

Structural investigations by neutron diffraction of equi-atomic Zr–Ti(V)–Ni(Co) compounds and their related hydrides

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Abstract

Crystal structure refinements based on neutron diffraction experiments performed on the ternary compounds ZrTiNi, ZrVCo and ZrVNi allow to confirm the stability of the C14 Laves type of structure in a large extent of formula. Besides, SEM/EDX analyses reveal the presence of minor additional phases that precipitate parallel to the main one. Neutron diffraction experiments performed on the corresponding ZrMM' hydrides indicate that after hydrogen (deuterium) absorption the crystal structure remained unchanged, except for ZrTiNi, where further investigations are underway.

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1. Introduction

Several binary Zr-based Laves compounds show relatively high mass capacities, fast kinetics, and in some cases a relatively low cost, in comparison with other intermetallic compounds (TiFe and LaNi₅ related systems, etc.). However, the corresponding ternary hydrides are too stable at room temperature, e.g. ZrV₂H_{5.3}, ZrMn₂H_{3.6}, ZrCr₂H_{3.4}, to develop applications in terms of reversible storage. Many studies have been reported aiming to bring the pressure of the reversible phase transformation AB₂ + H_x ↔ AB₂H_x to practical values by metal substitutions on both the A=Zr and B=M sites, respectively [1,2]. Besides, multi-component Ti/Zr-based Laves phase compounds have yet retained attention in terms of potential applications involving electrochemical reactions; however, they exhibit often poor activation characteristics and lower electrochemical capacities in comparison with their somewhat promising solid–gas reactions. Zr/Ti-containing AB₂ Laves phase powders are oxygen sensitive and the formation of dense and mainly based Ti-phases onto the surface, diminishes the molecule dissociation effectiveness, and

subsequently limits the reversible hydrogen atom or proton diffusion within the solid material.

This paper is the first report of a more systematic analysis aiming to better understand some of the intrinsic and extrinsic parameters that might be considered to have significant impact on the performances in terms of reversible kinetics and of reversible capacity of absorption. The crystal structure of the ZrTiNi, ZrVCo and ZrVNi compounds and their related hydrides (deuterides) have been investigated by neutron diffraction. Besides, the microstructure and the chemical composition of the materials were checked by microprobe analysis.

2. Experimental

The 3N-purity starting elements were melted in a 5N-purity argon atmosphere by using the HF induction technique in a water-cooled copper crucible. Formula of the starting alloys was chosen as 1:1:1. Hydrides (deuterides) with maximum hydrogen (deuterium) content were prepared following the procedure reported elsewhere by using 5N-purity gases, by applying one to two thermal and pressure cycles [3]. The hydrogen concentration as effectively stabilised under normal conditions of temperature and determined on the bulk materials were found to be

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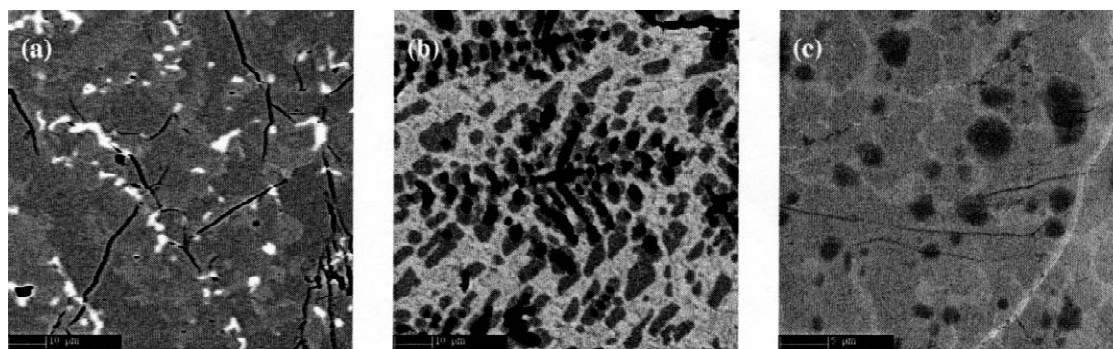


Fig. 1. Selected SEM images of (a) ZrVCo, (b) ZrVNi and (c) ZrTiNi, well displaying the polyphased aspects of the as-cast intermetallic materials.

3.15, 3.75, 3.55, respectively, for ZrVCo, ZrVNi and ZrTiNi.

All the materials were systematically checked by using a conventional X-ray diffractometer ($\lambda_{\text{K-Cu}}$) equipped with a backscattering monochromator. Characterisation of the microstructure and the chemical composition was carried out by X-ray fluorescence analysis using a Kevex EDX probe attached to a Philips EM400T TEM. Neutron diffraction experiments were carried out at the Institute Laue-Langevin Grenoble, using both the high-resolution D2B and D1A powder diffractometers, equipped with banks of independent detectors and Soller slit collimators. The neutron diffraction patterns were analysed by using either the profile refinement method Fullprof [4] or the MXD [5] software which is based on the determination integrated intensities routine ABFFIT [6].

3. Results and discussion

3.1. Chemical analysis

For the ZrVCo compound, the SEM images as reported in Fig. 1a, shows the presence of a mass matrix having grey (M1) and light grey (M2) aspects, and the presence of bright precipitates which size ranges from 1 to 5 μm . The

chemical analysis as displayed in Table 1, reveals that the two brightness matrix compounds have an almost uniform composition, which does not exactly correspond to the starting composition, even if not by much. In fact, the minor precipitates have Zr-rich and V-low contents, meaning that a small amount of Zr is disproportionate from the matrix.

For the ZrVNi compound, the SEM images show clearly that the system is a multiphase one thus containing three components as seen in Fig. 1b. A grey matrix (M) is the dominating one, in which a light bright intermediate phase (IP) is homogeneously distributed, moreover accompanied with dispersed dark dendrites (D). As shown in Table 1, the chemical analysis reveals that the composition of the matrix is rather close to the starting composition whereas the intermediate phase is a (Zr,Ni)-rich one with a minor V content (close to 1 at.%). Conversely, the dendrites contain more than 95 at.% of V, which means that probably particles of a (V-rich, Ni, Zr)-bcc solid solution was precipitated during the solidification process. It is worth noting that the latter phase was not formally identified by X-ray, and therefore cannot be detected and moreover quantified since V is a neutron coherently poor-scattering element.

For ZrTiNi, the SEM images as in Fig. 1c, reveal the presence of a main single-phase sample as a grey matrix.

Table 1
Microprobe chemical analysis of the ZrVCo, ZrVNi and ZrTiNi alloys

Compound	Phases	Chemical composition (at.%)				
		Zr	Ti	V	Co	Ni
ZrVCo	Matrix 1	27.2(2)		36.1(3)	36.7(2)	
	Matrix 2	25.7(3)		37.6(2)	36.6(3)	
	Precipitates	54.6(7)		12.5(10)	32.9(3)	
ZrVNi	Matrix	33.4(4)		34.0(8)		32.7(8)
	Interm.	51.3(2)		1.3(7)		47.5(2)
	Dendrites	0.5(1)		95.6(4)		3.9(2)
ZrTiNi	Matrix	34.2(3)	32.5(1)			33.3(2)
	Clusters	39.5(12)	30.7(9)			29.3(4)
	Precipitates	54.6(19)	12.7(18)			30.7(5)

This matrix shows two different levels of brightness, but the microprobe analysis indicates clearly they have identical chemical compositions. The origin of such a difference could be attributed to typical grain orientations within the phase. It can be noticed also the presence of clusters and fine intergranular structures (light grey, even bright) that are homogeneously dispersed within the matrix with a typical thickness of less than 1 μm .

3.2. Crystal structure determination of the starting compounds by neutron diffraction

The crystal structure refinements carried out using the powder neutron diffraction data confirm that in the three ZrMM' compounds, the main phase crystallises within the C14-type of structure. The relative stability of the C14 hexagonal structure within the ternary compositions of the ZrVCo, ZrVNi and ZrTiNi alloys is rather interesting to note. For instance, in both the Zr–Ni and Zr–Ti phase diagrams no AB₂ Laves phases was shown to exist on one hand, and both ZrCo₂ and ZrV₂ crystallise within the C15 cubic Laves phase type of structure, on the other hand. The model of structure used for the profile type analysis was based on the hexagonal C14-type of structure [1,2]. For both ZrVCo and ZrVNi, all the 3d transition metals M and M' occupy the B-sites that have 2a and 6h positions in the

P6₃/mmc space group [1,2,7]. The Riedvelt refinement and the chemical analysis agree with the presence of about 93% of the main AB₂ phase, the rest being dominantly of the, e.g. ZrNi₂ type of structure.

The main atom parameters calculated from the structure refinements are reported in Table 2. It is worth to note that according to the stoichiometry, the distribution of 3d metal atoms within the 2a and 6h positions do not reveal preferentially marked site occupancies and at a first order it seems to not vary so much with the nature of transition metals.

However, the structural model for ZrTiNi was found to be somewhat different. It was supposed that Ti could occupy partly both the A and the B sites. Refinement of the crystal structure of ZrTiNi was revealed to be less simple than expected, compared to ZrVM' compounds. Because titanium has a negative neutron scattering cross-section, those of Zr and Ni being positive, and of the possible presence of titanium on all the A and B sites, the site scattering cross-sections are all determined by the relative occupation numbers, which are variables to refine. First, the cell parameters were determined independently from the peaks positions. Then, the intensities of the Bragg peaks were integrated using the ABFFIT program [6] and finally the structure refinement was made by using the MXD program [5]. It is noteworthy that finally the Ti atoms were found to be distributed on the three metal

Table 2
Crystal structure analysis of ZrVNiCo, ZrVNi and ZrTiNi by neutron diffraction

	Lattice parameters	Atom	x	y	z	B (\AA^2)	Occupancy
C14	a=5.0737(1) c=8.2831(2)	Zr(4f)	0.333	0.667	0.063(2)	0.23(2)*	0.166
		Co(2a)	0.000	0.000	0.000		0.026(1)
		V(2a)	0.000	0.000	0.000		0.057(1)
		Co(6h)	0.832(2)	0.666(2)	0.25		0.112(1)
		V(6h)	0.832(2)	0.666(2)	0.25		0.138(2)
Reliability factor: R=0.06 Refined formula: ZrV _{1.17} Co _{0.83}							
C14	a=5.0806(1) c=8.3080(2)	Zr(4f)	0.333	0.667	0.063(2)	0.27(10)	0.166
		Ni(2a)	0.00	0.000	0.000	0.03(1)	0.032(1)
		V(2a)	0.00	0.000	0.000	0.03(1)	0.051(1)
		Ni(6h)	0.829(1)	0.658(1)	0.25	0.03(1)	0.128(2)
		V(6h)	0.829(1)	0.658(1)	0.25	0.03(1)	0.122(2)
Zr–Ni	a=3.2712(1) b=9.9310(3) c=4.1072(1)	Zr(4f)	0.00	0.360(0)	0.25	0.5	0.5
		Zr(4f)	0.00	0.084(0)	0.25	0.5	0.5
Reliability factor: R=0.04 Refined formula: ZrV _{1.04} Ni _{0.96} and ZrNi							
C14	a=5.1274(5) c=8.5342(1)	Zr(4f)	0.333	0.667	0.034(1)	0.8(2)*	0.147(1)
		Ti(4f)	0.333	0.667	0.034(1)		0.019(1)
		Ni(2a)	0.00	0.00	0.00		0.036(1)
		Ti(2a)	0.00	0.00	0.25		0.47(1)
		Ni(6h)	0.800(4)	0.600(4)	0.25		0.115(1)
		Ti(6h)	0.800(4)	0.600(4)	0.25		0.135(1)
Reliability factor: R=0.05 Refined formula: Zr _{0.89} Ti _{1.2} Ni _{0.91} *Overall B							

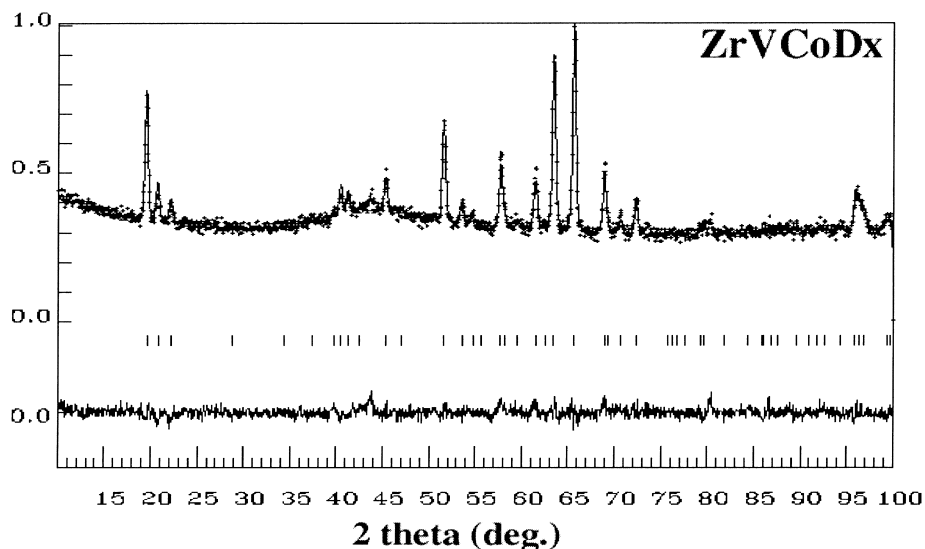


Fig. 2. Neutron diffraction pattern of $ZrVCoD_x$ analysed by profile method (+, experimental data; upper solid line, calculated pattern; lower solid line, intensity difference).

positions A-(4f), B-(2a) and B-(6h), respectively. In fact, refinement of the formula leads to a higher Ti content compared to the starting composition. However the relative distribution of Ti atoms on the two B-metal positions is found rather comparable to that deduced for $ZrVCo$ and $ZrVNi$. The refined parameters are displayed in Table 2.

3.3. Crystal structure determination of the hydrides by neutron diffraction

All metallic site occupancies were fixed according to the results of the refinements obtained previously on the C14 compounds. Neutron diffraction patterns both of the

Table 3
Structure analysis by neutron diffraction of the $ZrVCo$ and $ZrVNi$ hydrides

Hydrides	Lattice parameters	Atom	x	y	z	Overall B (\AA^2)	Occupancy
C14	$a=5.4034(1)$	Zr(4f)	0.333	0.667	0.061(1)	0.20(5)	0.166
	$c=8.8243(2)$	Co(2a)	0.00	0.00	0.00	0.20(5)	0.026(1)
		V(2a)	0.00	0.00	0.00	0.20(5)	0.057(1)
		Co(6h)	0.849(2)	0.699(2)	0.25	0.20(5)	0.112(2)
		V(6h)	0.849(2)	0.699(2)	0.25	0.5(1)	0.138(2)
		D1(24I)	0.047(7)	0.337(7)	0.568(7)	0.5(1)	0.266(4)
		D2(12k)	0.456(7)	0.911(7)	0.630(7)	0.5(1)	0.141(4)
		D3(6h)	0.460(7)	0.920(7)	0.25	0.5(1)	0.086(4)
	D4(6h)	0.191(7)	0.382(7)	0.25	0.5(1)	0.049(4)	

Reliability factor: $R=0.09$

Refined formula: $ZrV_{1.17}Co_{0.83}D_{3.26}$

$\Delta V/V=20.8\%$

C14	$a=5.3955(1)$	Zr(4f)	0.33	0.667	0.066(1)	0.188(5)	0.166
	$c=8.8023(2)$	Ni(2a)	0.00	0.00	0.0	0.50(5)	0.032(1)
		V(2a)	0.00	0.00	0.0	0.50(5)	0.051(1)
		Ni(6h)	0.838(5)	0.676(5)	0.25	0.28(5)	0.128(2)
		V(6h)	0.0838(5)	0.676(5)	0.25	0.28(5)	0.122(2)
		D1(24I)	0.069(4)	0.356(7)	0.563(3)	1.5(1)	0.252(4)
		D2(12k)	0.482(28)	0.965(28)	0.627	1.5(1)	0.046(4)
		D3(6h)	0.470(7)	0.940(7)	0.25	1.5(1)	0.144(4)
ZrNiDx	$a=3.5263(4)$	D4(6h)	0.180	0.360	0.25	1.5(1)	0.016(6)
	$b=10.4839(16)$	Zr(4f)	0.0	0.434(1)	0.25	0.2	0.50
	$c=4.3083(6)$	Ni(2a)	0.0	0.137(1)	0.25	0.5	0.50
		D1(24I)	0.00	0.954(3)	0.00	3.0(9)	0.293(14)
	D2(24I)	0.00	0.305(1)	0.526(2)	0.5(3)	0.966(26)	

Reliability factor: $R=0.09$

Refined formula: $ZrV_{1.04}Ni_{0.96}D_{2.75}$ and $ZrNiD_{2.52}$

$\Delta V/V=19.4$ and 19.4%

ZrVCo and ZrVNi deuterides reveal that the original structure of the parent compounds with C14 type was kept after hydrogenation. Conversely, the neutron diffraction pattern of the ZrTiNi deuteride is far from being so well resolved since a very marked tendency to amorphisation is pointed out. In fact this diffuse scattering prevents application of any conventional refinement procedure. So, to further study in detail this deuteride, the particularly high reaction to hydrogen of the starting compound must be accounted for a careful management of the reaction.

A typical neutron diffraction pattern of the ZrVCoD_x compound is shown in Fig. 2. The results of the profile method refinements applied to the two first deuterides are reported in Table 3. The distribution of the hydrogen (deuterium) atoms within the interstitial sites, reveals preferential occupancies in the ZrVNi as well as in the ZrVCo hydrides. The refined amounts of absorbed hydrogen are, respectively, of 2.75 and 3.26 for the Ni and Co compounds. These numbers agree well with the experimental ones for the latter compound, but it is much less than experimentally for the former sample, which is a diphasic material with a Zr-rich phase that should absorb the difference amount. An estimate of the absorbed amount of the ABH₃ normalised by the effective number of metal atom consideration to the refined amount of this compound, makes quite coherent the estimated and the refined hydrogen amounts to be present in ZrVNiH_x.

In spite of unexpectedly lower cell parameters for ZrVCo, reference to ZrVNi (since the atomic radius r_{Co} is larger than r_{Ni} , moreover the latter element being more substituted by the bigger V in the Co compound!), more hydrogen appears to be stabilised under normal conditions in the cobalt compound. A detailed analysis of the structures reveals that the D1(24l) and D2(12k) sites exhibit randomly more attractive neighbourhood (more V atoms, e.g. the 2a site) in the cobalt compound than in the nickel one. Thus, the occupation numbers of the large multiplicity sites D1 (24l) and D2 (12k) sites are larger (at least equal) in ZrVCo than in ZrVNi, for a total correspondingly larger amount of absorbed hydrogen. This is well supported by an effectively larger increase of the cell parameters of the corresponding hydrides: $V_{\text{ZrVCo-H}} > V_{\text{ZrVNi-H}}$.

4. Conclusion

The ZrVCo, ZrVNi and ZrTiNi compounds were found to crystallise in the hexagonal C14-type Laves phase structure type. Refinement of the crystal structure of these compounds, based on neutron diffraction data, allows to confirm the structure-type and to quantify the effective metal atom repartition. However, relatively small but significant departure from the initial composition has been found. In all the cases, the ternary intermetallics have been

found to be more M'-poor (M'=Co, Ni) than expected. The M' element (end of the 3d series) appears to form less strong bonds when occupying the 2a position than the 6h ones on which M (Ti, V) and M' are more equally distributed. Rather large amounts of extra phases are formed with the ZrVNi compound which was found to be the closest to the 1-1-1 composition. ZrTiNi appears as a titanium-rich compound where the excess of titanium is distributed in both the A-(4f) position (slight proportion of Ti) and the B-(2a and 6h) positions (major proportion of Ti).

After hydrogenation, the C14-type of ZrMM' compounds keep the same structure. Analysis of the crystal structure reveals that the deuterium atoms are distributed in four different A2B2 interstitial sites in agreement with Ref. [1]. The total hydrogen content was refined to be very close to the initial composition as measured before on the bulk materials. The distribution of the deuterium (hydrogen) atoms within the interstitial sites reveals preferential site occupancy effects, that are shown to be dependent on the nature and may be the size of the next neighbour metal atoms [2].

It fact, slight changes in the nature and the proportions of B metals (M and M') can affect not only the relative stability of the formed phases, but also their distribution between the different metal atom position in the main one of C14 type. Consequently, the hydrogen absorption parameters of the materials can be made very sensitive to somewhat limited changes of proportion operated when selecting the alloyed elements.

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