



# Effect of substitution on F.C.C. and B.C.C. hydride phase formation in the $\text{TiCr}_2\text{-H}_2$ system

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## Abstract

Phase transformations of  $\text{TiCr}_{1.8}$ ,  $\text{ZrCr}_2$ ,  $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Cr}_{1.8}$ ,  $\text{Ti}_{0.7}\text{Zr}_{0.3}\text{Cr}_{1.8}$  and  $\text{TiCr}_{1.7}\text{Fe}_{0.1}$  intermetallic compounds during their interaction with hydrogen at pressures from 1 to 200 MPa and temperatures of 195 and 295 K are studied. Formation of three types of hydride phases are stated by X-ray diffraction method: (I) hexagonal Laves phase preserving the  $\text{MgZn}_2$  structure of the initial intermetallic, (II) F.C.C. phase of  $\text{CaF}_2$  structure type which can be considered as a solid solution in the pseudobinary  $\text{TiH}_2\text{-CrH}_2$  system and (III) B.C.C. phase with W-structure type—high temperature  $\beta$  solution in the metallic Ti–Cr system stabilized by hydrogen. It was shown that partial substitution of titanium by zirconium up to 30% did not change the general scheme of phase transformations, while the addition of iron suppressed the formation of phases (II) and (III) in all experimental pressure and temperature ranges. The conditions of formation, X-ray parameters and thermal stability have been determined for synthesized hydride phases in the  $\text{TiCr}_2\text{-H}_2$  and substituted systems. © 1999 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

## 1. Introduction

The formation of  $\text{CaF}_2$ -type F.C.C. (face centered cubic) hydride at hydrogen interaction with  $\text{TiCr}_2$  hexagonal Laves phase in high pressure and low temperature ranges was found by J.R. Johnson and co-workers [1]. Later, it was shown in our work [2] that this phase transformation took place for both cubic C15 and hexagonal C14 modifications of the  $\text{TiCr}_2$  compound. Besides, the study of thermal desorption of the F.C.C. hydrides allowed us to establish the existence of an intermediate hydrogen containing phase with W-type B.C.C. (base centred cubic) lattice. In the present work we consider the effect of alloy component substitution on the regularities of the F.C.C. and B.C.C. hydride formation in the  $\text{TiCr}_2$ -based systems.

## 2. Experimental details

In this work we studied the  $\text{TiCr}_{1.8}$ ,  $\text{ZrCr}_2$ ,  $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Cr}_{1.8}$ ,  $\text{Ti}_{0.7}\text{Zr}_{0.3}\text{Cr}_{1.8}$  and  $\text{TiCr}_{1.7}\text{Fe}_{0.1}$  alloys pre-

pared by arc melting in an inert atmosphere. All samples represented single phase intermetallic compounds of C14 ( $\text{MgZn}_2$ -type) structure (Table 1). The procedure of hydride synthesis at high pressures and their analysis were described previously [2, 3]. In order to stabilise high pressure hydride phases, the samples were frozen under hydrogen pressure by liquid nitrogen, then passivated at 80 K by air or  $\text{SO}_2$ . Properties and structure of hydrides with intermediate composition were studied during their prolonged exposure in air after stabilisation and by step-

Table 1  
Structure parameters of initial intermetallic compounds

Compound	Structure type	Lattice parameters		
		<i>a</i> (nm)	<i>c</i> (nm)	<i>V</i> (nm <sup>3</sup> )
$\text{TiCr}_{1.8}$	$\text{MgZn}_2$	0.4912 (1)	0.7943 (4)	0.1660
$\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Cr}_{1.8}$	$\text{MgZn}_2$	0.4951 (1)	0.7991 (5)	0.1696
$\text{Ti}_{0.7}\text{Zr}_{0.3}\text{Cr}_{1.8}$	$\text{MgZn}_2$	0.5003 (2)	0.8073 (5)	0.1750
$\text{TiCr}_{1.7}\text{Fe}_{0.1}$	$\text{MgZn}_2$	0.4898 (1)	0.7969 (4)	0.1656
$\text{ZrCr}_2$	$\text{MgZn}_2$	0.5088 (2)	0.8252 (5)	0.1848

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by-step thermal desorption in vacuum at temperature up to 1200 K.

### 3. Results and discussion

The ‘pressure-composition’ isotherms measured for the studied samples in the pressure range from 0.1–200 MPa are presented in Figs 1, 2 and 3.

Hydrogen absorption at 293 K was completely reversible for all  $\text{TiCr}_2$ -based compounds. Corresponding curves had no particular parts like plateaus for phase transformations. The temperature decrease to 195 K did not lead to significant changes in sorption capacity and reaction reversibility for the  $\text{Ti}_{0.7}\text{Zr}_{0.3}\text{Cr}_{1.8}$  and  $\text{TiCr}_{1.7}\text{Fe}_{0.1}$  alloys. X-Ray analysis of the  $\text{Ti}_{0.7}\text{Zr}_{0.3}\text{Cr}_{1.8}\text{H}_{3.5}$ ,  $\text{TiCr}_{1.7}\text{Fe}_{0.1}\text{H}_{3.3}$  and  $\text{ZrCr}_2\text{H}_{4.5}$  hydrides synthesized at a pressure of 200 MPa and a temperature of 195 K and then passivated, showed that reaction products were single phase and preserved the hexagonal  $\text{MgZn}_2$  structure of the initial compounds (Table 2).

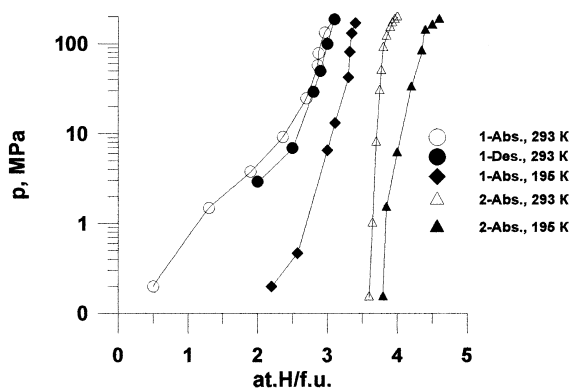


Fig. 1. ‘Pressure-Composition’ isotherms for the  $\text{TiCr}_{1.7}\text{Fe}_{0.1}\text{-H}_2$  and  $\text{ZrCr}_2\text{-H}_2$  systems.

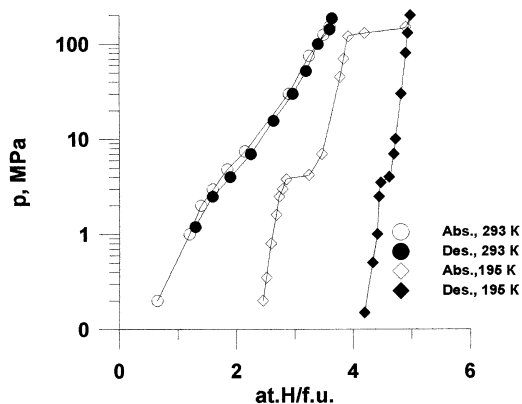


Fig. 2. ‘Pressure-Composition’ isotherms for the  $\text{TiCr}_{1.8}\text{-H}_2$  system.

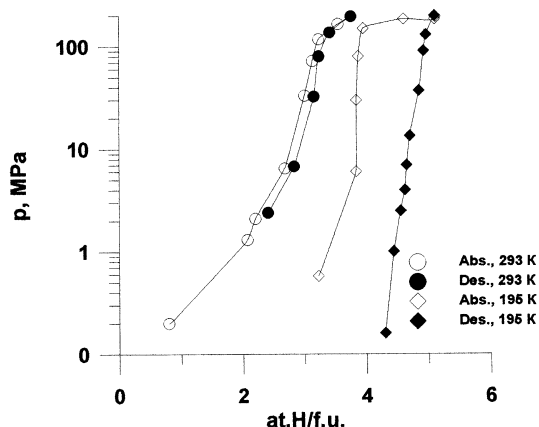


Fig. 3. ‘Pressure-Composition’ isotherms for the  $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Cr}_{1.8}\text{-H}_2$  system.

In the  $\text{TiCr}_{1.8}\text{-H}_2$  and  $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Cr}_{1.8}\text{-H}_2$  systems, a considerable additional hydrogen uptake proceeded at this temperature in pressure range above 120–150 MPa. This reaction was very slow and characterized by the plateaus of 1 atom H per formula unit at the absorption isotherms (Figs 2 and 3). It is necessary to note that these plateaus were not reproduced at hydrogen desorption indicating the irreversibility of the phase transformation.

Structure data confirm qualitative changes in these systems (Table 2). While the hydrides synthesized at room temperature preserved  $\text{MgZn}_2$  structure type like the above described compounds, the hydrogen absorption at low temperature and high pressures resulted in drastic reformation of the intermetallic matrix from hexagonal to F.C.C. fluorite-type structure. The comparison of the high-pressure hydrides of the  $\text{TiCr}_{1.8}$  and Zr-substituted  $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Cr}_{1.8}$  alloys showed that there was no noticeable difference in structure parameters between these phases.

The study of stability under ambient conditions of the synthesized hydrides revealed that  $\text{TiCr}_{1.8}\text{H}_{4.5}$  lost 70% of absorbed hydrogen during 10 days. This fact led to the conclusion that the fluorite-type phase was metastable, and decomposes with formation of new W-type phase with B.C.C. coordination of metallic atoms. Meanwhile, 10% Zr-substituted high-pressure hydride did not change its phase composition, even during 60-days of exposure at normal conditions. The hydrogen loss in this case did not exceed 24% and was caused only by hydrogen desorption from  $\text{MgZn}_2$ -type phase (Table 3). At the same time, heating in vacuum for both  $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Cr}_{1.8}\text{H}_{5.1}$  and  $\text{TiCr}_{1.8}\text{H}_{4.5}$  hydrides was accompanied by similar phase transformations: the hydrogen release had an intermediate stage of formation of W-type phase. We have to note that complete hydrogen desorption at 1000–1200 K resulted in restoration of initial C14 structure for both compounds.

Table 2  
Structure parameters of synthesized hydrides

No.	Hydride composition after passivation	Structure type	Lattice parameters		
			<i>a</i> (nm)	<i>c</i> (nm)	$\Delta V/V_0(\%)$
1*	TiCr <sub>1.8</sub> H <sub>3.40</sub>	MgZn <sub>2</sub>	0.5210 (4)	0.8506 (8)	20.5
2**	TiCr <sub>1.8</sub> H <sub>4.50</sub>	MgZn <sub>2</sub>	0.5147 (3)	0.8486 (5)	17.1
		CaF <sub>2</sub>	0.4259 (6)		30.3
3**	Ti <sub>0.9</sub> Zr <sub>0.1</sub> Cr <sub>1.8</sub> H <sub>5.10</sub>	MgZn <sub>2</sub>	0.5248 (2)	0.8668 (6)	22.0
		CaF <sub>2</sub>	0.4295 (5)		30.7
4**	Ti <sub>0.7</sub> Zr <sub>0.3</sub> Cr <sub>1.8</sub> H <sub>3.50</sub>	MgZn <sub>2</sub>	0.5314 (2)	0.8734 (6)	22.0
5**	TiCr <sub>1.7</sub> Fe <sub>0.1</sub> H <sub>3.30</sub>	MgZn <sub>2</sub>	0.5186 (1)	0.8545 (3)	20.2
6**	ZrCr <sub>2</sub> H <sub>4.50</sub>	MgZn <sub>2</sub>	0.5505 (3)	0.8989 (6)	27.9

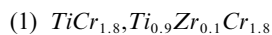
Synthesis conditions: \* –  $T = 293$  K,  $P = 200$  MPa; \*\* –  $T = 195$  K,  $P = 200$  MPa.

Table 3  
Structure parameters of desorption products

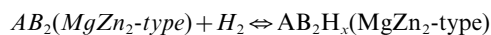
Composition	Structure type	Lattice parameters		Composition of initial hydride and desorption conditions
		<i>a</i> (nm)	<i>c</i> (nm)	
TiCr <sub>1.8</sub> H <sub>1.4</sub>	MgZn <sub>2</sub>	0.4976 (2)	0.8190 (5)	TiCr <sub>1.8</sub> H <sub>4.50</sub> , $T = 293$ K, $P = 0.1$ MPa, 10 days
TiCr <sub>1.8</sub> H <sub>1.2</sub>	W	0.3091 (5)		
	MgZn <sub>2</sub>	0.4989 (3)	0.8093 (5)	TiCr <sub>1.8</sub> H <sub>4.50</sub> , $T = 373$ K, $P = 0.01$ MPa
Ti <sub>0.9</sub> Zr <sub>0.1</sub> Cr <sub>1.8</sub> H <sub>3.9</sub>	W	0.3087 (6)		
	MgZn <sub>2</sub>	0.5089 (4)	0.8294 (5)	Ti <sub>0.9</sub> Zr <sub>0.1</sub> Cr <sub>1.8</sub> H <sub>5.10</sub> , $T = 293$ K, $P = 0.1$ MPa, 60 days
Ti <sub>0.9</sub> Zr <sub>0.1</sub> Cr <sub>1.8</sub> H <sub>1.6</sub>	CaF <sub>2</sub>	0.4274 (6)		
	MgZn <sub>2</sub>	0.4977 (4)	0.8175 (5)	Ti <sub>0.9</sub> Zr <sub>0.1</sub> Cr <sub>1.8</sub> H <sub>5.10</sub> , $T = 423$ K, $P = 0.01$ MPa
	W	0.3096 (5)		

#### 4. Conclusions

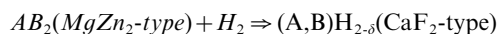
The studies carried out in this work allowed us to propose the following phase transformation scheme for TiCr<sub>2</sub>-based systems.



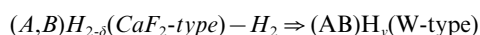
$$T = 293 \text{ K}, P \leq 200 \text{ MPa}$$



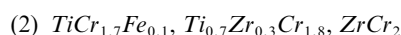
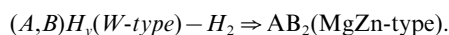
$$T = 195 \text{ K}, P \geq 120 \text{ MPa}$$



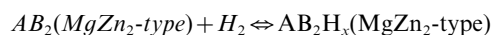
$$T = 373 - 423 \text{ K}, P = 0.01 \text{ MPa}$$



$$T > 973 \text{ K}, P = 0.01 \text{ MPa}$$



$$T = 195 - 293 \text{ K}, P \leq 200 \text{ MPa}$$



The F.C.C. (A,B)H<sub>2-δ</sub> phases of CaF<sub>2</sub> structure type formed in the TiCr<sub>1.8</sub>-H<sub>2</sub> and Ti<sub>0.9</sub>Zr<sub>0.1</sub>Cr<sub>1.8</sub>-H<sub>2</sub> systems were isostructural to binary titanium (TiH<sub>2</sub>) and chromium (CrH<sub>2-δ</sub>) hydrides. Taking into account known structure data on the analogous hydride phase obtained for cubic TiCr<sub>1.8</sub> [1], the high-pressure phases synthesized in this work could be considered as the pseudobinary hydride (Ti,Cr)H<sub>2-δ</sub> and (Ti,Zr,Cr)H<sub>2-δ</sub> with statistic distribution of Ti, Zr and Cr atoms.

The (A,B)H<sub>y</sub> phases found at thermal desorption of (Ti,Cr)H<sub>2-δ</sub> and (Ti,Zr,Cr)H<sub>2-δ</sub> dihydrides were isostructural to high-temperature solid solution with B.C.C. W-type lattice in binary Ti–Cr system. The comparison of lattice parameters of (A,B)H<sub>y</sub> ( $a = 0.308$ – $0.310$  nm) and stoichiometric Ti<sub>34</sub>Cr<sub>66</sub> solid solution ( $a = 0.302$ –

0.303 nm [4]) indicated the existence of dissolved hydrogen in obtained intermediate phases that stabilize this structure type.

The above mentioned regularities of phase transformations accompanied by reformation of metallic matrix from hexagonal (MgZn<sub>2</sub>-type) to F.C.C. (CaF<sub>2</sub>-type) and B.C.C. (W-type) are unusual for intermetallic-hydrogen systems. Even slight variation in the chemical composition of the initial compound significantly influences these transformations. Thus, the substitution of 5% of Cr by Fe completely suppressed the formation of the fluorite-type phase. In the case of the Zr-containing compounds, a similar effect took place at substitution of 30% of Ti. It is necessary to note that these phenomena cannot be explained only by crystallographic par-

ticularities of substituted alloys because they have the same structure and very close values of lattice periods, i.e., interatomic distances and dimension of interstitial sites. Probably, the difference in behavior of studied systems is mainly due to variations in electronic structure of substituted compounds.

### References

- [1] Johnson JR, Reilly JJ et al. *J Less-Common Metals* 1982;88:107–14.
- [2] Klyamkin SN, Demidov VA, Verbetsky VN. *Vestnik MGU, Khimiya* 1993;34:412–16.
- [3] Klyamkin SN, Verbetsky VN. *JALCOM* 1993;194:41–5.
- [4] Cuff FB, Grant NJ, Floe CF. *J Metals* 1952;4(8):848–52.