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Some peculiarities of interactions in the Hf_2Fe-H_2 system at low temperatures and high pressures

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Hydride formation was studied in the Hf_2Fe-H_2 system at a hydrogen pressure of up to 2000 atm in a temperature range from 195 to 295 K. Hydride phases of different compositions were studied by the X-ray diffraction method. The hydrogenation reaction in the system can take two pathways to form two stable hydride phases depending on the conditions of initial hydrogenation. Absorption of hydrogen at a pressure of about 2000 atm yields a hydride which contains two H atoms per metal atom. Models of the arrangement of hydrogen atoms in the crystal lattice of hydride phases were suggested.

Key words: hydrides, hafnium, iron, intermetallic compounds; high pressure.

In the previous work,[1] hydride phases based on intermetallic compounds (IMC) of hafnium and zirconium, which crystallize in the $MoSi_2$ structural type, have been obtained and studied at high pressure. The concentrations of hydrogen in these phases run to 6 H atoms per formula unit. A distortion of the crystal lattice of the initial intermetallic compound allows the hydrogen atoms that are inserted to occupy crystallographic positions which are characterized by anomalously short intermolecular H—H distances.

In this work, we studied the hydride phases which are based on the Hf_2Fe intermetallic compound and formed at an H_2 pressure of up to 2000 atm and temperatures of 195—295 K.

Experimental

The Hf_2Fe intermetallic compound was prepared by fusing a mixture of pure metals in an electric-arc furnace under an atmosphere of argon. The initial melt and the products of its hydrogenation were studied by the X-ray powder diffraction method on a DRON-2 diffractometer (Cu-Kα radiation, Ni filter, crystalline silicon was used as the internal standard).

The alloy that was obtained contained only one phase of the Ti_2Ni structural type (the unit cell parameter a = 12.036 Å).

The interaction in the Hf_2Fe-H_2 system was studied on a high-gas-pressure instrument. The scheme and technical characteristics of the instrument were reported previously.[2] We developed an experimental procedure which allows precision $p-V-T$ measurements in purified hydrogen (99.9999%) in a pressure (p) range from 0.01 to 2000 atm and temperature (T) range from 78 to 600 K. The use of the equation of state for a highly compressed hydrogen[3] makes it possible to calculate compositions of the hydride phases formed under the experimental conditions with an accuracy of 0.05 H atoms per 1 mole of the intermetallic compound (H/IMC).

Compositions of the hydride compounds were controlled, and their thermal stabilities were studied by the high-temperature hydrogen extraction method *in vacuo*.

After the preliminary evacuation at 670 K for 3 h, the initial hydrogenation of Hf_2Fe samples was carried out by two different procedures.

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Table 1. Conditions of the synthesis, compositions, and X-ray diffraction parameters of hydride phases **1** and **2** in the Hf_2Fe-H_2 system

T/K	p/atm	H/Hf_2Fe		a/Å		$\Delta V/V_0$ (%)	
		1	**2**	**1**	**2**	**1**	**2**
295	10	4.6	5.0	12.766	12.889	19	23
240	5	—	5.3	—	—	—	—
295	2000	5.2	5.6	—	—	—	—
195	2000	5.6	6.0	—	—	—	—
295	1*	4.8	5.2	12.769	12.887	19	23

* Desorption after treatment with hydrogen at 2000 atm and 195 K.

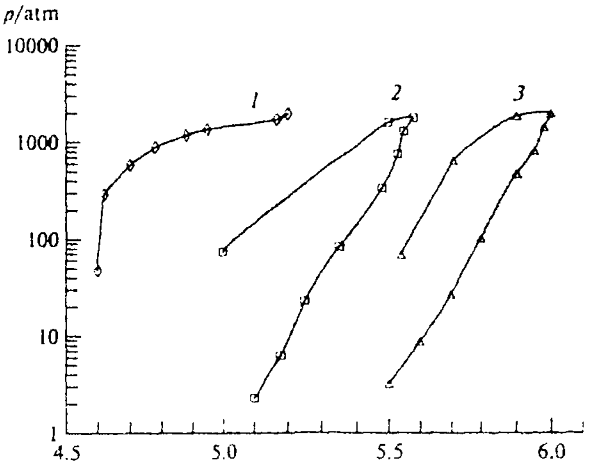

Fig. 1. Absorption and desorption isotherms of hydrogen in the Hf_2Fe-H_2 system: *1*, hydride **1**, 295 K; *2*, hydride **1**, 195 K; *3*, hydride **2**, 195 K.

A. A reactor containing a sample was filled with hydrogen until the pressure became 30—50 atm at 295 K. After a short induction period (20—60 s), adsorption of hydrogen proceeded almost immediately to form the hydride phase of composition $Hf_2FeH_{4.6}$ (**1**). The data of X-ray diffraction phase analysis of this phase indicated that the structure of the initial intermetallic compound was retained for the product, and the volume of the unit cell increased by 19% (Table 1). The composition of the hydride phase and its X-ray diffraction parameters are close to those determined previously.[4,5] The hydride phase that was synthesized is characterized by high stability: its hydrogen content remains virtually unchanged in the pressure range from 0.01 to 50 atm and, according to the results of analysis by the high-temperature hydrogen extraction method, is completely retained upon contact of the sample with air.

B. After outgassing, the reactor containing the sample was cooled to 240 K, and the sample was slowly "titrated" with hydrogen at this temperature, *i.e.*, hydrogen was introduced portionwise at 1—2 atm. The reaction proceeded very slowly (the induction period was 5 h), and hydrogenation was completed only after several days. Under these conditions, the hydride phase of composition $Hf_2FeH_{5.25}$ formed. When the temperature was increased to room temperature, the concentration of hydrogen in this phase decreased to 5.0 H/IMC. It is of particular interest that, as in the first case (procedure *A*), the hydride phase $Hf_2FeH_{5.0}$ (**2**) obtained according to procedure *B* is very stable: when the phase was heated *in vacuo*, release of hydrogen started only at $T \approx 570$ K.

The X-ray diffraction study demonstrated that the $Hf_2FeH_{5.0}$ phase also retained the initial cubic structure. However, in this case, the volume of the unit cell increased by 23% (see Table 1).

The interactions of hydride phases **1** and **2** with hydrogen were studied up to p = 2000 atm at 295 and 195 K. The results of the measurements are presented in Fig. 1 in the form of the absorption and desorption isotherms for hydrogen.

Results and Discussion

The crystal structure of Hf_2Fe was studied previously[6,7] and was then repeatedly refined.[8—10] The Hf_2Fe compound crystallizes in the complex lattice of the Ti_2Ni structural type (a = 12.0246 Å, space group $Fd3m$, Z = 32). The Hf atoms occupy two positions: 48f with coordinates (0.815, 0.125, 0.125) and 16c with coordinates (0, 0, 0); Fe atoms occupy the position 32e with coordinates (0.212, 0.212, 0.212).[10] The unit cell contains 456 tetrahedral interstitial sites of six types (two A_3B (A = Hf and B = Fe), two A_2B_2, one AB_3, and one B_4) and 24 octahedral interstices A_6 of two types, which are formed by identical Hf atoms but differ in the positions in the crystal structure and in the volume (insignificantly).

An interesting feature of the Ti_2Ni structural type (Hf_2Fe belongs to this type) is the presence of a complex system of octahedra A_6, which are linked together. Each A_6 octahedron shares four (A'_6) or two (A''_6) triangular faces with the adjacent octahedra. The effective radii of the corresponding octahedral interstitial sites in the structure of Hf_2Fe are 0.68—0.70 Å. The centers of the shared triangular faces of the octahedra are the centers of the "trigonal" interstices with effective radius in the undistorted initial lattice of about 0.26 Å. The unit cell of Hf_2Fe contains 32 such trigonal interstitial sites. The total of these positions within the A'_6 and A''_6 octahedra located in the shared triangular faces can be considered as a single bulky cavity, a complex branched "channel", or a "honeycomb" system.

When the channels are filled with H atoms, which occupy the centers of octahedra and trigonal cavities, the hydrogen sublattice in the structure of the hypothetical hydride phase of composition Hf_2FeH_x, where x = 1.75, will have the configuration of the n-atom three-dimensional hydrogen cluster with interatomic H—H distances of about 1.40 and 1.25 Å and bond angles in the hydrogen chain of ~120°.

The second characteristic feature of the Ti_2Ni structural type lies in the fact that tetrahedra formed by atoms of transition metals occur in which the interatomic B—B distance is substantially larger than the corresponding distance in the crystal lattice of free metal. Thus, for example, in the structure of Hf_2Fe, the interatomic Fe—Fe distance is 3.01 Å (the sum of the standard van der Waals radii is 2.52 Å). It can be suggested that these tetrahedral interstitial sites with an effective radius of about 0.45—0.50 Å are stereochemically quite suitable for the insertion of isolated hydrogen atoms. Apparently, the probability of this process, which could result in a substantial change in the magnetic properties of the hydride, is the highest at low temperatures and high hydrogen pressures.

The interaction in the $Hf_2Fe—H_2$ system at low (not over 40—50 atm) hydrogen pressures was studied many times.[4,5,11] On the whole, the results obtained in the works with the use of different methods are not contradictory. These results made it possible to consider the $p—C$ diagram for the $Hf_2Fe—H_2$ system as follows. Apparently, absorption of hydrogen at low pressure yields two individual hydride phases of composition Hf_2FeH_x (a = 12.22—12.30 Å, where $x \approx$ 1.5—2.0,[4,5] and a = 12.65 [5] or 12.58 Å,[4] where $x \approx 3$). According to the published data,[5] the heats of formation of two these hydride phases are close to each other (60—80 kJ (mol $H_2)^{-1}$). Taking into account the substantial slope of the plateau on the isotherms corresponding to this phase transition, this equilibrium can be arbitrarily considered as invariant.

Further dissolution of hydrogen in the trihydride phase, apparently, follows the pattern seen in solid solutions with a relative increase in the volume of the unit cell ($\Delta V/V_0$) by ~5%. For the hydride phase with the maximum concentration of hydrogen ($x \approx 4.5$ and a = 12.82 Å),[4] the total volume effect of formation was 20%.

The results of neutron diffraction studies of the structures of hydride (deuteride) phases containing 3.0, 4.2, and 4.4 atoms of D per Hf_2Fe formula unit[8] allow the authors to relate the formation of the $Hf_2FeH_{3.0}$ hydride phase to the fact that hydrogen (deuterium) atoms occupy virtually only the centers of one type of tetrahedra $[Hf_3Fe]$ and, what is most interesting, to the unexpected and unpredictable *a priori* process of introduction of H atoms into "trigonal" interstices located in the centers of the faces shared by the A'_6 and A''_6 octahedra. In the $Hf_2FeH_{4.2}$ and $Hf_2FeH_{4.4}$ samples, the above-mentioned two positions in the $[Hf_3Fe]$ tetrahedra and $[Hf_3]$ triangles are subsequently occupied almost completely upon formation of the solid-solution phase based on Hf_2FeH_3. According to the data in the literature,[8] in the low-pressure phases studied previously,[4] the occupancies of other positions suitable for H atoms are low.

When considering the relationships shown in Fig. 1, the following features should be noted. The isotherms established for phases **1** and **2** virtually reproduce each other with a shift in the composition of about 0.4 H/IMC, which corresponds to the difference in the composition of the initial hydride phases $Hf_2FeH_{4.6}$ and $Hf_2FeH_{5.0}$ obtained upon initial absorption of hydrogen. An increase in the hydrogen pressure to 2000 atm at 295 K results only in the additional absorption of H_2 by the samples up to 5.2 and 5.6 H/IMC, respectively. This process is virtually reversible and is characterized by an insignificant hysteresis.

When the experimental temperature decreased to 195 K, not only the hydrogen content of hydrides increased (at 2000 atm, their compositions were $Hf_2FeH_{5.6}$ and $Hf_2FeH_{6.0}$), but the character of the interaction changed as well. First, the hysteresis increased substantially upon absorption and desorption of hydrogen (up to tens and even hundreds of atmospheres). Second, even upon subsequent heating to room temperature and lowering of the hydrogen pressure to atmospheric, the initial compositions of the hydride phases were not restored. An analysis of the samples by the high-temperature hydrogen extraction method demonstrated that the hydrogen concentrations in these samples increased by 0.15—0.2 H/IMC compared to the initial hydride phases. In this case, the X-ray phase analysis did not reveal a noticeable change in the unit cell parameters. However, the profiles of reflections for phase **1** are indicative of a high degree of crystallinity of the sample, whereas the X-ray diffraction patterns of phase **2** are characterized by a diffuse character of the lines.

In spite of the above-mentioned differences between hydride phases **1** and **2**, the processes of thermal decomposition of these phases proceed similarly. When heated *in vacuo*, hydrogen release started at 570—620 K and was completed at 1200 K. In both cases, thermal decomposition is accompanied by restoration of the structure of the initial intermetallic compound with the typical unit cell parameters.

Based on the experimental data considered in this work, the following conclusions can be made. However, some conclusions are hypothetical and call for further verification and refinement.

1. Absorpion of hydrogen by the Hf_2Fe compound up to very high concentrations (the H/IMC ratio is $\approx$ 5.2) proceeds with retention of the structural type of the initial intermetallic compound, namely, the metal matrix for hydrogen insertion.

2. Depending on the conditions of the initial absorption of hydrogen, the reaction can take two pathways. The slowed-down initial absorption at a reduced temperature made it possible to obtain a stable hydride phase of composition $Hf_2FeH_{5.0-5.2}$ regardless of the p,T conditions of the subsequent cyclization in the pressure range from 1 to 2000 atm and the temperature range from 195 to 295 K. The concentration of hydrogen in this phase is 10% higher than that in the $Hf_2FeH_{4.7}$ hydride, which we described previously[4,5,8] and obtained by the procedure *A*, *i.e.*, when initial absorption of hydrogen proceeds at room temperature without additional cooling of the sample.

Apparently, "excess" H atoms in the crystal lattice of the $Hf_2FeH_{5.0-5.2}$ phase, which are inserted during very low absorption of hydrogen upon additional cooling to 240 K, occupy the interstitial sites, which are virtually blocked when the reaction proceeds by an alternative mechanism or through an alternative pathway. It can be assumed that these interstices are A''_6 octahedral sites. Actually, the data of the crystal chemical analysis demonstrated that in this case the concentration of hydrogen in the hydride phase should increase by 0.5 H/IMC. As was demonstrated above, when the lattice expands, these interstices, together with the trigonal interstices, form a bulky channel, which can accommodate more than one hydrogen atom.

3. Broadening of reflections in the diffraction patterns of the samples of hydride phase **2** treated with hydrogen at high pressure and low temperature can be interpreted as evidence of the "strain" of its structure. Actually, it is easy to demonstrate that an increase in the volume of the crystal lattice by 20% or more corresponds to an average increase in the interatomic M—M distances by 5—7%. This is a limiting value, after which the bonds are cleaved and the structure is destroyed irreversibly. However, the hydride phase stable under normal conditions has the $Hf_2FeH_{5.0-5.2}$ composition, which is characterized by an expansion of 23%. The maximum absorption capacity of the Hf_2Fe structure that we obtained in the experiment corresponds to the $Hf_2FeH_{6.0}$ formula. This composition was obtained at 195 K and 2000 atm and corresponds, apparently, to the phase which is thermodynamically stable under these conditions.

It is very likely that the interstitial sites responsible for additional absorption of hydrogen are initially present in the structure, but hydrogen is not held in these sites because of their shape. Actually, in the structure of Hf_2Fe, the following interstices occur: the $[Fe_4]$ tetrahedra with effective radius of about 0.45—0.50 Å and $[HfFe_3]$ tetrahedra with effective radius of 0.40 Å (32 sites per unit cell, *i.e.*, one site per Hf_2Fe formula unit). When these positions are partially occupied (~50%), the composition of the hydride phase should be close to $Hf_2FeH_{6.2}$, which virtually corresponds to the composition of the high-pressure phase, which we obtained at 195 K.

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