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Pseudobinary intermetallic compounds in Hf_2M'–Hf_2M'' (M', M''=Mn, Fe, Ni, Cu) systems and their interaction with hydrogen at high pressures

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Abstract

Ternary alloys in the Hf_2Ni–Hf_2Mn, Hf_2Ni–Hf_2Fe, Hf_2Ni–Hf_2Cu and Hf_2Fe–Hf_2Cu systems have been prepared and characterised by X-ray diffraction and pressure–composition isotherm measurements. Single phase compounds have been obtained for all Ni-containing alloys with a general composition of $Hf_2Ni_{0.5}M_{0.5}$. These compounds retained the structure type of parent Hf_2M intermetallics: cubic Ti_2Ni type for $Hf_2Ni_{0.5}Fe_{0.5}$ and $Hf_2Ni_{0.5}Mn_{0.5}$ and tetragonal $MoSi_2$ type for $Hf_2Ni_{0.5}Cu_{0.5}$. The new hydrides obtained from ternary intermetallics had the composition of $Hf_2Ni_{0.5}M_{0.5}H_x$ where x=3.1 (M=Cu) and 4.9–5.0 (M=Mn, Fe). Formation of hydride phases from cubic Mn- or Fe-containing compounds occurred without any change in structure type but was accompanied by unit cell volume expansion of 23–24%. In the case of Cu, there was a tetragonal to orthorhombic transformation. An absence of phase transformations in high pressure range of 100 to 2000 atm for new compounds unlike the earlier studied Hf_2M–H_2 systems has to be noted.

Keywords: Intermetallic hydrides; High pressure

1. Introduction

Hf_2M binary intermetallic compounds, where M is a 4d element, crystallise in three structure types, namely: Ti_2Ni (M=Mn, Fe, Co), $CuAl_2$ (M=Ni) and $MoSi_2$ (M=Cu) [1]. According to earlier experimental studies [2] all of them form hydrides with high hydrogen concentrations. Analysis of those intermetallics and hydrides structure and available data on hydrogen localisation [3–5] allowed us to suppose that additional hydrogen intercalation, for example, under high pressure, might lead to formation of new hydrogen-rich phases. This has been experimentally confirmed for Hf_2Fe and Hf_2Cu (as well as for isostructural Hf_2Pd and Zr_2Pd) [6–8]. However, it is not yet quite clear which of the factors, lattice structure or chemical composition, is responsible for the observed high pressure effects. The present work investigates the constitution of ternary $Hf_2M'_{0.5}M''_{0.5}$ alloys (M', M''=Mn, Fe, Ni, Cu) and their interaction with hydrogen at pressures up to 2000 atm.

2. Experimental details

The sample preparation and hydriding techniques have been described in Ref. [9,10]. The hydrogen contents in the hydrides were calculated from the p–V–T measurements under pressure and analysed by high temperature vacuum extraction. In order to retain composition of the high pressure hydrides they have been treated by SO_2. This poisoning procedure is described in Ref. [7].

3. Results and discussion

Single phase ternary alloys have been obtained in all Ni-containing systems. These $Hf_2Ni_{0.5}M_{0.5}$ compounds retained the structure type of the parent Hf_2M intermetallics (Table 1). An interesting feature of a series of Ti_2Ni-type compounds (taking into account known data for binary Hf_2Mn and Hf_2Fe) should be noted. For most

Table 1
X-ray diffraction data for $Hf_2M'_{0.5}M''_{0.5}$ alloys

Alloy composition,	Structure type	Unit cell parameters, nm
$Hf_2Ni_{0.5}Mn_{0.5}$	Ti_2Ni	a=1.1976
$Hf_2Ni_{0.5}Fe_{0.5}$	Ti_2Ni	a=1.2076
$Hf_2Cu_{0.5}Ni_{0.5}$	$MoSi_2$	a=0.3154, c=1.1006
$Hf_2Fe_{0.5}Cu_{0.5}$	Ti_2Ni	a=1.2024
	$MoSi_2$	a=0.3163, c=1.1112

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intermetallic compounds a substitution of one of the components by another element with higher atomic radius leads to an increase in lattice parameters. However, the sequence $Hf_2Mn \rightarrow Hf_2Ni_{0.5}Mn_{0.5} \rightarrow Hf_2Fe \rightarrow Hf_2Ni_{0.5}Fe_{0.5}$ of isostructural binary and pseudobinary Hf_2M compounds demonstrates an opposite trend: unit cell parameter '*a*' increases with decreasing average atomic radius of M-component.

In contrast to the $Hf_2Ni_{0.5}M_{0.5}$ sample, $Hf_2Fe_{0.5}Cu_{0.5}$ was not single phase. According to XRD data both cubic Ti_2Ni-type and tetragonal $MoSi_2$-type phases from parent Hf_2Fe and Hf_2Cu compounds appeared in the alloy. Their lattice parameters indicated a rather limited mutual solubility that agreed with the known constitution of the Fe–Cu binary system [1].

$Hf_2Ni_{0.5}Mn_{0.5}$ and $Hf_2Ni_{0.5}Fe_{0.5}$ reacted with hydrogen at room temperature and low (10 atm) pressures without an incubation period. The hydrides formed in both systems had a hydrogen content close to five atoms per formula unit (Table 2). It should be noted that in the case of the parent Hf_2Fe compound such a high concentration has been obtained only under special conditions, namely a low temperature (240 K) and very slow hydrogenation reaction proceeded by small discrete hydrogen portions ('hydrogen titration') [8]. Another significant distinction between Hf_2Fe and isostructural pseudobinary compounds studied in this work was a complete absence of the high pressure phase transformation. Additional hydrogen absorption at pressures up to 2000 atm did not exceed 0.3 H/A_2B rather than the 1 H atom in the Hf_2Fe.

Substitution of Cu in Hf_2Cu by Ni resulted in a dramatic change in hydrogenation mechanism at low pressures. In contrast to the parent compound, $Hf_2Cu_{0.5}Ni_{0.5}$ interacted with hydrogen only on heating at 400 K. Hydrogen concentrations in the hydride phase formed under those conditions was remarkably lower than earlier observed for both binary compounds: 3.0 H atoms per formula unit instead of 5.0 H/A_2B [5,6]. Moreover, any temperature–pressure variation including cooling to 195 K and pressure rise up to 2000 atm provoked no visible additional hydrogen uptake. XRD study showed that an orthorhombic distortion of intermetallic matrix occurred on hydride formation. However, the nature of the distortion differed strongly from that observed in the Hf_2Cu-, Hf_2Pd- and $Zr_2Pd–H_2$ systems [6]. New $Hf_2Cu_{0.5}Ni_{0.5}H_3$ phase possessed an extremely high specific volume expansion for this structure type: more than 3×10^{-3} nm^3 per one intercalated hydrogen atoms instead of 1.8×10^{-3} nm^3 for Hf_2CuH_3 synthesised in our previous work [6,7].

We can suppose that the main reason for such a difference in hydrogen contents and lattice distortion parameters was not a change of intermetallic composition but an increase in synthesis temperature. In fact, R.M.Van Essen and K.H.J.Buschow [2] have reported that maximal hydrogen absorption capacity of Hf_2Cu was close to three H atoms. The hydrogenation has been carried out at elevated temperature and crystallographic parameters of hydride phase were nearly alike to those obtained in the present work for $Hf_2Cu_{0.5}Ni_{0.5}H_3$. That is, the observed type of phase transformation which was a result of a temperature increase in the case of the $Hf_2Cu–H_2$ system (compare the data from Refs. [2] and [6]) remained the only reaction path for $Hf_2Cu_{0.5}Ni_{0.5}$ when hydrogenation cannot be performed at room temperature.

Such an effect of synthesis temperature on hydride formation reaction discussed previously for the $Hf_2Fe–H_2$ system [8], might be attributed to a different sequence of interstitial positions filling with intercalated hydrogen atoms at different temperatures and, probably, 'blocking' of some interstitial sites. We also presume that the changes in high-pressure phase transformations mentioned above ($Hf_2Ni_{0.5}Mn_{0.5}$ and $Hf_2Ni_{0.5}Fe_{0.5}$ in comparison with Hf_2Fe) caused by substitution in $TiNi_2$-type compounds were of a similar nature.

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References

[1] F.A. Shunk, Constitution of Binary Alloys, 2nd Suppl, McGraw-Hill, N.Y, 1969.

[2] R.M. Van Essen, K.H.J. Buschow, J. Less-Common Metals 64 (1979) 277.

[3] A.F. Andresen, A.J. Maeland, J. Less-Common Metals 129 (1987) 115.

Table 2
Characteristics of hydrides in the $Hf_2M'_{0.5}M''_{0.5}–H_2$ systems

Hydride composition	Structure type	Unit cell parameters, nm				Maximal hydrogen contents, H/A_2B	
		a	*b*	*c*	$\Delta v/v_0$ (%)	$p=10$ atm, $T=293$ K	$p=2000$ atm, $T=195$ K
$Hf_2Ni_{0.5}Mn_{0.5}H_{4.9}$	Ti_2Ni	1.286			24	4.9	5.2
$Hf_2Ni_{0.5}Fe_{0.5}H_{4.9}$	Ti_2Ni	1.294			23	4.9	5.1
$Hf_2Cu_{0.5}Ni_{0.5}H_{3.0}$	(Rhomb.)	0.634	0.693	1.171	17	3.0 (400 K)	3.2

[4] J.L. Soubeyroux, D. Fruchart, S. Derdour et al., J. Less-Common Metals 129 (1987) 187.
[5] F. Aubertin, U. Gonser, J.M. Pope, S.J. Campbell, Z. Phys. Chem, N.F. 163 (1989) 249.
[6] K.N. Semenenko, S.N. Klyamkin, Russ. Chem. Bull. 42 (1993) 794.
[7] S.N. Klyamkin, K.N. Semenenko, J. Alloys Comp. 204 (1994) 65.
[8] S.N. Klyamkin, V.V. Burnasheva, K.N. Semenenko, Russ. Chem. Bull. 46 (1997) 28.
[9] S.N. Klyamkin, K.N. Semenenko, J. Alloys Comp. 253–254 (1997) 41.
[10] S.N. Klyamkin, V.N. Verbetsky, J. Alloys Comp. 194 (1993) 41.