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Study of the system $Zr(Cr_{0.8-x}Co_xV_{0.2})_2$–$H_2$

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Abstract

Alloys of composition $Zr(Cr_{0.8-x}Co_xV_{0.2})_2$ have been synthesised with the C14-type Laves phase. They are very active and readily absorb large amounts of hydrogen. The effects of the $(Co_xV_{0.2})/(Cr_{0.8-x})$ substitution have been studied with regard to alloy and hydride stability and maximum hydrogen content.

Keywords: $Zr(Cr_{0.8-x}Co_xV_{0.2})_2$; Ternary hydrides; *P–c–T* diagrams; Hydrogen storage

1. Introduction

Many of the Laves phase alloys exhibit excellent hydrogen sorption properties. Theoretically they can absorb up to 6 H/formula unit (f.u.) for the C14 and C15 structured compounds [1].

The stoichiometric compound $ZrCr_2$ can be stabilised in either of the C14 or C15 types. At room temperature, it absorbs up to 3.4 H/f.u. for the former [2], and 4 H/f.u. for the latter [3]. Although it exhibits such a good hydrogen storage capacity, it cannot be used for practical applications because it has too high stability; at 323 K, the equilibrium pressure is only 1.2 kPa [3].

However, a partial substitution of chromium by less hydrogen attractive elements may strongly modify the dissociation pressure of the corresponding hydride. In the recent past, several studies have been devoted to these substitutions: vanadium [4,5], iron [3,6–11], cobalt [3,12], nickel [11,13,14], copper [15], aluminium [16], silicon and germanium [17]. A parallel question concerned the phase stability in the systems $Zr(Cr_{1-x}M_x)_2$ with M = Mn, Fe, Co, Ni, Cu [18].

The aim of this study was to synthesise substituted compounds having the C14-type structure, and from absorption–desorption isotherms, determine the reversible hydrogen capacity.

2. Experimental details

The starting elements (99.9% purity) were melted under highly pure argon atmosphere (99.999% purity) by using the h.f. induction furnace technique in a water-cooled copper crucible. The alloys were crushed in a stainless steel mortar and then 200 μm mesh sieved. In order to synthesise the hydrides with the maximum hydrogen content, the fine powders were placed into glass tubes, then introduced into a stainless steel autoclave dedicated to work up to 10 MPa hydrogen gas pressure and 800°C. After several evacuations of the reactor and H_2 rinsing cycles, hydrogen gas was admitted at 0.1 MPa pressure. Activation of the samples was achieved during the first hydridation cycle, by smoothly increasing temperature until hydrogen absorption occurred. Then the reactor was evacuated (primary vacuum) and the sample was cooled to room temperature. This operation was repeated again, but hydrogen gas pressure was finally increased to some megapascals in order to reach the maximum hydrogen content when the sample was cooled to room temperature. The hydrogen uptake was determined from the difference in weight before and after the charging procedure.

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All the samples—alloys and hydrides—were systematically analysed by the powder diffraction technique using a Philips diffractometer (Cu Kα $\lambda = 1.5418$ Å), equipped with a backscattering graphite monochromator.

The pressure–composition isotherms (P–c–T) were measured over the temperature range 20–180°C, by using either a conventional constant volume apparatus [19] or a thermogravimetric system [20].

3. Results and discussion

3.1. Guideline for substitutions

As vanadium is a hydrogen attractive element, ZrV_2 absorbs a markedly large amount of hydrogen, up to 5.2 atom. H/f.u. [3], and the dissociation plateau pressure at room temperature is rather low ($P \approx 10^{-3}$ MPa). Indeed, substitution of chromium by vanadium must increase the hydrogen capacity and decrease the plateau pressure at room temperature.

On the contrary, Shaltiel and al. [3] have found that the substitution of chromium by cobalt in $ZrCr_2$, decreases the hydrogen capacity and increases the plateau pressure.

From the systematic study of the structure stability of the systems $Zr(Cr_{1-x}M_x)_2H_y$, where M is a 3d element or molybdenum [21], we have confirmed the opposite effects of the two substitution elements V and Co. Such a phenomenon has been previously observed and quantified in the parent series $Zr(Mn_{1-x}M_x)_2H_y$ [22]. It has been correlated to the continuous but opposite effects on the cell volume of the two elements V and Co, and the composition relative to Cr.

Depending on the rate of substitution, combination of these two elements should provide interesting trends, i.e. a good hydrogen storage capacity and a substantial increase of the equilibrium plateau pressure. In this paper, we focus on the properties of the ternary hydrides where chromium is substituted by selected amounts of both vanadium and cobalt.

3.2. Structural parameters

The as-cast alloys of general formula $Zr(Cr_{0.8-x}Co_xV_{0.2})_2$ crystallise in the C14 structure type. The X-ray diagrams show some weak extra peaks (Figs. 1 and 2).

Table 1 reports the refined cell parameters measured by X-ray diffraction and the corresponding maximum hydrogen uptake.

It is known that the Laves phase $ZrCr_2$ crystallises in the hexagonal C14 or C15 type, while ZrV_2 exclusively crystallises in the cubic C15 type [3]. In the previous study of the system $Zr(Cr_{1-x}V_x)_2$ [19], we found that the composition of the structure transition C14→C15 is close to $x = 0.1$. Moreover, the pseudobinary alloys $Zr(Cr_{1-x}Co_x)_2$ crystallise in the C14-type structure in the range of $0 \leq x \leq 0.5$ [3]. So, by substitution of some Cr by $(Co_xV_{0.2})$ for $x = 0.4$ and 0.5, we expect to form a cubic C15 structure. However, analysis of the as-cast samples by X-ray diffraction reveals a hexagonal type of structure. A similar result has been reported by Shaltiel et al. [3] in their study of the system $Zr(V_{1-x}Co_x)_2$. For $Zr(V_{1-x}Co_x)_2$ compositions in the range $0.1 \leq x \leq 0.6$, a C14-type structure was found. Table 2 reports the heat of formation of the binary systems $Zr(Cr–V–Co)_2$ calculated using the Miedema model [23]. It should be noted that the heat of formation of a substituted compound is smaller than that of the prototype $ZrCr_2$ (C14 structure), except when only the more electropositive vanadium is substituted for chromium. From the rules established in Ref. [24] on structure stability, a more negative heat of formation compared with $ZrCr_2$ corresponds to hexagonal structures.

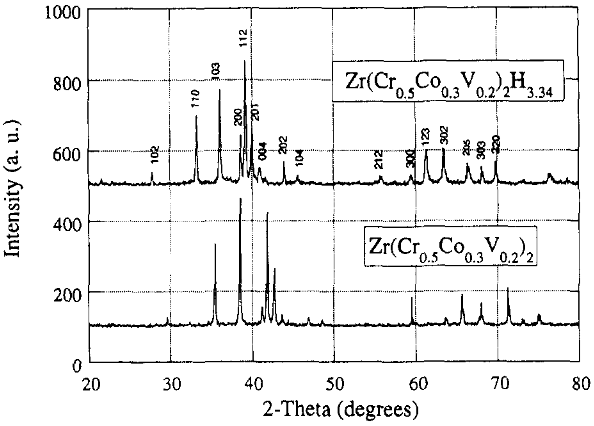

Fig. 1. Powder X-ray diffraction patterns of $Zr(Cr_{0.5}Co_{0.3}V_{0.2})_2$ as-cast alloy and its hydride recorded at $\lambda = 1.5418$ Å.

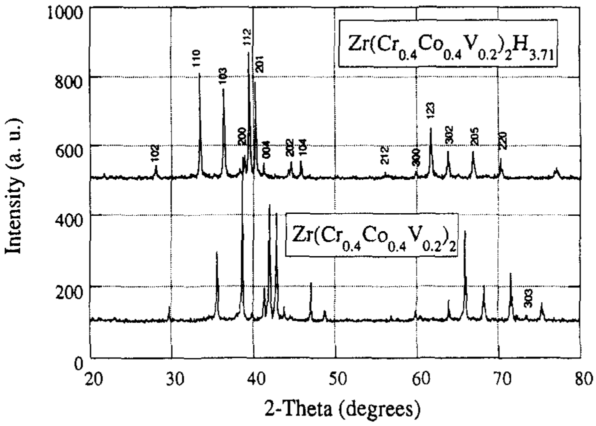

Fig. 2. Powder X-ray diffraction patterns of $Zr(Cr_{0.4}Co_{0.4}V_{0.2})_2$ as-cast alloy and its hydride recorded at $\lambda = 1.5418$ Å.

Table 1
Cell parameters and hydrogen maximum capacity of alloys and hydrides synthesised in the C14-type structure for the as-cast samples

	Alloys			Hydrides				
	a (Å)	c (Å)	V (Å^3)	N_H	a (Å)	c (Å)	V (Å^3)	$\Delta V/V$ (%)
$ZrCr_2$	5.102(1)	8.294(2)	186.97	3.44	5.385(1)	8.830(2)	221.74	18.60
$Zr(Cr_{0.5}Co_{0.3}V_{0.2})_2$	5.059(1)	8.296(2)	183.90	3.34	5.382(1)	8.811(2)	221.06	20.21
$Zr(Cr_{0.4}Co_{0.4}V_{0.2})_2$	5.042(1)	8.260(2)	181.87	3.71	5.366(1)	8.782(2)	218.97	20.40

Table 2
Heats of formation using the Miedema model

Compounds	ΔH (kJ mol^{-1} of alloy)
$ZrCr_2$	−16.77(1)
$Zr(Cr_{0.8}V_{0.2})_2$	−11.41(1)
$Zr(Cr_{0.7}Co_{0.3})_2$	−27.73(1)
$Zr(Cr_{0.6}Co_{0.4})_2$	−31.62(1)
$Zr(Cr_{0.5}Co_{0.3}V_{0.2})_2$	−24.37(1)
$Zr(Cr_{0.4}Co_{0.4}V_{0.2})_2$	−28.07(1)

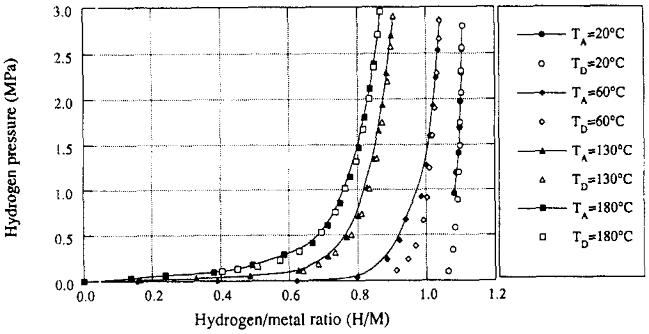

Fig. 3. Pressure–composition isotherms recorded in the temperature range 20–180°C for the $Zr(Cr_{0.5}Co_{0.3}V_{0.2})_2$–$H_2$ system. Full symbols relate to absorption curves and empty ones to desorption curves.

3.3. *P–c–T diagrams*

Figs. 3 and 4 report some selected isotherms curves measured for two compositions, $Zr(Cr_{0.5}Co_{0.3}V_{0.2})_2H_y$ and $Zr(Cr_{0.4}Co_{0.4}V_{0.2})_2H_y$ respectively.

These isotherms show fairly good hydrogen capacities with the ratio H/M in the range 1.1 to 1.2 at room temperature. Comparison of the two series of plots reveals that the larger the cobalt substitution, the higher are the plateau pressures. Nevertheless, the chosen alloy compositions correspond to a relatively high stability of the parent hydrides. Since the desorption isotherms stop at high H/M values, we were not able to experimentally determine the values of the thermodynamic parameters ΔH and ΔS. We also noticed that the hysteresis phenomenon (absorption–desorption curves) decreases with increasing temperature. At 130°C the two curves are nearly the same.

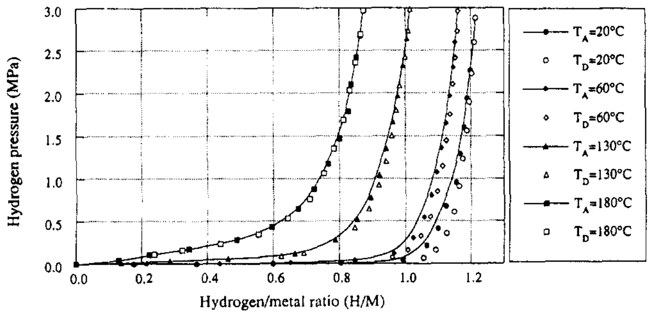

Fig. 4. Pressure–composition isotherms recorded in the temperature range 20–180°C for the $Zr(Cr_{0.4}Co_{0.4}V_{0.2})_2$–$H_2$ system. Full symbols relate to absorption curves and empty ones to desorption curves.

4. Conclusions

Compounds of formula $Zr(Cr_{0.8-x}Co_xV_{0.2})_2$ have been synthesised with the C14 hexagonal type of Laves phases. These alloys readily form ternary hydrides with a good hydrogen capacity (3.5 ± 0.2 H/f.u.). *P–c–T* diagrams reveal a rather high stability of these hydrides close to room temperature. However, at 130°C, the hydrides can be fully desorbed under normal pressure. The alloys seem to be good candidates for a reversible hydrogen storage. In order to use such types of alloy as negative electrodes for batteries, higher plateaux pressures must be achieved.

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