

## Interaction of NbVNi with Hydrogen

S. A. Lushnikov and V. N. Verbetsky

Moscow State University, Moscow, 119899 Russia

e-mail: lushnikov@hydride.chem.msu.ru

Received November 3, 2002

**Abstract**—The interaction of NbVNi with hydrogen is studied over wide pressure and temperature ranges. Hydrogen absorption–desorption isotherms are measured, and the compositions of the resulting hydride phases are determined. X-ray diffraction analysis demonstrates that the incorporation of hydrogen into NbVNi leads to an isotropic expansion of its crystal lattice.

### INTRODUCTION

Intermetallic compounds with the general formula  $RT_2$  and Laves-phase structures find wide application as hydrogen-storage materials. Detailed data on hydride formation have been reported for  $RT_2$  compounds with  $R = \text{Ti, Zr, and rare earth}$  and  $T = 3d$ -transition metal. Data on the interaction between NbT<sub>2</sub> intermetallics and hydrogen are not available in the literature.

### EXPERIMENTAL

NbVNi was prepared by arc-melting in an inert atmosphere and then annealed at 1120 K for 240 h. The reactions between NbVNi and hydrogen were studied using the high-pressure apparatus ( $p_{\text{H}_2}$  up to 0.2 GPa) described previously [1]. The hydrogen content of high-pressure hydrides was evaluated using a modified van der Waals equation for hydrogen [2]. In addition, the synthesized hydrides were analyzed for hydrogen by high-temperature vacuum extraction. The hydride phases were cooled to liquid-nitrogen temperature at a high pressure and then passivated in air for about 40 min. The intermetallics and hydrides were characterized by x-ray diffraction (XRD) on a DRON-1 powder diffractometer (Ni-filtered  $\text{CuK}_\alpha$  radiation). Structural data were refined by the Rietveld method.

### RESULTS AND DISCUSSION

The ternary Laves phase in the Nb–V–Ni system was first described in [3]. According to Prima *et al.* [4], this phase melts congruently and has a vast homogeneity region, extended along the 33 at. % Nb section. The crystallographic data for the NbVNi synthesized in this work are presented in Table 1, and its XRD pattern is shown in Fig. 1a. According to XRD data, we obtained phase-pure NbVNi with a  $\text{MgZn}_2$ -type structure.

In the structure of NbVNi (Table 1), most of the Nb atoms sit in position  $4f$ , position  $2a$  is occupied predominantly by vanadium atoms, and position  $6h$  is occupied by a mixture of V and Ni ( $\text{V}_{0.33} + \text{Ni}_{0.67}$ ).

Figure 2 shows the hydrogen absorption–desorption isotherms in the NbVNi–H<sub>2</sub> system. It can be seen that, at room temperature and  $p_{\text{H}_2} \leq 0.02$  GPa, nonactivated NbVNi does not react with hydrogen. At  $p_{\text{H}_2} = 0.02$  GPa, the amount of absorbed hydrogen rises stepwise. The resulting hydride has the composition NbVNiH<sub>2.2</sub>. Further increase in pressure causes gradual hydrogen absorption, with the formation of NbVNiH<sub>3.8</sub> at  $p_{\text{H}_2} = 0.1858$  GPa. Hydrogen desorption to  $p_{\text{H}_2} = 0.065$  MPa leads to the formation of NbVNiH<sub>1.4</sub>.

Low-temperature (223 K) absorption at  $p_{\text{H}_2} = 0.1928$  GPa results in the formation of NbVNiH<sub>5.0</sub>.

**Table 1.** Crystallographic data for NbVNi

| Lattice parameters, nm | $V, \text{nm}^3$ | Atoms                             | Position | $x$     | $y$  | $z$     | $R_w, \%$ |
|------------------------|------------------|-----------------------------------|----------|---------|------|---------|-----------|
| $a = 0.496 \pm 0.002$  | 17.2             | Nb                                | $4f$     | 0.33    | 0.67 | 0.06(3) | 6.74      |
| $c = 0.809 \pm 0.001$  |                  | V                                 | $2a$     | 0       | 0    | 0       |           |
|                        |                  | $\text{V}_{0.33}\text{Ni}_{0.67}$ | $6h$     | 0.83(1) | 0.66 | 0.25    |           |

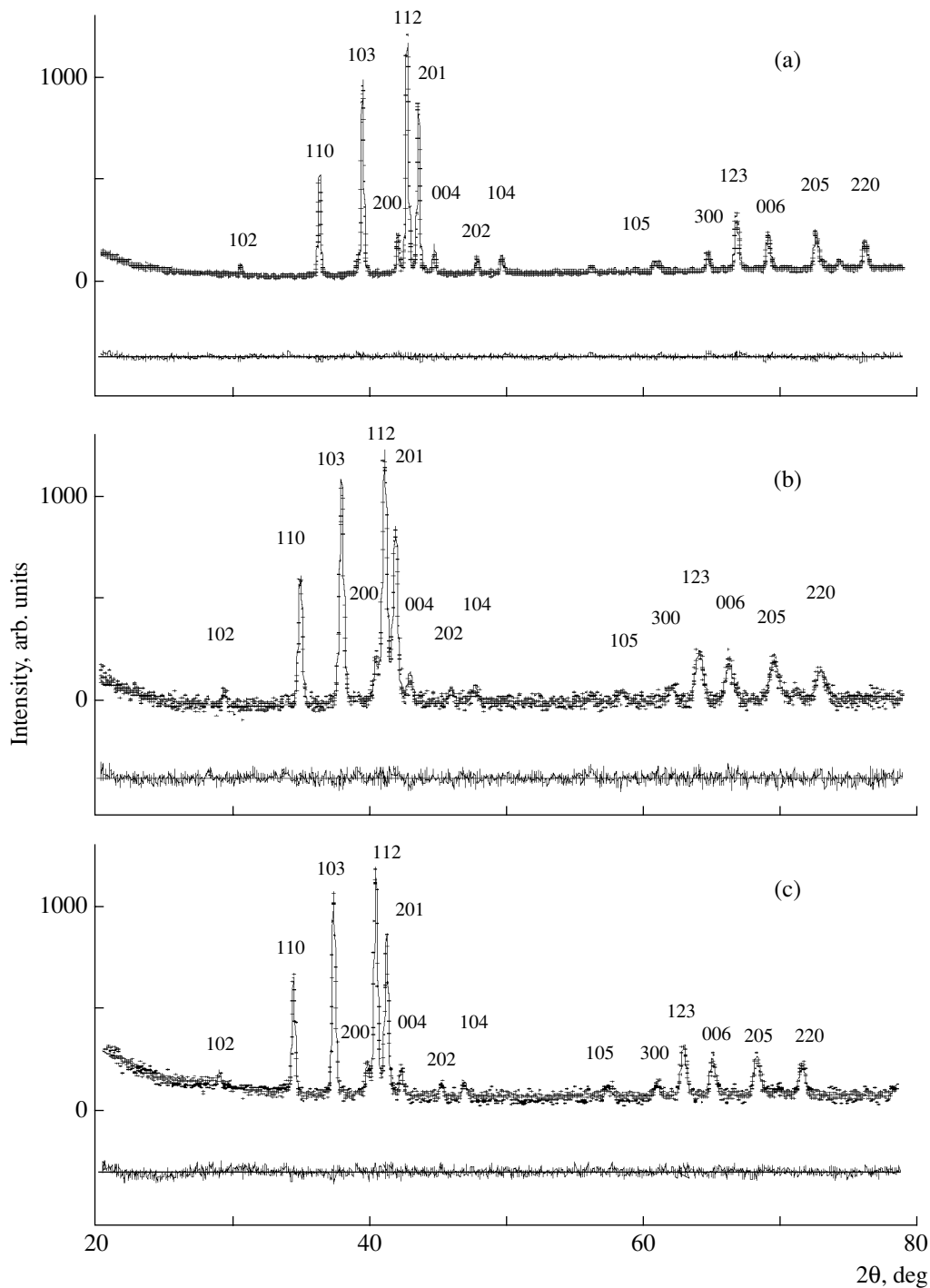


Fig. 1. XRD patterns of (a) NbVNi, (b) NbVNiH<sub>2.6</sub>, and (c) NbVNiH<sub>3.6</sub>.

Hydrogen desorption at this temperature to  $p_{\text{H}_2} = 0.68$  MPa yields NbVNiH<sub>2.6</sub>.

At 670 K, nonactivated NbVNi reacts with hydrogen starting at  $p_{\text{H}_2} \approx 5$  MPa to form NbVNiH<sub>0.7</sub>. After complete hydrogen desorption in vacuum at 620 K, activated NbVNi is capable of reacting with hydrogen under milder conditions: at  $p_{\text{H}_2} = 5$  MPa and room tem-

perature. The process continues for a day, and the resulting hydride has the composition NbVNiH<sub>0.7</sub>. The reaction rate is very slow in comparison with Zr- and Ti-containing Laves phases.

It seems likely that the slow reaction kinetics are associated with the high strength of niobium alloys and intermetallics [5, 6]. A similar correlation between the hydriding pressure and lattice "rigidity" was revealed

**Table 2.** Crystallographic data for NbVNi-based hydrides

| Composition           | Structure type    | $a$ , nm      | $\Delta a/a$ , % | $c$ , nm      | $\Delta c/c$ , % | $V$ , nm <sup>3</sup> | $\Delta V/V$ , % |
|-----------------------|-------------------|---------------|------------------|---------------|------------------|-----------------------|------------------|
| NbVNiH <sub>0.7</sub> | MgZn <sub>2</sub> | 0.501 ± 0.002 | 1.0              | 0.816 ± 0.001 | 0.9              | 17.7                  | 3.1              |
| NbVNiH <sub>2.6</sub> | MgZn <sub>2</sub> | 0.513 ± 0.001 | 3.5              | 0.837 ± 0.001 | 3.5              | 19.0                  | 10.9             |
| NbVNiH <sub>3.6</sub> | MgZn <sub>2</sub> | 0.520 ± 0.002 | 4.9              | 0.852 ± 0.002 | 5.4              | 19.9                  | 15.9             |

by Takeshita and Gschneider [7, 8] for compounds with the CaCu<sub>5</sub> structure (CaNi<sub>5</sub>, YNi<sub>5</sub>, LaNi<sub>5</sub>, and ThNi<sub>5</sub>).

The crystallographic data for the hydrides synthesized in this work are presented in Table 2, and the XRD patterns of two NbVNi-based hydrides are displayed in Figs. 1b and 1c.

As follows from the XRD data, NbVNiH<sub>0.7</sub>, NbVNiH<sub>2.6</sub>, and NbVNiH<sub>3.6</sub> have the same structure as NbVNi. The data in Table 2 demonstrate that the incorporation of hydrogen into NbVNi leads to a nearly isotropic expansion of its crystal lattice. At the highest hydrogen content (NbVNiH<sub>3.6</sub>), the relative increase in unit-cell volume is 15.9%.

Structure refinement by the Rietveld profile analysis method showed that the metal atoms in NbVNiH<sub>2.6</sub> and NbVNiH<sub>3.6</sub> occupied the same sites as in NbVNi ( $R_w = 8.51$  and  $8.26\%$ , respectively). Thus, the incorporation

of hydrogen caused no redistribution of the niobium, vanadium, or nickel atoms over the lattice sites.

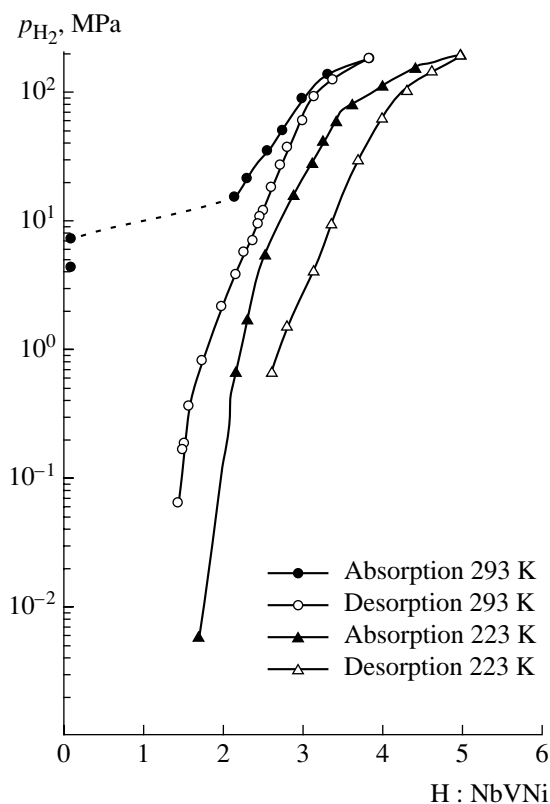
## CONCLUSIONS

Under ordinary conditions (room temperature and low pressure), the intermetallic compound NbVNi does not react with hydrogen. Hydrogen absorption begins at 623 K and  $p_{H_2} = 5$  MPa and takes as much as 24 h to reach completion, in striking contrast to Zr- and Ti-containing Laves phases.

At high pressures,  $p_{H_2} \leq 0.2$  GPa, we were able to obtain hydride phases at room temperature and even at 223 K. According to XRD data, the incorporation of hydrogen into NbVNi leads to an isotropic expansion of its crystal lattice and causes no redistribution of the niobium, vanadium, or nickel atoms over the lattice sites.

## REFERENCES

- Verbetsky, V.N., Klyamkin, S.N., Kovriga, A.Yu., and Bespalov, A.P., Hydrogen Interaction with RNi<sub>3</sub> (R—Rare-Earth) Intermetallic Compounds at High Gaseous Pressures, *Int. J. Hydrogen Energy*, 1996, vol. 11/12, pp. 997–1000.
- Hemmes, H., Driessen, A., and Griessen, R., Thermodynamic Properties of Hydrogen at Pressures up to 1 Mbar and Temperatures between 100 and 1000 K, *J. Phys. C: Solid State Phys.*, 1986, vol. 19, pp. 3571–3585.
- Teslyuk, M.Yu., *Metallicheskie soedineniya so strukturalami faz Lavesa* (Metallic Compounds with Laves-Phase Structures), Moscow: Nauka, 1969, pp. 1–196.
- Prima, S.B., Tret'yachenko, L.A., and Kuz'ma, Yu.B., Ternary Compound in the Nb–V–Ni System, in *Diagrammy sostoyaniya v materialovedenii* (Phase Diagrams in Materials Research), Kiev, 1984, pp. 24–30.
- Chu, F., Thoma, D.J., and Kotula, P.J., Phase Stability and Defect Structure of the C15 Laves Phase Nb(Cr,V)<sub>2</sub>, *Acta Mater.*, 1998, vol. 46, no. 5, pp. 1759–1769.
- Samsonov, G.V. and Konstantinov, V.I., *Tantal i niobii* (Tantalum and Niobium), Moscow: Metallurgizdat, 1959, pp. 1–208.
- Takeshita, T. and Gschneider, K.A., High Pressure Hydrogen Absorption Study on YNi<sub>5</sub>, LaPt<sub>5</sub>, and ThNi<sub>5</sub>, *J. Less-Common Met.*, 1981, vol. 78, pp. 43–47.
- Takeshita, T. and Gschneider, K.A., Low-Temperature Heat Capacity of Haucke Compounds CaNi<sub>5</sub>, YNi<sub>5</sub>, LaNi<sub>5</sub>, and ThNi<sub>5</sub>, *Phys. Rev. B: Condens. Matter*, 1980, vol. 21, pp. 5636–5641.



**Fig. 2.** Hydrogen absorption-desorption isotherms in the NbVNi–H<sub>2</sub> system.