INTERACTION IN NbVCo-H_2 AND NbVFe-H_2 SYSTEMS UNDER HYDROGEN PRESSURE UP TO 2000 ATM

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Abstract

Interaction IMC (intermetallic compounds) NbVCo and NbVFe with hydrogen in wide temperatures and pressures intervals have been investigated with PCT (pressure-composition) method. X-ray analyses has been shown that hydrogen introduction in lattice was accompanied with volume increasing without rearrangement of metallic atoms.

Keywords: Intermetallic Compounds (IMC); Hydrides; Hydrides; High pressure of hydrogen

1. Introduction

For the first time ternary Laves phase in Nb-V-Co and Nb-V-Fe systems have been described in [1]. Intermetallic compounds AB_2 with Laves phases structure are perspective material for hydrogen storage. Under usual pressure (up to 100 atm.) hydrides, formed in AB_2-H_2 system, are able to absorb about two weigh percent of hydrogen. In such systems A-component is usually titanium, zirconium and earth-rare elements. At present work interaction IMC, containing niobium as A-component with hydrogen has been investigated.

2. Experimental

Samples of NbVCo and NbVFe alloys have been obtained by electrical furnace in inert atmosphere. For homogenization obtained samples were quenched at 850^0C during 240 hours in evacuated quartz ampoules. Investigation of interaction IMC with hydrogen was carried out on apparatus of high pressure (up to 2000 atm.), described in [2]. For calculation of hydrogen amount in obtained hydride phases in situ the equation of high pressed hydrogen have been used [3]. Fixing of the composition obtained hydrides of high pressure has been conducted by transferring them into passive state. For this sample of hydride obtained under high pressure first was cooled at temperature of liquid nitrogen and then has been left at air about forty minutes at this temperature.

Amount of hydrogen in the passive hydrides has been checked with thermal desorption. X-ray analyses of alloys and hydrides have been conducted on DRON-2

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(Co,CuK_α-emission, Ni filter). Obtained X-ray data were refined with the Rietveld method.

3. Results and discussions

X-ray analyses of IMC NbVCo and NbVFe have shown that obtained samples are single-phase and have $MgZn_2$ structure type. Obtained X-ray data are presented in table1 and on figures 1(a, b).

TABLE 1. Results of X-ray analyses of IMC

Composition of IMC	Cell parameters, Å	V,Å^3	Atoms	Position	Rw-factor,%
NbVCo	a=4,932±0,002; c=8,03±0,01	169	Nb $V_{0,75}Co_{0,25}$ $V_{0,42}Co_{0,58}$	4(f) 2(a) 6(h)	3,62
NbVFe	a=4,932±0,002; c=8,06±0,01	170	Nb $V_{0,98}Fe_{0,02}$ $V_{0,34}Fe_{0,66}$	4(f) 2(a) 6(h)	5,19

Data from table 1 have been shown that in the NbVCo and NbVFe structure Nb atoms occupied 4(f) position. In NbVCo 2(a) position preferentially occupied V and Co atoms, and in NbVFe 2(a) position practically fully occupied of V atoms.

Position 6(h) atoms of B-component occupied approximately equally, in correlation ($V_{0,42}$ +$Co_{0,58}$) for NbVCo and ($V_{0,34}$ +$Fe_{0,66}$) for NbVFe.

Remarkable interaction hydrogen with NbVCo starts under increasing of pressure to 355 atm. and room temperature. Under such conditions hydrogen absorption has been occurred to composition $NbVCoH_{0,3}$. Plateau on absorption isotherm with pressures interval from 350 atm. to 750 atm. is corresponded to further absorption of hydrogen and forming hydride with composition $NbVCoH_{2,2}$ (fig.2(a)). Subsequently pressure increasing in this system is accompanied with hydrogen absorption and forming hydride phase $NbVCoH_{2,9}$ under pressure 1800 atm.

However on desorption isotherm plateau at this temperature hasn't been observed. Under decreasing of pressure gradual hydrogen desorption is occurred until composition $NbVCoH_{1,2}$ under pressure 10 atm.

Unlike from inactive IMC, the $NbVCoH_{1,2}$ rapidly interacts with hydrogen even under low temperatures. Decreasing temperature to (-50^0C) in this system leads to additional hydrogen absorption and forming hydride $NbVCoH_{3,8}$ under pressure 1800 atm. At this hydrogen absorption occurs monotonously, without a plateau on the isotherm.

In NbVFe-H_2 system interaction of NbVFe with hydrogen starts under 300 atm., as in case with NbVCo. After exceeding the pressure more 1200 atm., remarkable hydrogen absorption has been observed. This is corresponded of the plateau on the absorption isotherm (fig. 2(b)) with pressure interval from 1200 atm. to 1280 atm. Under this phase composition has been changed from $NbVFeH_{1,1}$ until $NbVFeH_{2,2}$.

Subsequently pressure increasing to 1600 atm. leads to forming hydride phase $NbVFeH_{3,0}$. Hydrogen desorption under pressure decreasing has been occurred without plateau on isotherm. Under this phase composition was equally $NbVFeH_{1,2}$ under 10 atm.

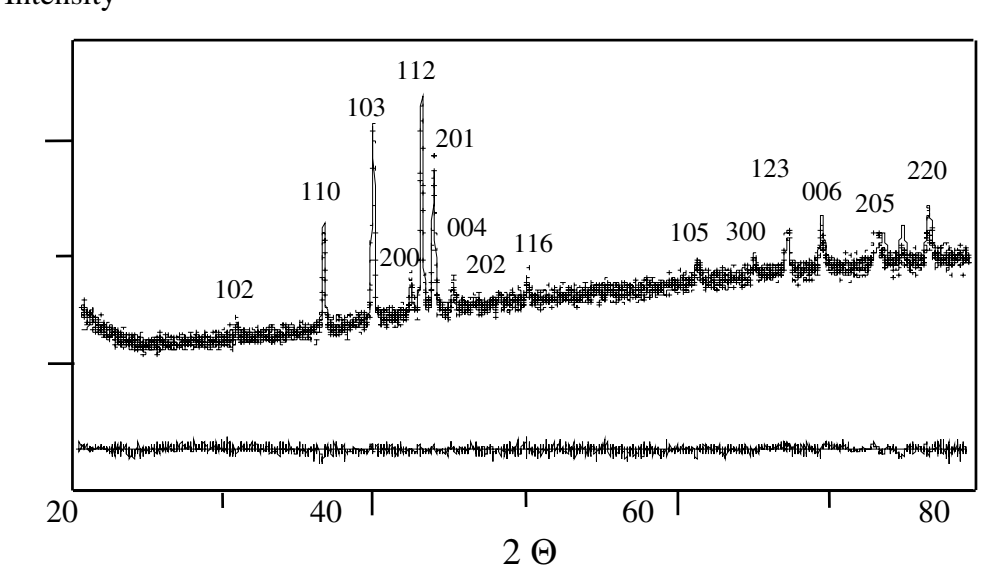

Figure 1 (a). Diffractogram of NbVCo

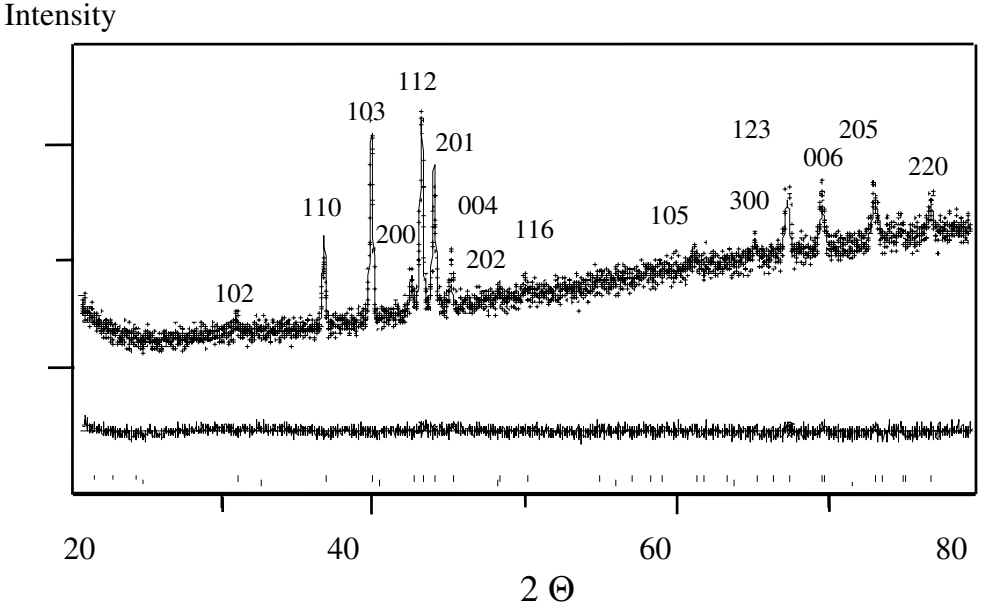

Figure 1 (b). Diffractogram of NbVFe

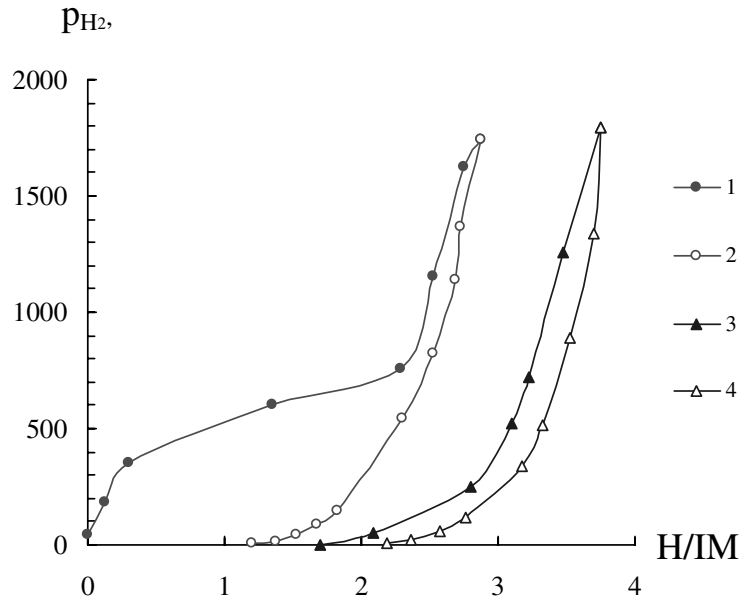

Figure 2 (a). Hydrogen absorption (1,3) and desorption (2,4) isotherms in NbVCo-H_2 system at temperatures 20^0C (1,2) and -50^0C (3,4)

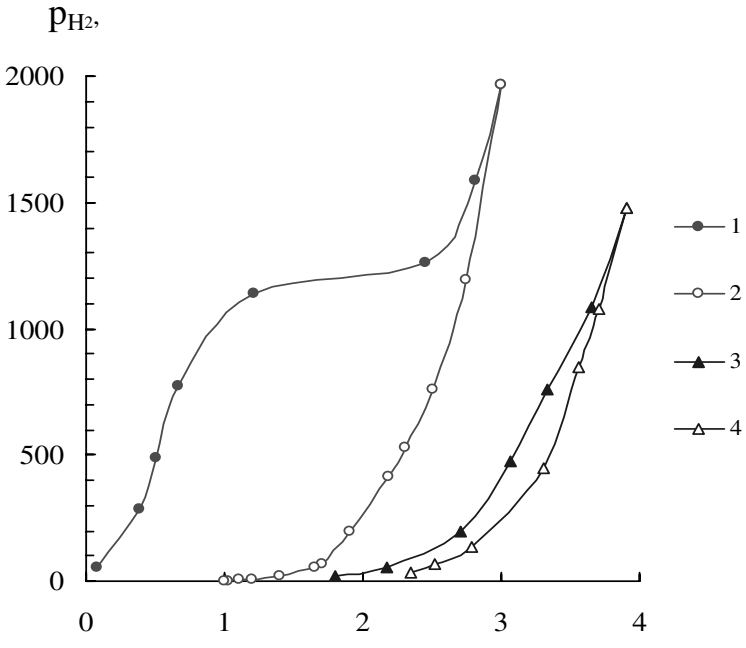

Figure 2 (b). Hydrogen absorption (1,3) and desorption (2,4) isotherms in NbVFe-H_2 system at temperatures 20^0C (1,2) and -50^0C (3,4)

After decreasing temperature to (-50^{0}C) in this system hydrogen absorption was occurred monotonously by formed hydride phase until composition $NbVFeH_{3,9}$ under 1500 atm.

Inactive NbVFe interacts with hydrogen at increasing temperature to 350^{0}C and pressure about 50 atm. Obtained hydride phase has composition equally $NbVFeH_{0,8}$ at 35 atm. and room temperature.

After the sample was evacuated at temperature 350^{0}C and hydrogen was fully extracted, active NbVFe interacted with hydrogen under lower pressure – about 20 atm. at room temperature. Obtained hydride also has composition $NbVFeH_{0,8}$.

Obtained samples of hydrides under high pressure are unstable. Passivation these hydrides, carried out before X-ray analyses has shown their less composition comparatively of composition calculated in situ.

Results of X-ray analyses of synthesized hydrides are presented in table 2 and diffractograms are on fig.3 (a,b).

TABLE 2. X-ray data of hydrides IMC NbVCo and NbVFe

Composition	Str. type	a, Å	Δ a/a %	c, Å	Δc/c %	V,Å^3	ΔV/V%	Rw,%
$NbVCoH_{2,5}$	$MgZn_2$	5,140±0,002	4,2	8,39±0,03	4,5	191	13,0	9,7
$NbVFeH_{2,2}$	$MgZn_2$	5,145±0,001	4,3	8,43±0,02	4,6	193	13,5	8,7

Carried out X-ray analyses have shown that under forming NbVCo and NbVFe hydrides, structure type of initial IMC didn't change. Data presented in table 2 have shown, that forming hydrides in NbVCo-H_2 and NbVFe-H_2 systems is accompany equable expansion of their lattice and increasing of «a» and «c» parameters. Cell increasing volume of hydrides formed under high pressure $NbVCoH_{2,5}$ and $NbVFeH_{2,2}$ are equally 13,0% and 13,5%. From X-ray data, refined by Rietveld method have been obtained, that introduction of hydrogen atoms in lattice didn't lead to relocation of metallic atoms.

4. Conclusions

High pressure of hydrogen allowed making synthesis of hydride phases based on IMC NbVCo and NbVFe with Laves structure. After first absorption cycle active samples interact with hydrogen even low temperature.

X-ray analyses have shown that forming of hydride phases is accompanied with equable volume expansion of lattice of initial IMC with introduction in lattice hydrogen atoms. Relocation of metallic atoms in lattice hasn't occurred.

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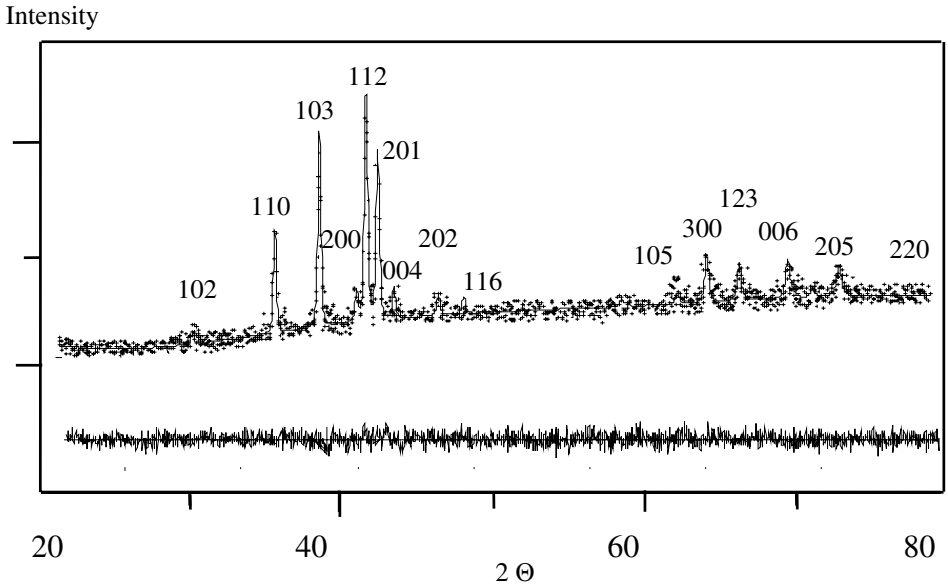

Figure 3 (a). Diffractogram of $NbVCoH_{2,5}$

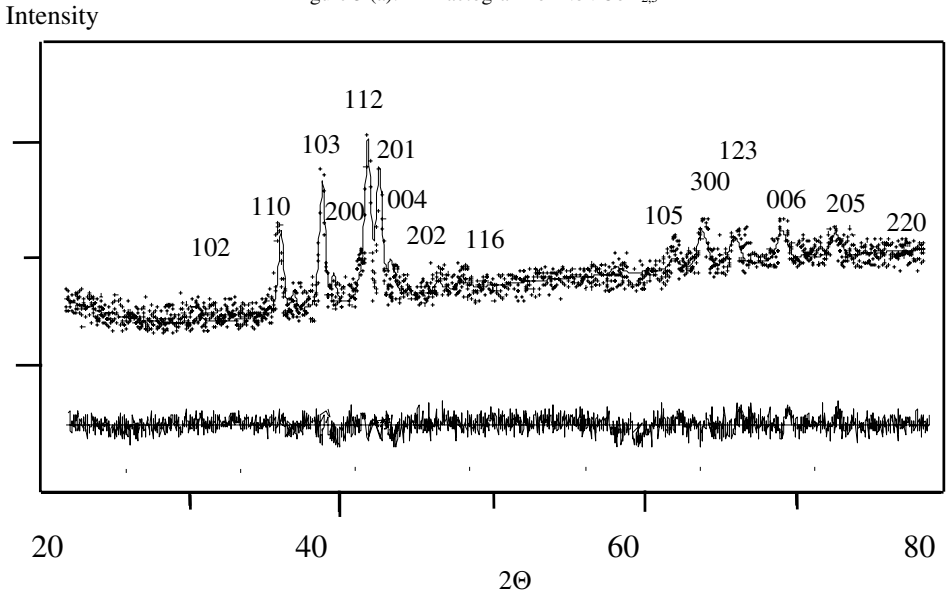

Figure 3 (b). Diffractogram of $NbVFeH_{2,2}$

5. References

1. Teslyk, M.Yu. (1969) Metallic compounds with structure of Laves phase, *M/Nauka*, 1-196.
2. Verbetsky, V.N., Klyamkin, S.N., Kovriga, A.Yu. and Bespalov, A.P. (1996) Hydrogen interaction with RNi_3 (R-rare-earth) Intermetallic compounds at high gaseous pressures, *Int. J. Hydrogen Energy* 11/12, 997-1000.
3. Hemmes, H., Driessen, A. and Griessen, R. (1986) Thermodynamic properties of hydrogen at pressure up to 1Mba and temperatures between 100 and 1000K, *J.Phys.C: Solid State Phys.* **19**, 3571-3585.