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Influence of Multiposition Filling on the Thermodynamic Isotope Effect in the Hydrogen–ZrV_{2-x}Ni_x System

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Abstract—The phase equilibrium in the ZrV_{2-x}Ni_x-H₂(D₂) system ($x = 0.1-0.4$) was studied over a temperature range from 273 to 323 K. For protium and deuterium, sorption isotherms, thermodynamic characteristics of hydride formation, and the isotope separation coefficient were obtained. Small additives of nickel cause an increase in the hydride formation pressure and H/D isotope separation coefficient and a small decrease in the capacity of the intermetallic compound (IMC) with respect to hydrogen. The results obtained were analyzed within the framework of a model describing the separation of hydrogen isotopes during sorption in metals and IMCs with filling of sites of various types (multiposition filling). Calculated and measured values of the isotope effect were found to be in close agreement.

INTRODUCTION

At present, the most effective methods for separating hydrogen isotopes are rectification and chemical isotope exchange. The scope of methods suitable for tritium is limited by low-temperature rectification of hydrogen and the capabilities of the available sorption technologies. Intermetallic compounds are promising sorbents for hydrogen sorption due to their radiation resistance. Intermetallic compounds (IMCs) are characterized by high isotope separation coefficients; in addition, a number of AB₂-type IMCs (Laves phases) exhibit a significant capacity for hydrogen [1].

The aim of the present work was to study, both experimentally and theoretically, the effect of filling of various internodes in ZrV_{2-x}Ni_x ($x = 0-0.4$) IMCs of substitution type by hydrogen atoms on the thermodynamic isotope effect, i.e., on the coefficient of separation of the hydrogen isotopes in the IMC hydride-gaseous hydrogen system. A ZrV₂-based IMC system was chosen not only because ZrV₂ exhibits a high capacity for hydrogen, but also because it is characterized by a significant thermodynamic isotope effect. Unfortunately, pure ZrV₂ exhibits getter properties with respect to hydrogen, a circumstance that complicates the construction of the lower unit of the separation column.

It was demonstrated [1, 2] that additives of other metals dissolved in IMC hydrides by substitution mechanism substantially change their properties. In [3], the effect of substitution of nickel for cobalt on the phase equilibrium in the LaCo₅ system was studied. The authors found that an increase in the nickel content results in a decrease in the stability of the hydrate and an increase in the pressure of hydrogenation. It is reasonable to assume that nickel should produce the same

effect on ZrV₂. This idea prompted us to study the effect of nickel on the properties of this compound.

EXPERIMENTAL

We studied the phase and isotope equilibria in the hydrogen–ZrV_{2-x}Ni_x hydride ($x = 0.1, 0.2, 0.3, \text{ and } 0.4$) system over a temperature range from 273 to 323 K. The experimental procedure was described in detail elsewhere [4]. At low hydrogen concentrations, when the H/Me atomic ratio for the solid phase is below unity, all four samples exhibited getter properties. The characteristics of the experimental setup prevented us from measuring adsorption isotherms in this region. According to [5], this region contains a plateau (the hydride formation pressure lies within 10⁻³–1.0 Pa), which is associated with the filling of A₂B₂ (Zr₂V₂)-type tetrahedral internodes in the IMC structure.

Typical adsorption isotherms measured at H/Me > 1 are displayed in Fig. 1. As can be seen, the isotherms have a characteristic plateau, which, according to the ZrV₂-D [6] phase diagram, corresponds to the α'–δ transition. This plateau is in part associated with the filling of AB₃ (ZrV₃)-type tetrahedral internodes. Neutron diffraction [6] and neutron inelastic scattering [7] show that internodes of two energetically nonequivalent types A₂B₂ and AB₃ in the initial IMC (ZrV₂) are filled. As x increases from 0.1 to 0.2, the pressure of formation of the δ phase increases, while the capacity for hydrogen slightly decreases (Fig. 1). As the nickel content increases to $x = 0.3$, a small decrease in the hydride formation pressure is observed, which is apparently associated with a new structure in the IMC, presumably, a C14 hexagonal (the initial IMC has a C15 cubic structure). This result agrees with the data reported in [2], in which the struc-

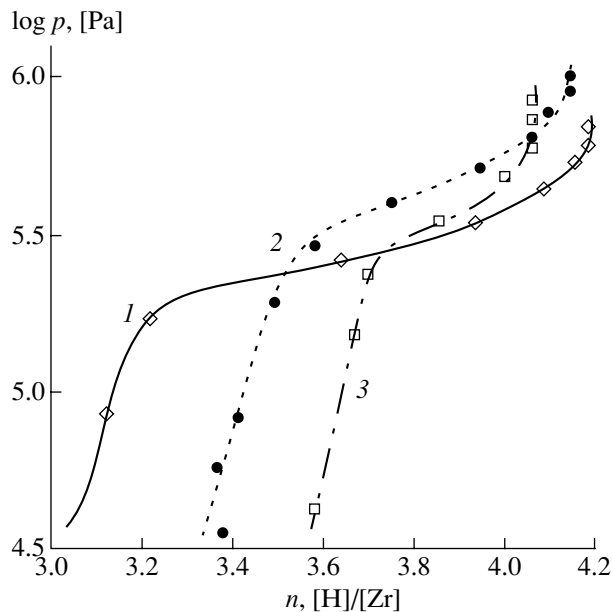
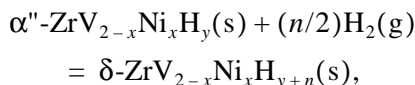


Fig. 1. Isotherms of sorption of protium at 283 K and various concentrations of nickel in solid $ZrV_{2-x}Ni_x$: $x = (1)$ 0.1, (2) 0.2, and (3) 0.3 and 0.4.

ture and properties of ZrV_2 containing iron and cobalt were studied, and with the XRD analysis performed in the present work. In addition, Fig. 1 shows that the concentration of hydrogen in the α'' phase increases with the nickel content.

Based on phase equilibrium data, we obtained the temperature dependence of the hydride (deuteride) formation pressure for the δ phases. In the temperature range covered, the dependence of the hydride formation pressure on $1/T$ is a straight line, a result that makes it possible to calculate the enthalpy and entropy changes for the reaction of hydride formation



from the van't Hoff equation

$$\ln p_{\text{H}_2(\text{D}_2)} = \Delta H_{\text{H}(\text{D})}/RT - \Delta S_{\text{H}(\text{D})}/R.$$

The results obtained are summarized in Table 1.

The temperature dependence of the isotope separation coefficient α_{HD} in the region of existence of the δ phase was studied by the single-equilibration method under static conditions. Typical experimental curves are

Table 1. Thermodynamic characteristics of hydrogenation of $\alpha''\text{-ZrV}_{2-x}\text{Ni}_x\text{H}(\text{D})_y$

| x | $-\Delta H^\circ$, kJ/mol H_2 | | $-\Delta S^\circ$, J/(K mol H_2) | |
|-----|---|----|---|-----|
| | H | D | H | D |
| 0.1 | 34 | 40 | 127 | 141 |
| 0.2 | 30 | 37 | 119 | 134 |
| 0.3 | 32 | 39 | 123 | 140 |
| 0.4 | 30 | 34 | 118 | 123 |

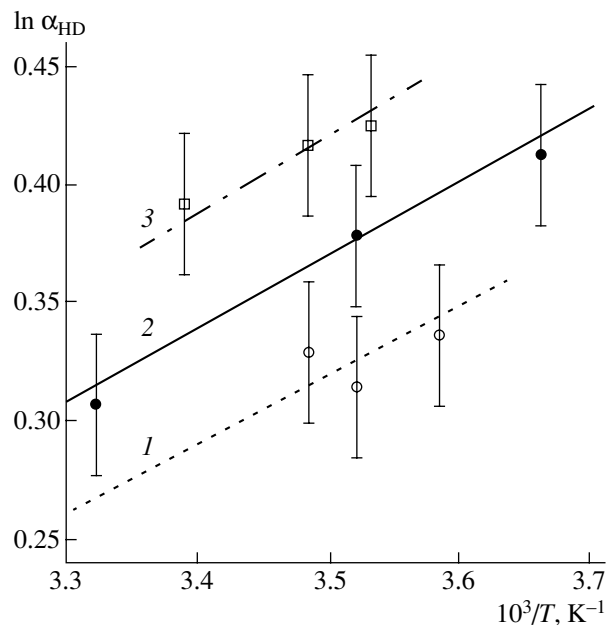


Fig. 2. Temperature dependences of the isotope separation coefficient for the δ phase at $x = (1)$ 0.1, (2) 0.2, and (3) 0.3.

shown in Fig. 2. In the temperature range covered, these dependences can be described by the equation

$$\ln \alpha = a + b/T.$$

The coefficients of the equation are given below:

| | | | | |
|------|------|------|------|------|
| x | 0.1 | 0.2 | 0.3 | 0.4 |
| $-a$ | 0.76 | 0.72 | 0.66 | 0.77 |
| b | 308 | 310 | 310 | 320 |

THEORETICAL

The pair interatomic interactions in the solid phase that accompany the formation of hydrides of metals in IMCs can be classified as shown in Table 2. This classification is based on the fact that a description of an effect normally involves only one type of interactions. It will be demonstrated, however, that an adequate description of the isotope effect in the hydrogen- $ZrV_{2-x}\text{Ni}_x\text{H}(\text{D})_y$ system should take into account both the Me-H and H-H interactions.

We used the Me-H interaction potential schematically displayed in Fig. 3; it can be presented as

$$U(r) = U_1(r) + U_2, \quad (1)$$

where r is the Me-H internuclear distance and

$$U_1(r) = A \exp[-(r/\rho)^2]. \quad (2)$$

The term $U_1(r)$ describes the short-range repulsion between the hydrogen atom and the electrons of the ionic core of the metal atom. The constant ρ depends on the position of the metal in the periodic table and plays the role of an effective radius of the ionic core. It is important that the value of ρ is constant for each metal irrespective of the IMC it enters into [8]. Thus, this characteristic holds for series of IMCs.

Table 2. Classification of pair interatomic interactions in the hydrides under study

| Interaction | Effects produced | |
|-------------|-------------------------------------|---|
| | Me–H | H–H |
| Long-range | Heat effect of formation of hydride | Lattice gas–lattice liquid transition The heat effect of hydride formation |
| Short-range | Equilibrium isotope effect | Blocking of neighboring internodes (limitation of the capacity) |

The second term in formula (1) describes the long-range (attractive) Me–H interaction of the hydrogen atom with the conduction electrons. It is this interaction that is responsible for the formation of the IMC hydride; its magnitude is determined by the energetic structure of the conduction band, in particular, by the density of electronic states near the Fermi level.

The H–H short-range interaction was described by taking into account only the effect of blocking of neighboring internodes. This assumption limits the highest possible concentration of hydrogen in the metal matrix. For example, if the matrix has N_m equivalent internodes, filling one of them blocks b_m nearest neighbors, with the largest number of hydrogen atoms in the sublattice composed of internodes of this type for a disordered solid solution being $N_m/(b_m + 1)$. The factor of blocking for internodes of type m is given by

$$f_m = 1/(b_m + 1). \quad (3)$$

When internodes of different types are filled, each quantity b_m should describe both intralattice and interlattice blocking.

The above consideration makes it possible to present the energy of a hydrogen atom at an internode of type m (without taking into account the vibrational component) as

$$E_m = \sum_i U(\mathbf{R}_i - \mathbf{R}_m), \quad (4)$$

where summation is performed over all metal atoms of the crystal lattice and \mathbf{R}_i and \mathbf{R}_m are the equilibrium positions of the hydrogen and metal atoms, respectively.

For a disordered solid solution, the condition of equilibrium between the gaseous and dissolved hydrogen yields the following relation between the population of internode n_m and the energy E_m of an interstitial hydrogen atom (this energy represents all interactions listed in Table 2):

$$\frac{1}{2}\mu_{\text{H}_2}(p, T) = \mu_{\text{H}} = E_m + RT \ln \frac{n_m}{1 - n_m}, \quad (5)$$

where $\mu_{\text{H}_2}(p, T)$ is the chemical potential of gaseous hydrogen, which can be calculated based on spectral data.¹ The dependence of n_m on E_m is given by the Fermi distribution:

$$n_m = \left[1 + \exp\left(\frac{E_m - \mu_{\text{H}}}{RT}\right) \right]^{-1}. \quad (6)$$

¹ The constant μ_0 in the expression for the chemical potential is included in the term U_2 of formula (1).

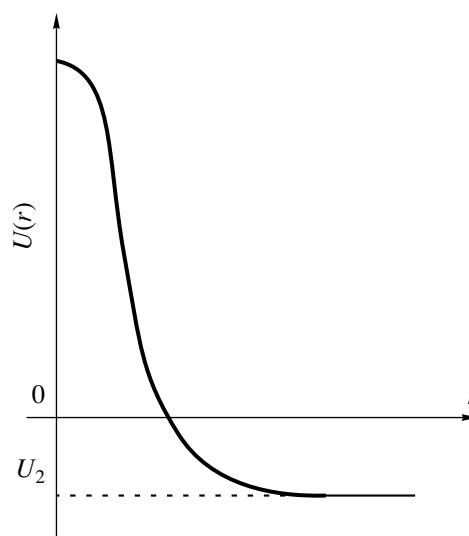
The frequencies of the optical vibrations of the hydrogen atoms (deuterium or tritium) are determined by solving (using the variational principle) the Schrödinger equation for an atom in the potential well of the corresponding internode. The solution of this problem in the spherical oscillator approximation was described by us in detail elsewhere [8]. For a pair of isotopes (for example, H and D) at internodes of type m for the case when the concentration of the heavy isotope is much smaller, the isotope separation coefficient is expressed through the vibrational frequencies ω_m of the isotopes as [1]

$$\alpha_{m\text{HD}} = \left[\frac{\sinh(\hbar\omega_{m\text{H}}/kT)}{\sinh(\hbar\omega_{m\text{D}}/kT)} \right]^3 \frac{Z_{\text{HD}}}{Z_{\text{H}_2}}, \quad (7)$$

where the ratio of the partition functions $Z_{\text{HD}}/Z_{\text{H}_2}$ for the isotopes is a tabulated function of the temperature [9]. For the harmonic oscillator, $\omega_{m\text{D}} = \omega_{m\text{H}}/\sqrt{2}$. We demonstrated that, when hydrogen atoms fill internodes of various types, the following additivity rule [4] is fulfilled at low concentration of the heavy isotope:

$$\alpha_{\text{HD}} = \sum_m N_m f_m n_m \alpha_{m\text{HD}} / \sum_m N_m f_m n_m. \quad (8)$$

The set of equations (1)–(8) constitute a closed model for calculating the isotope separation coefficient.


Fig. 3. A schematic of the Me–H potential.

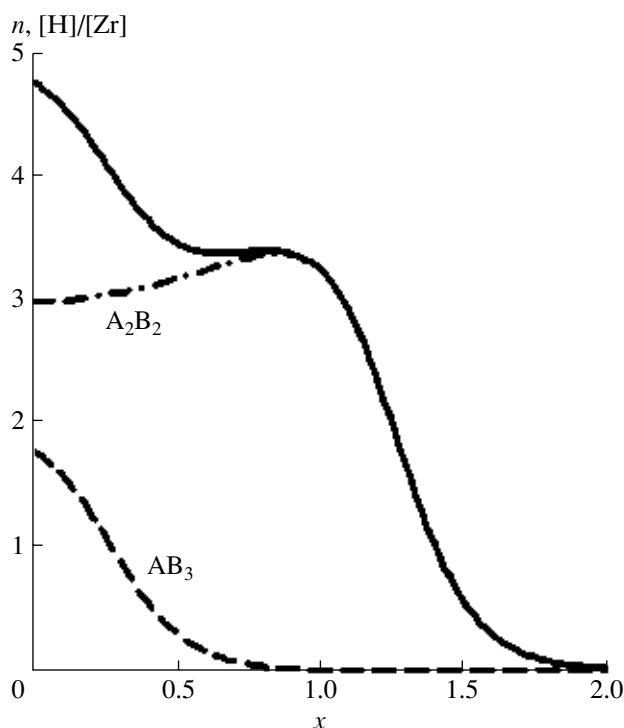


Fig. 4. Dependence of the capacity of $\text{ZrV}_{2-x}\text{Ni}_x$ on the degree of substitution x of nickel for vanadium. The contents of hydrogen in the sublattices composed of A_2B_2 and AB_3 internodes

cients for the hydrogen isotopes interaction hydrogen-metal hydride system when hydrogen atoms occupy an arbitrary number of energetically nonequivalent internodes. Note that the model does not describe structural phase transitions.

CALCULATION OF THE ISOTOPE SEPARATION COEFFICIENTS FOR THE HYDROGEN- $\text{ZrV}_{2-x}\text{Ni}_x\text{H(D)}_y$ SYSTEM

In the substituted IMCs under study at sufficiently high pressures of hydrogen ($\sim 10^6$ Pa), tetrahedral internodes of types A_2B_2 (12 internodes per formula unit of ZrV_2) and AB_3 (4 internodes per formula unit) are filled. Defining the degree of substitution as $s = x/2$ and

Table 3. Probabilities for internodes of various types to be occupied as functions of the degree of substitution

| A_2B_2 | | AB_3 | |
|--------------------------|-----------|-------------------------|-------------|
| type of internode | $P_m(s)$ | type of internode | $P_m(s)$ |
| Zr_2V_2 | $(1-s)^2$ | ZrV_3 | $(1-s)^3$ |
| Zr_2VNi | $2s(1-s)$ | ZrV_2Ni | $3s(1-s)^2$ |
| Zr_2Ni_2 | s^2 | ZrNi_2V | $3s^2(1-s)$ |
| | | ZrNi_3 | s^3 |

assuming there are no both long-range and short-range order in the arrangement of the nickel atoms, we found that the probability for an internode in the A_2B_2 or AB_3 sublattice to be of type m is given by the binomial distribution (Table 3); thus,

$$N_m = MP_m(s), \quad (9)$$

where $M = 12$ and 4 for the A_2B_2 and AB_3 sublattices, respectively.

The filling of one internode in the A_2B_2 sublattice of pure ZrV_2 results in the blocking of three neighboring internodes in the same sublattice and one internode in the AB_3 sublattice. When an internode is filled in the AB_3 sublattice, no blocking is observed. Therefore, according to formula (3), $f_m = 1/4$ and $1/2$ for the A_2B_2 and AB_3 sublattices, respectively; as a consequence, the maximum capacity of disordered solid solutions in this IMC for hydrogen cannot exceed five hydrogen atoms per formula unit [6].

The introduction of nickel changes the situation. According to the experimental data we obtained, at a hydrogen pressure of $\sim 10^3$ – 10^4 Pa, when only internodes in the A_2B_2 sublattice are filled, the capacity of the IMC with respect to hydrogen increases with the nickel content and even exceeds the ultimate value ($Mf = 3$). The result can only be explained by a decrease in the degree of blocking. Calculations based on potential (2) show that the presence of nickel (which is characterized by a smaller value of the ion core radius ρ) in the ZrV_2 matrix and an increase in the number of substituted internodes should cause this effect due to a shift of the hydrogen atom in the direction from the Zr – Zr bond. As a result of this shift, two neighboring internodes become accessible to the hydrogen atoms. For the completely substituted IMC, the factor of blocking for the A_2B_2 sublattice is $1/2$. In this case, without performing a detailed analysis, we assumed that the factor of blocking linearly depends on the number of internodes in Zr_2Ni_2 ; i.e., $f = (1 + s^2)/4$. For the AB_3 sublattice, this value is constant at $1/2$.

The energy of hydrogen atoms at internodes of the A_2B_2 and AB_3 sublattices is given by

$$E_{\text{A}_2\text{B}_2} = E_{\text{A}_2\text{B}_2}^0 + s\Delta E,$$

$$E_{\text{AB}_3} = E_{\text{AB}_3}^0 + s\Delta E,$$

where $E_{\text{A}_2\text{B}_2}^0 = -66$ kJ/mol H_2 , $E_{\text{AB}_3}^0 = -32$ kJ/mol H_2 , and $\Delta E = 70$ kJ/mol H_2 (the corresponding contributions from the potential U_2). These energetic parameters were selected with regard to the populations of internodes in hydride of ZrV_2 (the δ phase [6]) and the behavior of the adsorption isotherm. The values of E^0 thus obtained agree with the available experimental values of the differential heat of sorption [1]. The calculated populations of the internodes in the A_2B_2 and AB_3 sublattices and the total hydrogen content at $T = 273$ K and a pressure of 1.5×10^6 Pa as a function of the

degree of substitution of nickel for vanadium are shown in Fig. 4 (at high degrees of substitution, this dependence is hypothetical, because the phase diagram contains no such phases [10]).

When calculating the vibrational frequencies in formula (2), we took into account the dependence of the lattice constant on the hydrogen content. The corresponding dependence for hydride of ZrV_2 , as for most hydrides, is linear, with the slope being close to that determined for the crystal lattice of HfV_2 , a similar hydride. Thus, we assumed that the dependence of the lattice constant of $ZrV_{2-x}Ni_x$ on the hydrogen concentration is invariable, at least at moderate degrees of substitution. According to XRD data, the lattice constant of pure $ZrV_{2-x}Ni_x$ changes by 0.01 Å as x increases from 0.1 to 0.3; i.e., it is negligibly small in comparison with the expansion of the crystal lattice caused by hydrogen sorption.

The calculated vibrational frequencies for hydrogen atoms located at internodes of all types in hydrides of the substituted IMCs under study in conjunction with the data of Table 3 can be used for calculating α_{HD} (Table 4) by formulas (7), (8).

DISCUSSION

The average relative error in the values of α_{HD} (determined by the single-equilibration method) was below 5%; the calculated and measured values were found to be in close agreement. The optical vibrational frequencies for hydrogen atoms at various internodes in the IMCs under study lie within a relatively narrow range (135–160 meV). We previously demonstrated that the coefficients of separation of the hydrogen isotopes can be calculated by using an average frequency that lies within this range and most accurately describes the temperature dependence of α_{HD} [11]; a method for calculating this frequency was proposed.

We calculated the values of this frequency for hydrides of $ZrV_{2-x}Ni_x$ ($x = 0, 0.1, 0.2, 0.3,$ and 0.4) from experimental and calculation results. The theoretical $\alpha_{HD} = \alpha_{HD}(x)$ dependence was found to coincide with the experimental one within the error limits. At low degrees of substitution, the dependence passes through a weakly expressed maximum. As the degree of substitution increases still further, the effective frequency and the isotope separation coefficient decrease.

Thus, we found that small additives (to a certain limit) of nickel results in an increase in the hydride formation pressure. As the nickel content is increased, the capacity of IMC with respect to hydrogen slightly decreases, while the isotope separation coefficient for protium–deuterium mixtures in the δ phase increases.

Table 4. Measured (I) and calculated (II) values of the isotope separation coefficient α_{HD} for hydrides of $ZrV_{2-x}Ni_x$

| x | 273 K | | 284 K | | 301 K | |
|-----|-------|------|-------|------|-------|------|
| | I | II | I | II | I | II |
| 0 | 1.52 | 1.50 | 1.45 | 1.43 | 1.37 | 1.35 |
| 0.1 | 1.43 | 1.55 | 1.39 | 1.48 | 1.33 | 1.39 |
| 0.2 | 1.52 | 1.52 | 1.47 | 1.46 | 1.37 | 1.37 |
| 0.3 | 1.54 | 1.50 | 1.50 | 1.43 | 1.39 | 1.35 |
| 0.4 | 1.50 | 1.44 | 1.44 | 1.38 | 1.34 | 1.31 |

The experimental values of the isotope separation coefficients are closely described by the proposed model.

The model correctly describes the effect of multiposition filling and can be used for calculating the isotope separation coefficients for hydrides of other IMCs.

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