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High pressure hydride phases formation in Ti_2Ni- and $MoSi_2$-type intermetallic compounds

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Abstract

The effects of crystal structure and chemical composition of some Hf_2Me intermetallic compounds on their behavior at high hydrogen pressure have been studied. It was shown for Hf_2Fe that two ways of hydrogenation reaction were possible depending on the synthesis conditions. New hydrogen-rich hydrides have been obtained in all studied systems and characterized by the X-ray diffraction method. Some speculations on hydrogen localization in high-pressure phases have been proposed.

Keywords: Intermetallic hydrides; High pressure phases

1. Introduction

The present investigation is based on the following assumption (proposed by the authors in Ref. [1]). Intermetallic compounds (IMC), having a specific crystal structure, form in hydrogen atmosphere hydride phases which can be considered as matrices of zeolite or chlatrate type for additional hydrogen absorption. Under some conditions contributing to more profound reaction, especially at high pressure and low temperature, hydrogen intercalation in these phases might result in supersaturated hydrides characterized by short H–H interatomic distances, i.e., some ‘‘hydrogen clusters’’. In order to test this assumption we have chosen Hf_2Me (Me=Fe, Cu, Pd and $Ni_{0.5}Mn_{0.5}$) IMC of two structure types: Ti_2Ni and $MoSi_2$.

2. Experimental details

The alloys have been prepared by standard arc melting in inert atmosphere from pure metals. In the case of $Hf_2Ni_{0.5}Mn_{0.5}$ the commercial alloy NiMn has been used. The interactions in the metal–hydrogen systems have been studied in the pressure range up to 2000 atm at temperatures from 195 to 300 K by means of an original method for precise P–V–T measurements described in Ref. [2].

All hydride phases obtained, including unstable ones fixed using special treatments, have been analyzed by X-ray diffraction and high temperature vacuum desorption.

3. Results and discussion

For all compounds of $MoSi_2$ structure type the formation of two hydride phases was shown (Table 1). The first one, close to AB_2H_3 composition, preserved a tetragonal IMC lattice expanded by 10–11% In the second one (high pressure phase), hydrogen content increase to 5–5.5 at. H/f.u., led to a orthorhombic distortion of the lattice along with volume expansion of 22–24%. The chemical composition of the initial IMC influenced only the ratio of the above mentioned phases in hydrogenation products, i.e., the position of phase area limits in the P–C–T diagrams of these systems. This fact was in good correlation with appropriate isotherms of hydrogen absorption presented previously [3].

Other regularities have been revealed for Ti_2Ni-type compounds. Even phases with maximum hydrogen content, $Hf_2FeH_{5.2}$ and $Hf_2Ni_{0.5}Mn_{0.5}H_{4.9}$, preserved the cubic structure with volume expansion close to the limiting values for $MoSi_2$-type compounds (Table 2). Besides, chemical composition had a dramatic effect on the behaviour of IMC with Ti_2Ni-type structure at hydrogen absorption.

In the Hf_2Fe–H_2 system two reaction paths have been established (Fig. 1). During ‘‘classic’’ synthesis (at hydro-

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Table 1
X-ray characteristics of hydrides in the Zr_2Pd, Hf_2Pd and Hf_2Cu systems

IMC	A_2B (t)		A_2BH_3 (t)			$A_2BH_{5.5\text{-}6.0}$ (o)			
	a (Å)	c (Å)	a (Å)	c (Å)	$\Delta V/V_0$ (%)	a (Å)	b (Å)	c (Å)	$\Delta V/V_0$ (%)
Zr_2Pd	3.306	10.832	3.389	11.417	10.7	3.387	3.801	11.250	22.4
Hf_2Pd	3.260	10.893	3.288	11.586	9.1	3.063	4.061	11.181	20.5
Hf_2Cu	3.166	11.109	3.226	11.727	9.6	3.193	3.855	11.025	21.8

Table 2
Synthesis parameters, hydrogen content and X-ray characteristics of hydride phases in the $Hf_2Fe–H_2$ and $Hf_2Ni_{0.5}Mn_{0.5}–H_2$ systems

Hf_2Fe (a_0=12.03 Å)							
		Hydride (1)			Hydride (2)		
T (K)	P (atm)	(at.H/f.u.)	a (Å)	$\Delta V/V_0$ (%)	(at.H/f.u.)	a (Å)	$\Delta V/V_0$ (%)
295	10	4.6	12.77	19	5.0	12.89	23
240	5	-	-	-	5.3	-	-
295	2000	5.2	-	-	5.6	-	-
195	2000	5.6	-	-	6.0	-	-
295	1[a]	4.8	12.77	19	5.2	12.89	23
$Hf_2Ni_{0.5}Mn_{0.5}$ (a_0=11.98 Å)							
T (K)	P (atm)	(at.H/f.u.)		a (Å)		$\Delta V/V_0$ (%)	
240	5	4.9		12.86		24	
195	2000	5.2		-		-	
295	1[a]	4.9[b]		12.86[b]		24[b]	

[a] desorption after treatment at 195 K, 2000 atm.
[b] the same for all synthesis conditions.

gen pressure of 30–50 atm and room temperature) when the reaction proceeded practically instantly, a $Hf_2FeH_{4.6}$ hydride was obtained that had been described in Ref. [4]. This hydride was characterized by a hydrogen content increase up to 5.6 at.H/f.u. at P=2000 atm and T=195 K. However we failed to stabilize this maximum composition and pressure release led to hydrogen desorption to 4.8 at.H/f.u.

When the first synthesis proceeded under mild conditions (240 K and ''hydrogen titration'') hydrogen content in the hydride phase increased by 0.4–0.5 at.H/f.u. in comparison with ''classic'' synthesis products and reached 6.0 H/Hf_2Fe at 2000 atm.

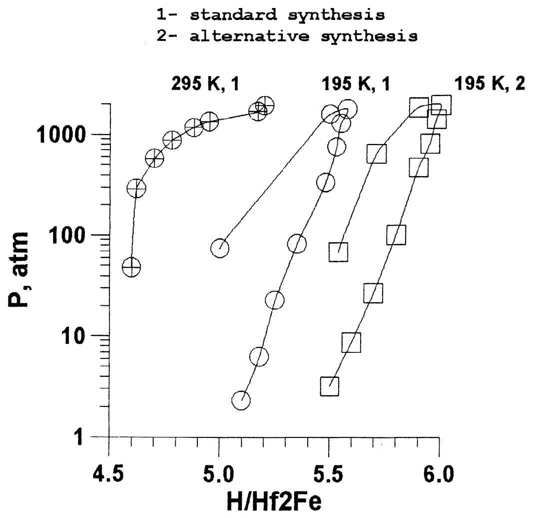

Fig. 1. P-C-isotherms in the $Hf_2Fe–H_2$ system.

It is necessary to note that this composition variation did not change during sample cycling in all the experimental pressure and temperature range. Furthermore, according to thermodesorption studies both hydride phases had the same thermal stability and desorbed hydrogen in vacuum only at heating to 550–600 K.

The substitution of iron in Hf_2Fe by nickel and manganese, where the latter was a stabilizer of Ti_2Ni structure type, resulted in considerable change of hydride formation. First, both synthesis methods gave identical products: $Hf_2Ni_{0.5}Mn_{0.5}H_{4.9}$. Second, pressure rise up to 2000 atm and temperature lowering to 195 K did not have an effect on hydrogen content in the hydride.

Comparison of results obtained in this work and recently published papers [1,3,5] with available literature data on the hydrogen interaction with IMC of these structure types leads us to make some statements, that need however further confirmation.

1. The used experimental methods combining high hydrogen pressure with low temperature allowed us to synthesize new hydride phases considerably exceeding all known analogues by hydrogen content. It could be noted that maximum registered hydrogen absorption reached 6.0 (Hf_2Fe) and even 6.4 at.H/f.u. (Hf_2Cu) and was reversible, but we failed in stabilizing the corresponding phases.

2. The shape of measured isotherms [3,5] showed that

hydrogen absorption in the high pressure range differed significantly for compounds of various structure types. While for Hf_2Fe and $Hf_2Ni_{0.5}Mn_{0.5}$ hydrogen content did not change in the pressure range from 1000 to 2000 atm, i.e., observed values of absorption capacity were close to saturated ones, all $MoSi_2$-type IMC demonstrated noticeable continuous absorption increase exactly at this pressure. This result implies that maximum hydrogen concentration had not been achieved.

3. The phenomenon of formation of two stable hydride phases with a hydrogen content difference of 10% discovered in the $Hf_2Fe–H_2$ system could be explained on the basis of the following notions. ''Extra'' hydrogen atoms in crystal lattice of $Hf_2FeH_{5.2}$ probably occupied interstitial sites that were ''blocked'' in another reaction path. Crystallochemical analysis of this structure type showed that $[Hf_6]$ octahedral positions remaining vacant according to structural studies in Ref. [4] could serve as above mentioned sites. Occupation of these sites should result in hydrogen concentration increase by 0.5 at.H/f.u. We have to note that the sites filling depended perhaps not only on P–T conditions of synthesis but also on the chemical nature of the second component of IMC: the effect detected for Hf_2Fe completely disappeared when iron was substituted by Ni–Mn.

4. The main conclusion that could be reached from crystallochemical analysis is the following. The additional absorption taking place at 2000 atm and 195 K (just in these conditions the hydrides with maximum hydrogen content have been obtained) could not be explained only by filling of the positions partially occupied in low-pressure phases [4,6]. The calculations indicated that the most probable locations of extra hydrogen atoms in $AB_2H_{5.5-6.5}$ phases of $MoSi_2$-type IMC were the B_4A_2 octahedra. As we have already noted in Ref. [1], the occupation of these sites should be accompanied by the orthorhombic distortion of the crystal lattice that was experimentally proved [3]. This distortion should result in formation of a hydrogen sub-lattice in the form of continuous planar layers or one-dimension chains and not in additional isolated sites as was usually observed for low-pressure phases. Such configuration could allow additional hydrogen intercalation at pressure rise owing to condensation of hydrogen atoms in these channels and not by occupation of new crystallographic positions. This speculation correlated with a character of experimental dependence of hydride composition on pressure in the range of 1000–2000 atm as was mentioned above for $MoSi_2$-type IMC.

Ti_2Ni-type IMC could have occupancies of B_4 and AB_3 tetrahedra with effective radii of 0.4–0.5 Å for complementary hydrogen absorption as the pressure increases. It is important to note that regarding the differences mentioned above for Hf_2Fe and $Hf_2Ni_{0.5}Mn_{0.5}$ occupation of these sites depended not only on cavity dimension (since both IMC had close values of lattice parameters) but also on chemical nature of metal atoms neighboring to the interstitial sites, i.e., metal–hydrogen bonding energy.

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