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**Study of the Interaction with Hydrogen  
and Ammonia of Titanium and Its Alloys with Iron**

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**Abstract**—Results of hydrogenation of titanium, intermetallic compound TiFe, and titanium-enriched alloys with iron, Ti<sub>67</sub>Fe<sub>33</sub> (Ti<sub>2</sub>Fe) and Ti<sub>80</sub>Fe<sub>20</sub> (Ti<sub>4</sub>Fe), with hydrogen and ammonia were summarized and analyzed. The phase transformations in the temperature range 20–500°C were found, the temperatures at which hydride phase are formed were determined, the alloy dispersion conditions were optimized, and the reaction products were analyzed. Specific features of the interaction of the polycrystalline systems with ammonia in the presence of ammonium chloride at various temperatures were revealed, and the conditions in which hydride, hydride-nitride, and nitride phases are formed were determined. Data were obtained about the possibility of using Ti–Fe alloys as the working material in reusable metal hydride hydrogen accumulators.

**Keywords:** hydrogen, ammonia, intermetallic compound, alloy, hydride, nitride, phase transformations, dispersion, metal hydride hydrogen accumulator

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One of the most important problems of hydrogen power engineering and technology using hydrogen as energy carrier is associated with a search for materials reversibly interacting with hydrogen to give hydrides with high content of hydrogen. Compounds of this kind are hydrogen accumulators and are widely used as working substances in compact and safe hydrogen-storage systems, hydrogen energy-accumulation systems, thermosorption compressors, heat pumps, and fuel cells [1–5].

At present, the increasing practical importance is gained by magnesium-based alloys due to the high content of hydrogen in magnesium hydride (7.6 wt %) [6]. Among magnesium-containing alloys stand out alloys of double and triple eutectics in the magnesium–nickel and magnesium–REE–nickel systems, respectively, with hydrogen-sorption capacity of up to 5.5 wt % [7, 8].

One of classical examples of using an intermetallic compound as a substance that reversibly sorbs hydrogen is, in addition to LaNi<sub>5</sub>, TiFe due to the comparatively high hydrogen capacity of the corresponding hydride (1.92 wt % for the TiFeH<sub>2</sub> composition), low equilibrium

hydride dissociation pressure (~0.2 MPa at 20°C), stability against hydrogenolysis in repeated hydrogenation–dehydrogenation cycles, ecological safety in operation, ready availability, and low cost of the metals constituting the intermetallic compound [1, 9–14].

However, the application of TiFe intermetallide as the working substance for a hydrogen accumulator is hindered by the severe alloy-activation conditions, stringent requirements to the purity of hydrogen to be absorbed, and difficulties in obtaining the stoichiometric composition of a prepared alloy. The activation of the intermetallide for its subsequent hydrogenation consists in a multiple treatment in the atmosphere of hydrogen at high temperatures (>500°C) and pressures (>6.5 MPa) or in a heating of the alloy to 400–450°C under hydrogen pressure of 0.7 MPa, followed by a vacuum treatment and repeated heating to 200°C under a hydrogen pressure of 6.5 MPa [9]. According to the constitution diagram of the Ti–Fe system, the TiFe compound has a homogeneity region [15]. Departure from stoichiometry toward a decreasing content of titanium (46–48 at % Ti) results in

that the compound  $\text{TiFe}_2$  not interacting with hydrogen appears in the alloy, and  $\text{TiH}_2$  is formed in hydrogenation in  $\text{Ti} + \text{TiFe}$  ( $\geq 52$  at % Ti) double alloys [9, 16].

To solve the problem of activation of the intermetallide, simplify procedures of operation with this compound, and improve its service characteristics, new approaches and procedures are being developed and implemented: alloying metal additives that cause a catalytic effect in hydrogenation, nanostructuring or amorphization of the alloy, mechanochemical treatment in ball mills, mechanical fusion, and replacement of hydrogen as hydrogenating agent with ammonia (hydronitrogenation reaction), etc. [14, 17–19]. For example, a procedure of the so-called “mild” synthesis of hydrides is known, which precludes the undesirable side reaction of disproportionation and consists in that hydrogen is delivered into an autoclave in small portions as it is absorbed by the metallic phase or in a mixture with an inert gas at room temperature [20, 21]. In fact, the treatment of a metallic or polymetallic phase is also an example of the mild synthesis because an equilibrium reaction of ammonia decomposition into hydrogen and nitrogen occurs under heating ( $\leq 250^\circ\text{C}$ ) in an ammonia-filled reactor with metal powder, and thus the hydronitrogenation occurs at a low hydrogen concentration without self-heating of the reactor and without hydrogenolysis [22].

Titanium dihydride that contains 4 wt % reversible hydrogen and is presently used as a source of hydrogen has an important shortcoming, high dehydrogenation temperature ( $>400^\circ\text{C}$ ). The direct hydrogenation of titanium also occurs at an elevated temperature. To make lower the hydrogenation temperature, it is possible, for example, to use intermetallide additives and, in particular,  $\text{TiFe}$  intermetallic compound as hydrogenation catalysts [23]. Thus, there is manifested the mutual influence of the components of the metallic mixture, titanium as an alloying additive to the intermetallide and intermetallic compound as a hydrogenation catalyst. It is quite real to regard the mixture of  $\text{TiFe}$  intermetallic compound and titanium from the standpoint of obtaining the corresponding reversible hydride phases in a single reactor. However, it is more promising to melt titanium-rich alloys in the  $\text{Ti-Fe}$  system, hydrogenate these alloys, and use, depending on requirements, as a high-temperature (Ti based) and low-temperature ( $\text{TiFe}$  based) hydrogen accumulator. Metal hydride accumulators of this kind can operate in the temperature range  $20\text{--}500^\circ\text{C}$ .

The reaction of interaction of metals and polymetallic phases with gaseous ammonia is used in the ammonia method of dispersion [18]. Compared with the hydride method, the ammonia dispersion can produce metallic powders with smaller particle size, which reaches in some cases the nanometer range.

In this study, we briefly summarized and analyzed the results obtained in studies of the hydrogenation with hydrogen and ammonia of the intermetallic compound  $\text{TiFe}$  and titanium-enriched alloys with iron of composition  $\text{Ti}_{67}\text{Fe}_{33}$  (henceforth  $\text{Ti}_2\text{Fe}$ ) and  $\text{Ti}_{80}\text{Fe}_{20}$  (henceforth  $\text{Ti}_4\text{Fe}$ ), determined the phase transformations in systems with ammonia and hydrogen in the temperature range  $20\text{--}500^\circ\text{C}$ , found the temperatures in which hydride phases are formed with the maximum possible content of hydrogen, analyzed the conditions and results of dispersion of the alloys, compared the results of using hydrogen and ammonia in the reactions with  $\text{Ti}_2\text{Fe}$  and  $\text{Ti}_4\text{Fe}$  alloys, and demonstrated the potentialities and prospects for use of the above alloys as working substances in metal hydride hydrogen accumulators.

It is known that the state diagram of the  $\text{Ti-Fe}$  system is characterized by the presence of two intermetallic compounds  $\text{TiFe}$  (CsCl structural type,  $a = 2.975 \text{ \AA}$ ) and  $\text{TiFe}_2$  ( $\text{MgZn}_2$  structural type,  $a = 4.77 \text{ \AA}$  and  $c = 7.79 \text{ \AA}$ ). The maximum solubility of iron in  $\alpha\text{-Ti}$  at  $600^\circ\text{C}$  is 0.05 at %, and that in  $\beta\text{-Ti}$  at  $800^\circ\text{C}$ ,  $\sim 20$  at % [15].

According to the literature [9, 24],  $\text{TiFe}$  interacts with hydrogen via the formation of a solid solution of  $\text{TiFeH}_{0.1}$  composition, with its subsequent additional hydrogenation to hydride phases that are unstable at room temperature on relieving the pressure: monohydride  $\text{TiFeH} \sim 1$  (tetragonal crystal system,  $a = 3.18 \text{ \AA}$  and  $c = 8.73 \text{ \AA}$ ) and dihydride  $\text{TiFeH} \sim 2$  (cubic structure,  $a = 6.61 \text{ \AA}$ ). The  $\text{TiFe}_2$  intermetallide does not interact with hydrogen under heating to  $600^\circ\text{C}$  under a pressure of up to 160 MPa [25].

The titanium dihydride  $\gamma$ -phase of composition  $\text{TiH}_{1.98}$  has at room temperature a face-centered cubic lattice ( $\text{CaF}_2$  type,  $a = 4.454 \text{ \AA}$ ), which undergoes tetragonal distortions at a higher hydrogen content (for  $\text{TiH}_2$  composition,  $a = 4.528 \text{ \AA}$  and  $c = 4.279 \text{ \AA}$ ) [26]. A direct hydrogenation of titanium occurs with a noticeable rate only at temperatures  $T > 400^\circ\text{C}$ .

Iron hydride of composition  $\text{H/Fe} = 0.65\text{--}0.7$  has been only obtained under a pressure of 6.7 GPa at  $250^\circ\text{C}$  [27].

## EXPERIMENTAL

The alloys and the intermetallic compound were prepared by fusion of a stock of metals with purity of >99.9% in a furnace with nonconsumable tungsten electrode in the atmosphere of high-purity argon under a pressure of 0.2 MPa, with the subsequent annealing of alloy beads at 800°C for two weeks and their quenching in cold water.

The alloys were ground in a titanium mortar, with the subsequent separation by sieving of a powder fraction with particle size of up to 100 µm. The solid solutions  $S_{sp}$  of the powder was ~0.04 m<sup>2</sup> g<sup>-1</sup>.

The alloys were hydrogenated with high-purity hydrogen (99.99%) from a metal hydride accumulator based on LaNi<sub>5</sub>H<sub>x</sub>. The hydronitrogenation was performed with ammonia of 99.99% purity, dried with metallic sodium. Ammonium chloride of chemically pure grade was dried via a vacuum treatment at 150°C for 9 h.

The hydrogenation and hydronitrogenation of the alloy was performed in a stainless-steel container placed in a 60 mL reactor-autoclave of a high-pressure installation.

Prior to being hydrogenated, the alloy was degassed in a vacuum at 200°C for 1 h. Then, the autoclave was filled with hydrogen to a pressure of 2 MPa and the heating was terminated. For equilibrium to be attained, the autoclave with a sample was kept at room temperature for several hours.

The interaction of the thus prepared powders with ammonia was performed in the presence of activator NH<sub>4</sub>Cl, added in an amount of 10 wt % relative to the mass of the alloy introduced into the reaction, in the temperature range 100–500°C at initial ammonia pressure of 0.6–0.8 MPa. A weighed portion (0.8–1.0 g) of the mixture was ground in a titanium mortar at room temperature in the atmosphere of argon, transferred to the reactor-autoclave, the reactor was evacuated to a pressure of ~1 Pa for 30 min at room temperature, ammonia was delivered, and the reactor was allowed to stay for 30 min. Further, the reactor was heated to prescribed temperatures, kept at a prescribed temperature for 3 h, and cooled to room temperature and again heated. The required number of heating–cooling cycles was determined from the termination of pressure variation because the pressure in the system grows in the course of the interaction (up to 1.5 MPa). As the last cycle ended, ammonia was dumped into a buffer vessel; the reaction products were discharged in an inert atmosphere and analyzed.

The activating effect of ammonium chloride is due to the reversible reaction that occurs as the temperature is elevated



Hydrogen chloride being released interacts with the surface metal oxide to give a chloride and thereby disintegrates the oxide film, which facilitates the hydrogenation of the metallic phase. Because the dissociation and recombination processes by reaction (1) in the atmosphere of argon are very fast, metal chloride is formed in insignificant amounts not recognized by the X-ray diffraction (XRD) analysis.

The products formed in hydronitrogenation of the alloys contained chemisorbed ammonia, which precluded the oxidation and dehydrogenation and enabled working in air with the powders obtained. According to differential thermal analysis data, chemisorbed ammonia is removed at 80–120°C. Thus, the treatment with ammonia is a convenient method for passivation of chemically active hydride and metallic phases.

NH<sub>4</sub>Cl was removed from the interaction products by treatment of the resulting mixture with absolute ethanol under mechanical agitation for 1 h at room temperature (the procedure was twice repeated) or by vacuum treatment of the mixture at ~1 Pa at 300°C for 3 h.

The composition of the alloys and products of hydrogen or ammonia treatment was determined by chemical analysis. The amounts of hydrogen and nitrogen were determined on a Vario Micro cube CHNS/O elemental analyzer (Elementar GmbH). The analysis for the content of chlorine was made by the turbidimetric method.

XRD studies were carried out on an ADP-1 diffractometer (CuK<sub>α</sub> radiation). The error in determining the crystal lattice constants did not exceed 0.005 Å. For all the phases, the lattice constants coincided with the published values. The average particle size of a powder was calculated from the specific surface area on the assumption of the spherical shape of particles.

The specific surface area  $S_{sp}$  of the samples was determined from low-temperature adsorption of krypton after degassing in a vacuum (residual pressure  $1.3 \times 10^{-3}$  Pa) at 300°C for 5 h and calculated by the Brunauer–Emmett–Teller method. Because hydrogen evolves from TiFe-based unstable compounds in the course of the vacuum treatment, the values measured

**Table 1.** Conditions and results of titanium hydrogenation

Sample no.	Metal	Hydrogenation conditions			Product composition	<i>H</i> , wt %	$T_{\text{decomp}}$ , °C
		<i>P</i> , MPa	<i>T</i> , °C	time, h			
Hydrogenation with hydrogen							
1	Powder	1.5	400	0.5	TiH <sub>2</sub>	4.0	550, 660
2	Small pieces	2.0	550	2	TiH <sub>2</sub>	4.0	550, 660
Hydrogenation with ammonia							
3	Powder	0.6–0.8	250	30	TiH <sub>2</sub> N <sub>0.15</sub>	3.8	540, 650

for the specific surface area actually refer to degassing products. However, these values give notion about the changes occurring in the starting alloys in the atmosphere of hydrogen or ammonia at various temperatures. The determination error was  $\pm 10\%$ .

The pycnometric density  $\rho$  of the powders was determined at 20°C in toluene with accuracy of  $\pm 3\%$ .

The pressure in the system was measured with a MO reference pressure gage of 0.4 accuracy class.

## RESULTS AND DISCUSSION

**Hydrogenation of metallic titanium.** The interaction of titanium in the form of pieces (1–10 mm) or powder (particle size up to 500  $\mu\text{m}$ ) with high-purity hydrogen at temperatures in the range 400–550°C and pressures of 1.5–2 MPa is accompanied by the formation of a dihydride of composition TiH  $\sim 2$ , which crystallizes in the cubic crystallographic system ( $a = 4.452 \text{ \AA}$ ) (Table 1 sample nos. 1 and 2 [28]).

The experiments performed in the study to examine the influence exerted by temperature, size of starting particles, cycling, and treatment duration on the direction of the titanium hydronitrogenation process demonstrated that the interaction of titanium powder with particle size of up to 50  $\mu\text{m}$  at a temperature of 250°C and contact duration of 30 h yields titanium hydride TiH<sub>2</sub> ( $S_{\text{sp}} = 57.4 \text{ m}^2 \text{ g}^{-1}$ ), which crystallizes in the tetragonal crystal system ( $a = 4.4710 \text{ \AA}$  and  $c = 4.3874 \text{ \AA}$ ) and contains, according to chemical analysis data,  $\sim 0.15$  nitrogen atom per formula unit of TiH<sub>2</sub> (Table 1, sample no. 3) [28].

Treatment of titanium with ammonia at 300°C yields a mixture of titanium hydride and nitride. Raising the hydronitrogenation temperature further is accompanied by a gradual decrease in the fraction of titanium hydride in

the products and by an increase in the amount of titanium nitride TiN, which is the only product at the interaction temperature of 400°C ( $a = 4.2347 \text{ \AA}$ ) with specific surface area of 53.5  $\text{m}^2 \text{ g}^{-1}$ .

An estimate of the average particle size (15–40 nm) demonstrated that nanocrystalline titanium hydride or titanium nitride is formed.

Thus, it follows from the above experimental results that using ammonia instead of hydrogen lowers the temperature at which titanium hydride is formed from 400–450°C to 250°C. As shown in [28], this is a convenient way to obtain nanodispersed powders of metal hydrides, hydronitrides, and nitrides, and, on removing hydrogen from the hydrides, to produce highly dispersed metal powders.

**Hydrogenation of the TiFe intermetallic compound.** An activated intermetallic compound TiFe is hydrogenated in the atmosphere of hydrogen under a pressure of 5 MPa in 20 min to give a dihydride of TiFeH<sub>2.0</sub> composition, which is preserved on relieving the pressure if the substance is preliminarily treated in the autoclave with carbon oxide (Table 2, sample no. 1).

The interaction of the intermetallic compound TiFe with ammonia was examined in the temperature range 150–500°C at treatment duration of about 30 h. The synthesis temperature and the characteristics of the resulting products are presented in Table 3 [29]. It should be noted that, for all the reactions of TiFe intermetallide with ammonia in the autoclave at room temperature, its hydride and hydridonitride phases do not exist above room temperature, being formed when the reactor is cooled to room temperature. This circumstance should be kept in mind when discussing the composition of the products obtained in the course of each synthesis.

**Table 2.** Conditions and results of interaction of TiFe intermetallide and Ti<sub>2</sub>Fe and TiFe<sub>4</sub> alloys with hydrogen

Sample no.	Alloy	Phase composition	Hydrogenation conditions			Product characteristics			
			<i>T</i> , °C	<i>P</i> , MPa	time, h	<i>H</i> , wt %	$\rho$ , g cm <sup>-3</sup>	phase composition	lattice constant <i>a</i> , Å
1	Ti <sub>50</sub> Fe <sub>50</sub> (TiFe)	TiFe	20 <sup>a</sup>	5.0	20	1.9	5.47	TiFeH <sub>2.0</sub>	6.61
2	Ti <sub>66.6</sub> Fe <sub>33.4</sub> (Ti <sub>2</sub> Fe)	TiFe + $\beta$ -(Ti,Fe)	350	3.0	15	2.5	4.70	TiFeH <sub>2.0</sub> <sup>b</sup> TiH <sub>2</sub>	6.61 4.457
3	Ti <sub>66.6</sub> Fe <sub>33.4</sub> (Ti <sub>2</sub> Fe)	TiFe + $\beta$ -(Ti,Fe)	150 <sup>c</sup>	3.0	30	2.5	4.70	TiFeH <sub>2.0</sub> <sup>b</sup> TiH <sub>2</sub>	6.61 4.457
4	Ti <sub>80</sub> Fe <sub>20</sub> (Ti <sub>4</sub> Fe)	$\beta$ -(Ti,Fe)	350	2.5	120	3.2	4.27	TiFeH <sub>2.0</sub> <sup>b</sup> TiH <sub>2</sub>	6.61 4.457

<sup>a</sup> After “severe” activation.

<sup>b</sup> The phases are formed when the reactor is cooled to room temperature.

<sup>c</sup> Powder with particle size of 200  $\mu$ m.

Interaction of TiFe with ammonia at 150°C (Table 3, sample no. 1) yields a solid solution of hydrogen in the intermetallide of composition TiFeH<sub>0.1</sub>. In the case of this treatment, the specific surface area increases from 0.04 m<sup>2</sup> g<sup>-1</sup> for the starting mixture to 0.9 m<sup>2</sup> g<sup>-1</sup> for the reaction product. Raising the interaction temperature to 200°C results in that a dihydride of composition TiFeH<sub>2</sub>N<sub>x</sub> (Table 3, sample no. 2), stabilized with ammonia and containing nitrogen, appears in the reaction products together with TiFeH<sub>0.1</sub>. The lattice constant of TiFeH<sub>2</sub>N<sub>x</sub> ( $a = 6.642$  Å) somewhat exceeds the published value for TiFeH<sub>2</sub> ( $a = 6.61$  Å), which is probably due to the incorporation of a certain amount of nitrogen into the octahedral voids of the TiFe matrix. It should be noted that the above hydride phases are present in the products of all the reactions performed in the temperature range 150–450°C: the corresponding diffraction patterns contain reflections characteristic of these phases (Table 3, sample nos. 1–7). Thus, the solid solution of hydrogen in TiFe is preserved in the atmosphere of ammonia in the above temperature range, and intermetallide dihydride is probably formed due to the additional hydrogenation of the solid solution in the course of cooling of the reaction products to room temperature.

A further increase in the amount of the dihydride phase of the intermetallide is observed in the reaction products at 250°C, but its decomposition occurs simultaneously with its formation: weak reflections of titanium dihydride and titanium nitride are observed in the corresponding diffraction patterns (Table 3, sample no. 3). These

reflections become stronger in the diffraction patterns of the reaction products obtained at 300°C, which makes it possible to determine the lattice constants of titanium hydride and nitride ( $a = 4.432$  Å for TiH<sub>2</sub> and  $a = 4.218$  Å for TiN) (Table 3, sample no. 4). It is known [30] that the formation of titanium hydride is an intermediate stage of the synthesis of titanium nitride. As the interaction temperature of the starting components is raised further to 350°C, the amount of the latter in the reaction products grows and is accompanied by the formation of iron nitride (for  $\gamma'_{\text{Fe}_4\text{N}}$ ,  $a = 3.792$  Å) (Table 3, sample no. 5). Unfortunately, the appearance of the Fe phase as an intermediate stage in a way to formation of iron nitride at 300–350°C could not be recorded.

Treatment of the intermetallide with ammonia at 400°C makes it possible to record the appearance of  $\alpha$ -Fe ( $a = 2.869$  Å) in the reaction products, together with titanium and iron nitrides (Table 3, sample no. 6). If the starting reaction mixture is kept at 450°C (Table 3, sample no. 7), iron nitride of composition Fe<sub>4</sub>N starts to decompose to Fe<sub>3</sub>N, which ends as the interaction temperature is raised further to 500°C (Table 3, sample no. 8). In this case,  $\alpha$ -Fe and the intermetallic compound TiFe<sub>2</sub>, which does not interact with the gas phase in the conditions under study, were observed in the products of the reaction performed at 500°C.

The results obtained for TiFe hydronitrogenation with ammonia (Table 3) make it possible to trace the stage-by-stage phase transformation upon an increase in temperature from the starting intermetallide to the

**Table 3.** Conditions and results of TiFe interaction with ammonia

Sample no.	$T_{\text{synth}}$ , °C	Interaction products		
		phase composition	lattice constant $a$ , Å	$S_{\text{sp}}$ , m <sup>2</sup> g <sup>-1</sup>
1	150	TiFeH <sub>0.1</sub>	2.985	0.9
2	200	TiFeH <sub>0.1</sub> <sup>a</sup>	2.983	4.5
		TiFeH <sub>2</sub> N <sub>x</sub> <sup>a</sup>	6.642	
3	250	TiFeH <sub>0.1</sub> <sup>a</sup>	2.980	4.3
		TiFeH <sub>2</sub> N <sub>x</sub> <sup>a</sup>	6.713	
		TiH <sub>2</sub> traces	–	
		TiN traces	–	
4	300	TiFeH <sub>0.1</sub>	2.975	2.3
		TiFeH <sub>2</sub> N <sub>x</sub> <sup>a</sup>	6.640	
		TiH <sub>2</sub>	4.432	
		TiN	4.218	
5	350	TiFeH <sub>0.1</sub> <sup>a</sup>	2.971	3.1
		TiFeH <sub>2</sub> N <sub>x</sub> <sup>a</sup>	6.710	
		TiN	4.235	
		γ'-Fe <sub>4</sub> N	3.792	
6	400	TiFeH <sub>0.1</sub>	2.983	4.5
		TiFeH <sub>2</sub> N <sub>x</sub> <sup>a</sup>	6.715	
		TiN	4.223	
		γ'-Fe <sub>4</sub> N	3.788	
		α-Fe	2.869	
7	450	TiFeH <sub>0.1</sub> <sup>a</sup>	2.987	5.7
		TiFeH <sub>2</sub> N <sub>x</sub> <sup>a</sup>	6.690	
		TiN	4.206	
		γ'-Fe <sub>4</sub> N	3.790	
		α-Fe	2.866	
8	500	TiFeH <sub>0.1</sub>	2.993	8.9
		TiN	4.233	
		α-Fe	2.870	
		Fe <sub>3</sub> N	$a = 2.715, c = 4.299$	
		TiFe <sub>2</sub>	$a = 4.762, c = 7.811$	

<sup>a</sup> The phases are formed when the reactor is cooled to room temperature.

products of its complete decomposition (TiN, γ'-Fe<sub>4</sub>N, and α-Fe) and to specify the particular role of ammonia in these processes, which consists in the decomposition of the TiFe metallic matrix. Certainly, the products cannot be used to trace all the processes occurring when the intermetallide is treated with ammonia in the presence of a promoting agent. For example, it is well known that the formation of TiFe intermetallide dihydride is accompanied, or, more precisely, preceded by the

appearance of a monohydride phase of composition TiFe ~ 1, which is also unstable at ~20°C and 0.1 MPa [9]. The diffraction patterns of the interaction products, the corresponding peaks are superimposed on each other, and it is impossible to unambiguously conclude that the monohydride phase is present in the products.

Thus, using ammonia instead of hydrogen for hydrogenation/hydronitrogenation of TiFe intermetallide enabled dispersion of this compound, i.e., made it

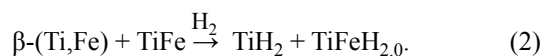
possible to transform it into a highly dispersed powder with nanometer particle size without any preliminary activation, without enhanced requirements to the purity of hydrogen used, and without stringent limitations on the composition of an alloy in its smelting.

**Hydrogenation of Ti<sub>2</sub>Fe alloy.** According to XRD data the double-phase Ti<sub>2</sub>Fe alloy (66.6 at % Ti, 33.4 at % Fe) has two phases: intermetallic compound TiFe ( $a = 2.976 \text{ \AA}$ ) and a solid solution of iron in  $\beta$ -titanium (solubility of iron in  $\beta$ -Ti is  $\sim 20$  at % at  $800^\circ\text{C}$ ,  $a = 3.174 \text{ \AA}$ ), in agreement with the Ti–Fe diagram of state [15].

Prior to being hydrogenated, the Ti<sub>2</sub>Fe alloy was subjected to a preliminary activation via heating in a vacuum (residual pressure  $\sim 1 \text{ Pa}$ ) at a temperature of  $350^\circ\text{C}$  for 1 h and cooled to room temperature [31].

On being degassed, the double-phase alloy taken as small pieces is fully saturated with hydrogen at  $350^\circ\text{C}$  in 15 min, with induction period of 30 min (Table 2, sample no. 2). The hydrogenation temperature decreases to  $150^\circ\text{C}$  if the starting sample is ground to a powder with particle size of up to  $200 \mu\text{m}$  (Table 2, sample no. 3) after pressure is relieved and samples are treated with carbon monoxide, the reaction products contain in both cases 2.5 wt % hydrogen. In the course of hydrogenation, the sample breaks up into a fine powder with metallic shine.

The process of hydrogenation of the Ti<sub>2</sub>Fe double-phase alloy is described by the scheme



That is, the components of the solid solution of iron in  $\beta$ -titanium interact in the course of hydrogenation to give an additional amount of the TiFe intermetallic compound. In addition to yielding titanium hydride under comparatively mild conditions, reaction (2) is also of interest because the TiFe intermetallic compound is formed in the ternary system Ti–Fe–H<sub>2</sub> at a low temperature.

According to XRD data, the hydrogenation product not stabilized with carbon monoxide is composed of titanium dihydride TiH<sub>2</sub> ( $a = 4.448 \text{ \AA}$ ) and a solid solution of hydrogen in the intermetallide, TiFeH<sub>0.1</sub> ( $a = 2.9865 \text{ \AA}$ ).

The temperature of treatment of the Ti<sub>2</sub>Fe double-phase alloy with ammonia in the presence of ammonium chloride and the results of hydronitrogenation are presented in Table 4 (the duration of the runs is  $\sim 30$  h). It can be seen that temperature affects the composition of the products.

**Table 4.** Chemical and phase transformations of Ti<sub>2</sub>Fe and Ti<sub>4</sub>Fe alloys in the atmosphere of NH<sub>3</sub> in relation to temperature

Alloy	$T, ^\circ\text{C}$	Reaction products
Ti <sub>2</sub> Fe	150	$\beta\text{-(Ti,Fe)} + \text{TiFeH}_{-2}^a$
	200	$\beta\text{-(Ti,Fe)} + \text{TiFeH}_{-2}\text{N}_{0.1}^a$
	250	$\beta\text{-(Ti,Fe)}\text{H}_x + \text{TiH}_{-2} + \text{TiFeH}_{-2}\text{N}_{0.1}^a$
	350–400	$\text{TiN}_{-1} + \text{TiFeH}_{-2}\text{N}_x^a$
	500	$\text{TiN}_{-1} + \text{Fe}_4\text{N} + \alpha\text{-Fe} + \text{TiFe}_2$
Ti <sub>4</sub> Fe	100	$\beta\text{-(Ti,Fe)}\text{H}_x + \text{TiFeH}_{-2}^a + \text{TiH}_2$
	150	$\beta\text{-(Ti,Fe)} + \text{TiFeH}_{-2}^a + \text{TiH}_2$
	200–300	$\text{TiFeH}_{-2}\text{N}_x^a + \text{TiH}_2$
	350	$\text{TiH}_2 + \text{TiN} + \text{TiFeH}_{-2}\text{N}_x^a$
	400	$\text{TiN} + \text{TiFeH}_{-2}\text{N}_x^a + \text{TiH}_2^b$
	450	$\text{TiN}_{-1} + \text{Fe}_4\text{N}^b + \text{TiFeH}_{-2}\text{N}_x^a$
	500	$\text{TiN} + \alpha\text{-Fe}$

<sup>a</sup> The phases are formed when the reactor is cooled to room temperature.

<sup>b</sup> Trace amounts.

The hydronitrogenation of the alloy begins at a temperature of  $150^\circ\text{C}$  and is accompanied by an increase in the specific surface area of the product (from  $0.04$  to  $0.35 \text{ m}^2 \text{ g}^{-1}$ ). Titanium is not hydrogenated at this temperature, whereas the intermetallide phase absorbs hydrogen to give TiFeH<sub>2</sub> ( $a = 6.6090 \text{ \AA}$ ). Beginning at a temperature of  $200^\circ\text{C}$ , insignificant amounts of nitrogen are incorporated into the lattice of intermetallide hydride, with a slight change in the lattice constant (for TiFeH<sub>2</sub>N<sub>0.1</sub>,  $a = 6.6890 \text{ \AA}$ ). As the temperature is raised further to  $250^\circ\text{C}$ , the titanium dihydride phase TiH<sub>2</sub> adds to the hydronitrogenation products already known at the preceding temperature.

The products formed when the double-phase alloy is treated with ammonia at  $350\text{--}400^\circ\text{C}$  are composed of the titanium nitride phase TiN<sub>1</sub> ( $a = 4.2332 \text{ \AA}$ ) and the phase with nitrogen incorporated into the lattice of intermetallide hydride TiFeH<sub>2</sub>N<sub>x</sub> ( $a = 6.6884 \text{ \AA}$ ). It should be noted that TiFe-based hydride phase with composition specified in Table 4 are formed when the reactor is cooled to room temperature.

At  $500^\circ\text{C}$ , iron nitride Fe<sub>4</sub>N ( $a = 3.8149 \text{ \AA}$ ) is quantitatively formed, which is due to the deeper

decomposition of the intermetallide. In addition to the iron and titanium nitride phases, the hydronitrogenation products contain, according to XRD data,  $\alpha$ -iron ( $a = 2.8656 \text{ \AA}$ ) and a new intermetallic compound  $\text{TiFe}_2$  (hexagonal crystal system,  $a = 4.7722 \text{ \AA}$  and  $c = 7.8012 \text{ \AA}$ ), which do not interact with hydrogen under these conditions.

It should be noted that the metal hydride phases formed in this system, as also in the  $\text{TiFe-NH}_3$  system, are "passivated" by ammonia, which enables an XRD analysis of the products at their preserved phase composition (which is particular important, as already noted above, for the  $\text{TiFeH}_{2-x}\text{N}_x$  phase).

Thus, it follows from the results obtained that using ammonia as hydrogenating agent makes it possible to avoid a labor-consuming and comparatively complicated preliminary activation of the components constituting the double-phase alloy.

To use the alloy under study as a working substance for accumulation of hydrogen, it is necessary to perform, on removing  $\text{NH}_4\text{Cl}$ , one more procedure for additional hydrogenation of the product with pure hydrogen directly in the accumulator. The thus prepared accumulator can be used at room temperature due to the evolution of hydrogen from the intermetallide hydride (~32% of the total amount of stored hydrogen) and under heating to 550–600°C due to the evolution of hydrogen in the decomposition of titanium dihydride. A metal-hydride accumulator based on the double-phase alloy  $\text{Ti}_2\text{Fe}$  can operate in the range from room temperature to 600°C and release up to 2.4 wt % hydrogen.

**Hydrogenation of  $\text{Ti}_4\text{Fe}$  alloy.** The  $\text{Ti}_4\text{Fe}$  alloy (80 at % Ti and 20 at % Fe) has the  $\beta$ -Ti structure and is a solid solution of iron in  $\beta$ -titanium (solubility of iron in  $\beta$ -Ti is ~20 at % at 800°C,  $a = 3.174 \text{ \AA}$ ), in agreement with the constitution diagram of the Ti-Fe system [15]. According to XRD data, the smelted  $\beta$ -(Ti, Fe) alloy is single-phase with cubic-lattice constant  $a = 3.1678 \text{ \AA}$ .

In [32], an analysis of the interaction of an alloy of this kind with hydrogen demonstrated that a hydride phase of composition  $\text{Ti}_4\text{FeH}_{8.3-8.8}$  crystallizing in the structural type of titanium dihydride, but with a substantially shorter lattice constant ( $a = 4.376-4.382 \text{ \AA}$ ), is formed at room temperature and pressure of 4 MPa. At 300–400°C in the atmosphere of hydrogen, the alloy undergoes hydrogenolysis and decomposes to give titanium dihydride and  $\text{TiFe}$  intermetallide [32].

Table 2 (sample no. 4) shows that the hydrogenation of the alloy with hydrogen at a temperature of 350°C yields a mixture of titanium dihydride and the hydride phase of the intermetallide with lattice constant coinciding with the values known from the literature [24, 26].

The results obtained in treatment of the alloy under study with ammonia are presented in Table 4.

The treatment of the alloy with ammonia at 100°C yields a mixture of products, one of which crystallizes in the cubic crystal system with lattice content  $a = 3.3797 \text{ \AA}$ , which differs from that for the starting alloy and suggests that a hydride phase of composition  $\beta$ -(Ti,Fe) is formed. This composition is probably the closest to the  $\text{Ti}_4\text{FeH}_{8.3-8.8}$  phase described in [32], but the synthesis temperature is too high for the starting alloy to be fully transformed to the corresponding hydride, which decomposes at this temperature to give hydride phases of titanium and  $\text{TiFe}$  intermetallide present in the reaction products. It should be noted that, as already mentioned above, the hydride phase  $\text{TiFeH}_2$  is formed as a product of the reactions performed at various temperatures when the reactor is cooled to room temperature. The products of the reaction at 100°C are characterized by a substantial rise in the specific surface area (from 0.04 to 1.3  $\text{m}^2 \text{ g}^{-1}$ ), which indicates that the powder dispersity becomes higher.

A slight increase in the hydronitrogenation temperature (to 150°C) results in that there is no hydride phase  $\beta$ -(Ti,Fe) in the reaction products. This means that this hydride does not exist at this temperature, being fully decomposed to the hydride phases of titanium and intermetallide. In addition, the reaction products are characterized by a decrease in the specific surface area to 0.3  $\text{m}^2 \text{ g}^{-1}$ .

The products of the hydronitrogenation performed at temperatures of 200–300°C contain the titanium dihydride phase and a phase based on dihydride of the  $\text{TiFe}$  intermetallic compound with a lattice constant ( $a = 6.7054 \text{ \AA}$ ) increased relative to the value known for  $\text{TiFeH}_2$  ( $a = 6.61 \text{ \AA}$ ) [9]. As already noted, this increase is due to the incorporation of insignificant amounts of nitrogen into the lattice of intermetallide hydride and to the corresponding formation, according to chemical analysis data, of the  $\text{TiFeH}_{2-x}\text{N}_x$  phase, which is also preserved as a product of reactions performed at subsequent temperatures.

When the alloy is treated with ammonia at a temperature of 300°C, a titanium nitride phase of composition  $\text{TiN}$



( $a = 4.2239 \text{ \AA}$ ) is added to the products known for the preceding hydronitrogenation temperatures. This phase remains one of hydronitrogenation products at all the subsequent treatment temperatures.

Raising the hydronitrogenation temperature to  $450^\circ\text{C}$  is characterized by the onset of decomposition of the  $\text{TiFeH}_{1.2}\text{N}_x$  phase and appearance of iron nitride  $\text{Fe}_4\text{N}$ . Metallic  $\alpha\text{-Fe}$  ( $a = 2.8607 \text{ \AA}$ ) appears, in addition to the titanium nitride phase, in the products of the hydronitrogenation reaction performed at  $500^\circ\text{C}$ .

Noteworthy is that the specific surface area of the reaction products sharply increases (from  $0.2$  to  $46.4 \text{ m}^2 \text{ g}^{-1}$ ) as the process temperature is raised from  $250$  to  $400^\circ\text{C}$ , which indicates that a mixture of highly dispersed powders is formed. The decrease in the specific surface area of the products on raising the hydronitrogenation temperature to above  $400^\circ\text{C}$  is due to the sintering of the powders.

A thermal analysis of hydronitrogenation products obtained at  $200\text{--}300^\circ\text{C}$  demonstrated the presence in the thermograms of three endothermic effects at  $90$ ,  $550$ , and  $660^\circ\text{C}$ , accompanied by the loss of mass. The first of these corresponds to the release of hydrogen from the "ammonia-stabilized" hydride phase of the intermetallide,  $\text{TiFeH}_{1.2}$ , and the subsequent two, to the decomposition of titanium dihydride. The composition of the decomposition products was confirmed by XRD data.

When hydronitrogenation products are washed to remove ammonium chloride, the stabilizing effect of ammonia is lost and hydrogen is released from the TiFe-based hydride phase, which is confirmed by XRD data.

To use the alloy under study as the working substance for a hydrogen accumulator, it is necessary to hydrogenate the starting  $\beta\text{-(Ti,Fe)}$  with ammonia at temperatures of  $200\text{--}250^\circ\text{C}$ , remove  $\text{NH}_4\text{Cl}$  by vacuum treatment of the hydronitrogenation products, place the thus prepared material into an accumulator, and perform a supplemental procedure of additional hydrogenation with pure hydrogen directly in the accumulator. The accumulator thus prepared for operation can be used at room temperature via evolution of hydrogen from  $\text{TiFeH}_{1.2}$  intermetallide hydride at room temperature and due to the release of hydrogen via decomposition of titanium hydride under heating to  $600^\circ\text{C}$ . The metal hydride accumulator based on the alloy under study can operate in the range from room temperature to  $600^\circ\text{C}$  and release up to 3 wt % hydrogen.

**Table 5.** Characteristics of the working substance for hydrogen accumulators

Material	Content of hydrogen in the hydride phases, wt %	$T$ , $^\circ\text{C}$
Ti	4.0	500–600
$\text{Ti}_4\text{Fe}$	3.2	20–600
$\text{Ti}_2\text{Fe}$	2.5	20–600
TiFe	1.9	20

Thus, the study aimed to obtain hydride phases by direct hydrogenation and hydronitrogenation of the intermetallide and alloys in the Ti–Fe system yielded data indicating that these alloys can be used as the working substance in reusable hydrogen accumulators. Table 5 lists the hydrogen capacities and working temperature ranges of the corresponding accumulators. It should be noted that, as expected, the alloys have, in contrast to the intermetallide, a wider working temperature range and higher hydrogen capacity.

## CONCLUSIONS

Titanium dihydride was obtained at a comparatively low temperature ( $250^\circ\text{C}$ ) in a treatment of titanium with ammonia as a hydrogenating agent. The interaction of ammonia with the TiFe intermetallide and alloy in the Ti–Fe system in the presence of ammonium chloride at various temperatures yields hydride, hydridonitride, and nitride phases of titanium and intermetallide.

The method of ammonia-based dispersion of alloys has a number of advantages over the hydride dispersion method and makes it possible to obtain highly dispersed powders with nanometer particle sizes.

The treatment of alloys with ammonia, as also that with hydrogen, can be used to prepare a working substance for reusable hydrogen accumulators.

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