

Neutron diffraction study of $\text{Zr}(\text{Cr}_{0.6}\text{Ni}_{0.4})_2\text{D}_{3.3}$

J-M Joubert ^a, M. Latroche ^a, A. Percheron-Guégan ^a, F. Bourée-Vigneron ^b

^a Laboratoire de Chimie Métallurgique et de Spectroscopie des Terres Rares, UPR 209, CNRS, 1 Pl. A. Briand, 92195 Meudon Cedex, France

^b Laboratoire Léon Brillouin, CE-Saclay, 91191 Gif sur Yvette Cedex, France

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Abstract

This paper deals with the structural study of $\text{Zr}(\text{Cr}_{0.6}\text{Ni}_{0.4})_2$ and its deuteride by means of both X-ray and neutron diffraction. The C14 (MgZn₂-type) structure of the intermetallic compound is conserved after deuteration. Determination of positions and occupancy factors of deuterium atoms has been achieved. Results will be compared to previously reported data on $\text{Zr}(\text{Cr}_{1-x}\text{Fe}_x)_2\text{-D}$ system, and the occupancy factor of each site will be discussed in terms of its chemical affinity.

Keywords: Hydrides; Laves phases; X-Ray diffraction; Neutron diffraction

1. Introduction

Cubic ZrCr_2 (C15-MgCu₂-type) absorbs 3.8 H atoms per formula unit at room temperature with an equilibrium pressure of 10^{-3} bar [1]. The crystal structure of its deuteride has been determined by Fruchart et al. [2] and Irodova et al. [3]. They found that A_2B_2 sites are occupied, and that AB_3 site filling is observed only for high deuterium concentration ($\text{D} > 3.1$). For practical applications, according to the relatively low equilibrium pressure, it is possible to increase it by substituting chromium by other transition metals (Fe, Co, Ni, etc.). This substitution leads to transformation of cubic ZrCr_2 into hexagonal C14 (MgZn₂-type) structure [4–5]. We have already studied some iron-substituted compounds by means of neutron diffraction [6]. The results have demonstrated that only A_2B_2 sites are occupied and that their occupancy factors are related to hole sizes in the deuteride. Boulghallat et al. [7] have compared the thermodynamic and kinetic hydriding properties of the two compounds $\text{Zr}(\text{Cr}_{0.6}\text{Fe}_{0.4})_2$ and $\text{Zr}(\text{Cr}_{0.6}\text{Ni}_{0.4})_2$. They have shown that the nickel-substituted compound has a larger capacity and that, in these two systems, the equilibrium pressure of the hydride is not related to the cell volume, as was observed for numerous systems [8], but to hole sizes in the host metal. So in order to complete these previously reported results and to make a comparison between hole sizes and occupancy factors in the two systems, we have performed a neutron diffraction experiment on $\text{Zr}(\text{Cr}_{0.6}\text{Ni}_{0.4})_2\text{D}_{3.3}$.

2. Experimental details

2.1. Synthesis

The compound $\text{Zr}(\text{Cr}_{0.6}\text{Ni}_{0.4})_2$ was prepared by induction melting of the pure components (Zr, 99.9%; Cr, 99.99%; Ni, 99.9%) in a water-cooled copper crucible under argon atmosphere. The sample was remelted five times, turned over between each melting and annealed for one month at 1000 °C in a silica tube sealed under secondary vacuum. The homogeneity was checked by metallographic examination and microprobe analysis.

About 7 g of the intermetallic compound were reduced to powder (less than 36 μm) in a glove box under argon atmosphere and introduced in a silica tube sample holder. The absorption was made by exposing the sample to deuterium pressure at room temperature. The capacity was measured from the pressure variation by a so-called volumetric method. We obtained a capacity of 3.3 D atoms per formula unit under a pressure of 3.3 bar.

2.2. X-Ray and neutron diffraction

The X-ray pattern of the intermetallic compound was performed on the same batch that was used for deuteration. It was recorded with an automated goniometer (Philips PW1170) using Cu K α radiation from 10° to 120° (2θ , step 0.02°, 10 s per step).

The deuteride was exposed to the neutron beam at room temperature in the silica tube closed under deu-

terium pressure. The experiment was performed at CE Saclay on the 3T₂ instrument. Wavelength was 1.226 Å and the pattern was recorded from 6° to 120° (2θ) in steps of 0.05°.

The two diffractograms were analysed using the Rietveld method with the standard software FULLPROF [9]. For X-ray pattern, the refinement was made assuming a statistical distribution of nickel-on-chromium sublattice because, owing to the small difference in their atomic numbers, they cannot be distinguished. For neutron pattern, the heavy background produced by the silica environment was interpolated between diffraction peaks. The distribution of nickel-on-chromium sublattice could be refined. The isotropic factors for thermal expansion were refined, but not at the same time as occupancy factors, because of high correlation between these two kinds of parameters.

3. Results

3.1. Intermetallic compound

The compound was found to be single phase by metallographic examination. Microprobe analysis shows that the compound is homogeneous and has a composition very near to the nominal one: Zr_{0.986(4)}(Cr_{0.61(1)}Ni_{0.40(1)})₂.

As for the iron substitution, increasing the amount of nickel in Zr(Cr_{1-x}Ni_x)₂ led to a change of the structure from the C15-MgCu₂-type of ZrCr₂ to C14-MgZn₂-type structure for $x \geq 0.2$ [5]. The diffractogram is shown in Fig. 1. The results of the refinement are given in Table 1. The X-ray diffractogram shows three very small supplementary diffraction lines which can be attributed to the presence of Cr and ZrNi phases. Any attempt

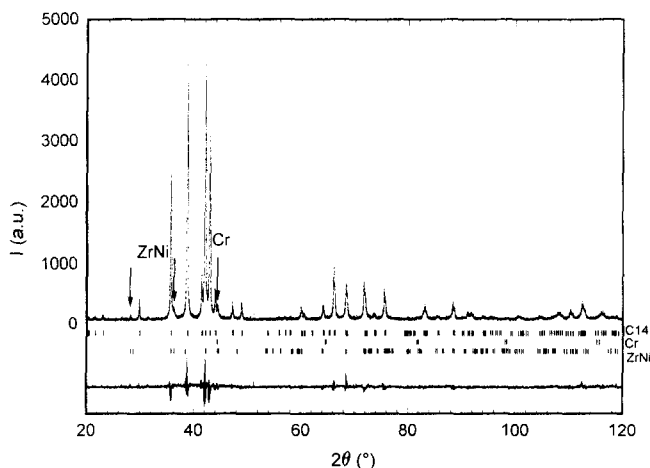


Fig. 1. X-ray diffraction pattern refinement of Zr(Cr_{0.6}Ni_{0.4})₂ (observed, calculated and difference curves). The first two arrows represent the extra lines which have been attributed to ZrNi phase, the third one to Cr phase.

Table 1

Determination of the structure of intermetallic compound from X-ray diffraction experiment (Zr(Cr_{0.6}Ni_{0.4})₂; S.G.: P 6₃/m m c (MgZn₂-type); $a = 5.0291(4)$ Å; $c = 8.2348(7)$ Å; $V = 180.4$ Å³; $R_1 = 5.7\%$; $R_F = 6.3\%$; $R_{wp} = 11.3\%$; $\chi^2 = 2.0$)

Atoms	Sites	x	y	z	B (Å ²)
Zr	4f	1/3	2/3	0.0632(5)	1.1(1)
Cr, Ni	2a	0	0	0	1.2(1)
Cr, Ni	6h	0.8307(13)	2x	1/4	1.2(1)

to prepare the compound as a single phase by a slight change of the composition failed. From X-ray pattern analysis, the weight ratios were evaluated as 2% for Cr and 3% for ZrNi.

3.2. Deuteride

The neutron diffraction pattern shows that the C14-MgZn₂-type structure is conserved after deuteration and that the totality of the intermetallic has been transformed into β phase. The very small quantity of secondary phases observed in the X-ray pattern was not detectable in the neutron pattern, so they were not taken into account. The cell parameters of the deuteride are $a = 5.351(1)$ Å, $c = 8.757(1)$ Å. The increase of the cell volume is 20.3%, which is comparable to the volume increase in the iron-substituted compounds [6]. The distribution of nickel on the two different possible positions (6h and 2a) could be refined. The occupancy factors observed are 0.44 for 2a site and 0.39 for 6h, to be compared to the 0.40 ideal value. It shows that the distribution is random, as was also observed with the iron-substituted compounds. Concerning the deuterium occupancy, any attempt to fill the AB₃ sites was unsuccessful (i.e. leading to negative occupancy factors) so the refinement was made assuming that only A₂B₂ sites were occupied. This fact corresponds well to the trend for deuterium to fill the tetrahedron constituted by atoms with high hydrogen affinity (Zr). The deuterium content found by neutron diffraction was 3.31(5) D atoms per formula unit, which is in very good agreement with the value determined by volumetric measurement (3.3).

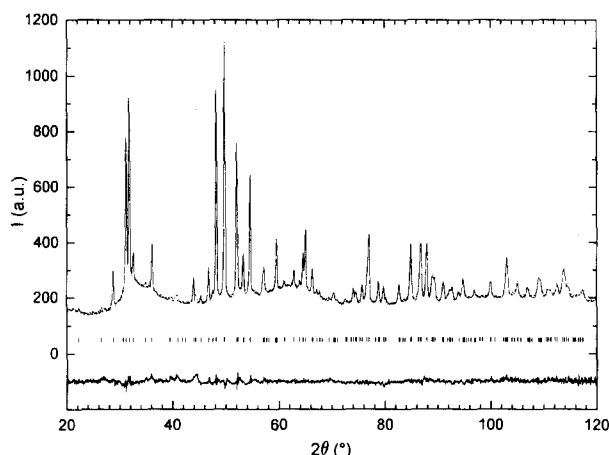
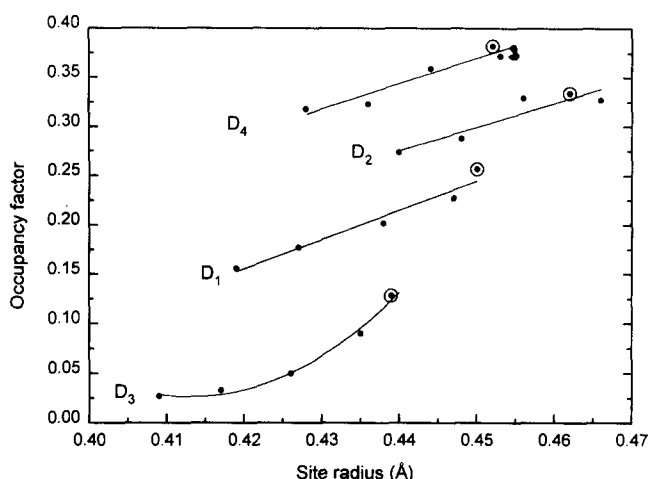
The determination of the cell parameters and atomic positions of metallic atoms allow the calculation of hole sizes for deuterium, defined as the radius of the largest sphere in contact with the four atoms of the coordination tetrahedron assuming an atomic radius of 1.60 Å for zirconium and the weighted radius of 1.276 Å for chromium substituted by nickel.

The diffractogram is shown in Fig. 2. The results of the refinement and site size calculations are listed in Table 2.

Table 2

Determination of the structure of deuteride from neutron diffraction experiment ($\text{Zr}(\text{Cr}_{0.6}\text{Ni}_{0.4})_2\text{D}_{3.3}$; S.G.: $P 6_3/m m c$; $a = 5.351(1) \text{ \AA}$ (+6.4%); $c = 8.757(1) \text{ \AA}$ (+6.3%); $V = 217.1 \text{ \AA}^3$ (+20.3%); $R_1 = 8.3\%$; $R_F = 6.9\%$; $R_{wp} = 2.9\%$; $\chi^2 = 2.5$). Total D content (refined): 3.31(5) D atoms per formula unit

Atom	Site	x	y	z	B (\AA^2)	n	Size (\AA)
Zr	4f	1/3	2/3	0.0636(2)	0.85(4)	1	
Cr	2a	0	0	0	1.01(3)	0.564(10)	
Ni	2a	0	0	0	1.01(3)	0.437(10)	
Cr	6h	0.8374(4)	2x	1/4	1.01(3)	0.612(10)	
Ni	6h	0.8374(4)	2x	1/4	1.01(3)	0.388(10)	
D ₁	24l	0.0443(6)	0.3275(9)	0.5657(5)	1.82(5)	0.257(3)	0.450
D ₂	12k	0.4560(8)	2x	0.6327(4)	1.82(5)	0.334(4)	0.462
D ₃	6h	0.2000(31)	2x	1/4	1.82(5)	0.128(6)	0.439
D ₄	6h	0.4666(12)	2x	1/4	1.82(5)	0.382(7)	0.452

Fig. 2. Neutron diffraction pattern refinement of $\text{Zr}(\text{Cr}_{0.6}\text{Ni}_{0.4})_2\text{D}_{3.3}$.Fig. 3. Evolution of the D occupancy as a function of the site radius for two different iron-substituted compounds at two different deuterium concentrations (●) [6] and for $\text{Zr}(\text{Cr}_{0.6}\text{Ni}_{0.4})_2\text{D}_{3.3}$ (○).

4. Discussion

From comparison between X-ray and neutron results, it is concluded that the $\text{MgZn}_2\text{C14}$ structure is conserved upon deuteration. Both atomic positions and temperature isotropic factors (B) of the metal atoms are identical within the error range. No ordering of the substituent is observed, and it is then assumed to be random. Absorption involves an isotropic increase of the cell volume of 20.3%.

The deuterium occupancy factors of A_2B_2 sites as a function of hole sizes for two different iron-substituted compounds at two different concentrations [6] and for $\text{Zr}(\text{Cr}_{0.6}\text{Ni}_{0.4})_2\text{D}_{3.3}$ have been plotted in Fig. 3. The larger capacity obtained for nickel-substituted alloy is due to a better filling of the A_2B_2 sites and not to the filling of AB_3 sites. This larger occupancy is related to larger hole sizes, as was noted by Canet et al. [6]. We can conclude that larger capacity and different thermodynamic properties for the hydride of the nickel-substituted compound are not due to a different absorption process, but only to larger hole sizes in the host metal [7] and in the deuteride.

In Fig. 3, we notice that the linear behavior of occupancy as a function of site sizes exists for each different given site except for D_3 , for which the data are less accurate owing to smaller occupancy. D_4 sites are always the most occupied sites before D_2 , D_1 and D_3 . This fact cannot be explained only by hole size because, for example, D_4 sites are smaller than D_2 and are more occupied. Thermodynamic considerations based on the Miedema model [10] fail because all these occupied sites have the same A_2B_2 environment. An ordered substitution of nickel-on-chromium sublattice could have been an explanation for a different occupancy factor in D_1 site, because this site is made of one 2a and one 6h B atom, while the other sites are built with two 6h B atoms. Such a preferential substitution was observed by Fruchart et al. [11] on $\text{Ti}_{1.2}\text{Mn}_{1.8}$, but here it is observed that the nickel distribution is random. To find an explanation, we have calculated the second neighbor atom environment for the sites which form a tetrahedron around the site. This second shell is

described as A_2B_2 for D_4 , AB_3 for D_2 and D_1 and B_4 for D_3 . This fact can explain the occupancies observed for each site ($D_4 > D_2 > D_1 > D_3$). So, for the same first-neighbor environment (A_2B_2), deuterium atoms prefer to fill the sites constituted by the most zirconium atoms among the second-neighbor atoms. We can conclude therefore that occupancy is directly related to the chemical affinity of the site if one considers two atomic shells around the deuterium atom.

5. Conclusion

We have studied by means of X-ray and neutron diffraction the crystallographic structure of $Zr(Cr_{0.6}Ni_{0.4})_2$ and its deuteride. The structure remains of the $MgZn_2$ type after deuteration. We have shown that only A_2B_2 sites were occupied by deuterium, and that better capacity of nickel-substituted compound compared to iron-substituted compounds was achieved only by a larger filling of these sites, related to a larger hole size. It has been shown that the larger occupancy of D_4 site before D_2 , D_1 and D_3 observed both for

iron- and nickel-substituted compounds can be directly related to the number of atoms with high hydrogen affinity (Zr) among the second neighbors of the site.

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