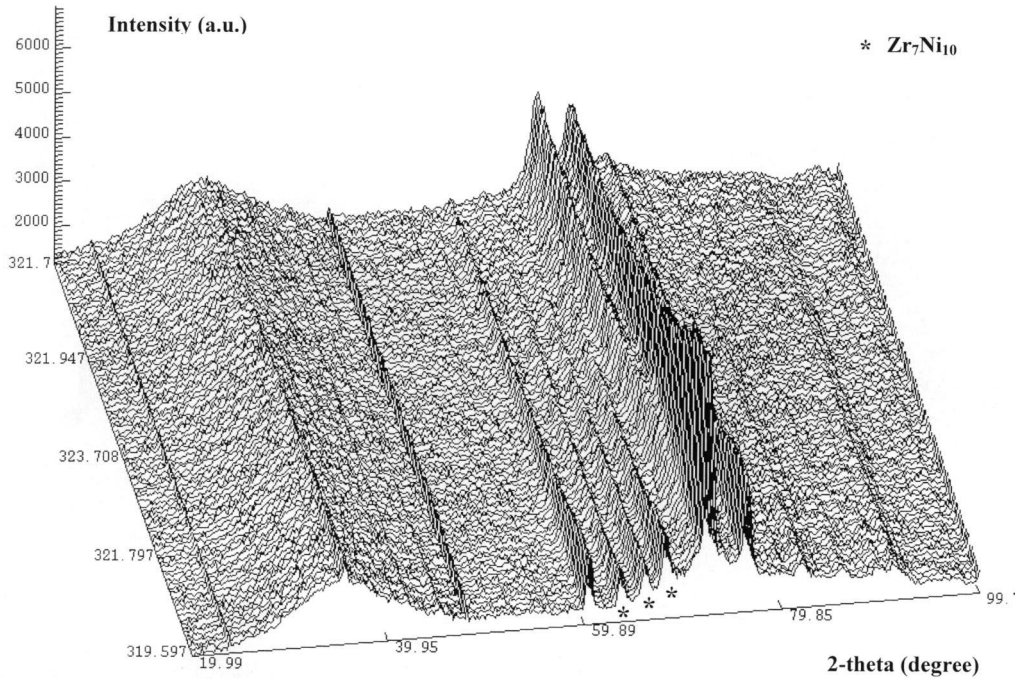


Fig. 1. 3-D diffraction patterns as recorded during the absorption process at  $T = 323$  K.

quite large amounts in the as-cast alloy ( $\approx 37$  wt.%). Alternatively, it might be related to the Laves phase, the hydride of which cannot desorb unless at very low pressures. Additional investigations are needed to better understand this point.

#### 4. Conclusion

Crystal structure investigations of the different components of the  $\text{ZrCr}_{0.7}\text{Ni}_{1.3}$  multiphased alloy show that the as-cast alloy crystallises in a cubic C15-type Laves

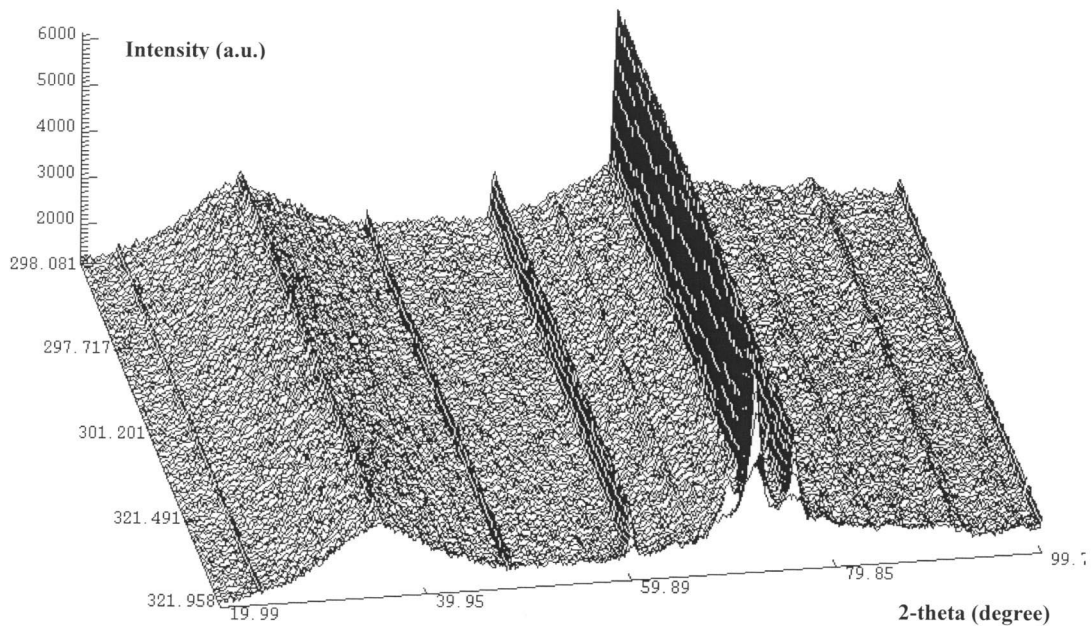


Fig. 2. 3-D diffraction patterns as recorded during the desorption process at  $T = 323$  K.

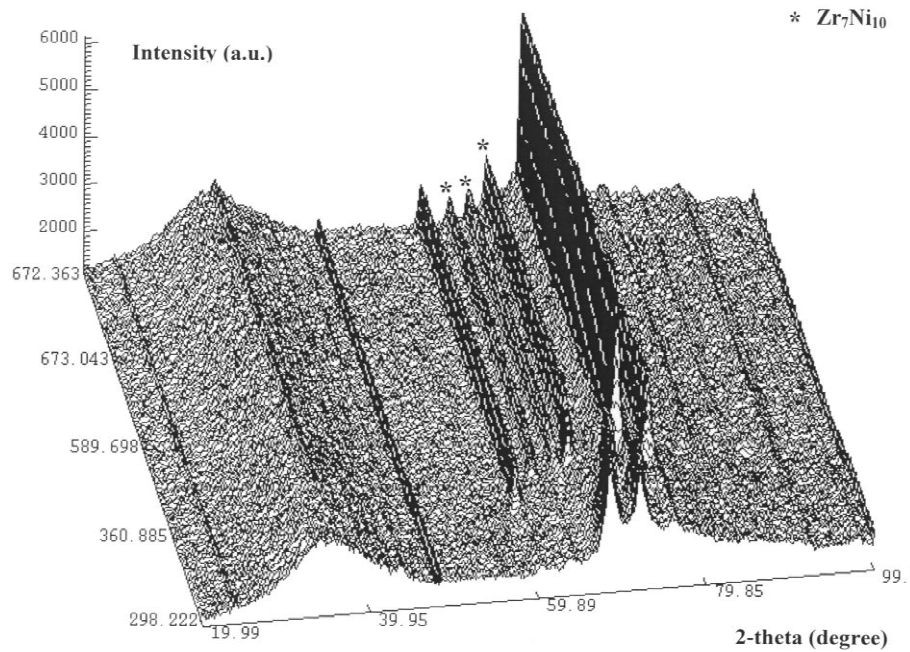


Fig. 3. 3-D diffraction patterns as recorded during heat treatment applied for recrystallisation of the  $Zr_7Ni_{10}$  phase.

phase with the precipitation of  $Zr_7Ni_{10}$  as a secondary phase and traces of chromium. After heat treatment performed at 1373 K for 3 days, the major part of the alloy is of the C15-type Laves phase. Furthermore, there is a significant reduction of  $Zr_7Ni_{10}$  by more than 50% and a complete dissolution of the chromium. From the 3-D diffraction patterns recorded during the absorption cycles, the diffraction peaks of the  $Zr_7Ni_{10}$  component disappear, probably due to an amorphisation process. After the desorption cycle, no new diffraction peaks are observed. During heat treatment up to 673 K under vacuum, a recrystallisation process of  $Zr_7Ni_{10}$  takes place after total release of the residual hydrogen.

### Acknowledgements

The neutron diffraction data were collected at the Institute Laue Langevin (ILL), Grenoble (France). Thanks are due to ILL for accepting the proposal and for the experimental support.

### References

- [1] M. Bououdina, Ph.D Thesis, University Joseph Fourier, Grenoble, 1995.
- [2] L. Yongquan, Y. Xiaoguang, W. Jing, W. Qidong, J. Alloys Comp. 231 (1995) 573.
- [3] J.-M. Joubert, M. Latroche, A. Percheron-Guégan, J. Bouet, J. Alloys Comp. 217 (1995) 245.
- [4] J. Huot, E. Akiba, Y. Ishido, J. Alloys Comp. 231 (1995) 85.
- [5] M. Bououdina, H. Enoki, E. Akiba, J. Alloys Comp. 281 (1998) 290.
- [6] M. Bououdina, J.L. Soubeyroux, P. Juen, C. Mouget, R. Argoud, D. Fruchart, J. Alloys Comp. 231 (1995) 422.
- [7] M. Bououdina, C. Lenain, L. Aymard, J.L. Soubeyroux, D. Fruchart, submitted for publication.
- [8] M. Bououdina, J.L. Soubeyroux, D. Fruchart, in press.
- [9] J.-M. Joubert, M. Latroche, A. Percheron-Guégan, J. Alloys Comp. 231 (1995) 494.