

Reviews

Dispersion and phase transformations of intermetallic compounds and alloys of Ti, Zr, and Y with iron and nickel in the reaction with ammonia

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The review collates the results of studies on the chemical dispersion and phase transformations of Ti, Zr, and Y alloys with iron and nickel during the reaction with ammonia at a pressure of 0.6–0.8 MPa in the temperature range of 100–500 °C in the presence of NH₄Cl as the activator. Promising working materials for metal hydride hydrogen storage, including alloys (Ti₉₀Mg₁₀, Y₆₇Fe₃₃, and Ti₆₇Fe₃₃) and intermetallics (Ti₂Ni, Zr₂Ni, Zr₃Al₂, ZrV₂), are considered. At 150–250 °C, the mentioned intermetallics absorb considerable amounts of hydrogen with conservation of the initial metallic lattice and formation of the highly dispersed hydrides Ti₂NiH_{3.3}, Zr₂NiH_{4.7}, Zr₃Al₂H_{1.1}, and ZrV₂H_{2.2}. The phase transformations taking place on heating of the intermetallics from 250 to 500 °C, resulting in mixtures of intermetallic hydridonitrides and metal nitrides, are elucidated. The transformation products of the Ti₉₀Mg₁₀, Y₆₇Fe₃₃, and Ti₆₇Fe₃₃ alloys in ammonia atmosphere in the temperature range of 100–500 °C are established.

Key words: hydrogen, ammonia, intermetallic compound, alloy, hydride, nitride, dispersion, phase transformation.

Introduction

The design of materials for permanent magnets and metal hydride electrodes, hydrogenation catalysts, and absorbents for bound hydrogen storage requires the preparation of powders with different size distribution by means of mechanical, physical, and chemical methods.¹ Chemical methods are generally most promising.^{1–2} The hydride dispersion method is based on the reversible chemical reaction of the metal, intermetallic compound, or an

alloy with hydrogen.^{3–4} The ammonia dispersion procedure involves the chemical reaction of metals or poly-metallic phases with gaseous ammonia,⁵ which may give metal powders with a smaller particle size, in some cases, down to the nanometer range.

Analysis of the published data on the ammonia dispersion⁶ of intermetallics and alloys in the temperature range of 20–500 °C at an ammonia pressure of 0.5–2.0 MPa demonstrated that this method is convenient for the preparation of nano-sized powders of metallic phases and metal

hydrides, hydridonitrides, and nitrides. The phase composition depends, in this case, on the temperature of treatment with ammonia (hydronitriding reaction); the use of ammonia does not require alloy preactivation or drastic restrictions on the alloy composition. The removal of hydrogen from hydride phases gives rise to highly dispersed powders of the metallic phase or powders with nanometer particle size containing some quantities of hydrogen and nitrogen. These powders are suitable for the fabrication of some functional composite materials.

A highly important task of hydrogen power engineering and technology is the search for materials that are able to reversibly interact with molecular hydrogen over a broad ranges of temperature and pressure. Compounds with high contents of bound hydrogen are used in the nuclear power engineering and preparative chemistry as working media for the fabrication of a compact and safe hydrogen storage devices and in hydrogen energy storage systems⁷ and in heat sorption compressors and heat pumps and as hydrogen sources for fuel cells.

In the search for materials promising for metal hydride hydrogen storage, it is necessary to develop and optimize procedures for the synthesis of hydride phases of metals, intermetallics, and alloys, establish the influence of the elemental and phase compositions on the hydrogen sorption characteristics of materials, study the recyclability of hydrogen storage characteristics, construct phase diagrams, and elucidate the hydrogen-induced phase transformations. In the development of hydrogenation and dehydrogenation procedures, considerable attention is paid to the pretreatment of a metallic phase: activation and the search for the optimal activation conditions. This pretreatment involves direct activation of the alloy or intermetallic compound under particular conditions or modification of polymetallic phases. For example, an alloy can be activated by mechanochemical treatment in ball mills, by addition of intermetallics to alloys, by hydrogen treatment at elevated temperature, by nanostructuring by plastic deformation, and by other methods. In some cases, the use of ammonia in the hydride and ammonia dispersion of metallic phases substantially decreases the hydrogenation temperature of intermetallic compounds. Owing to the mentioned benefits, ammonia treatment can be used for the search and development of promising hydrogen storage materials.

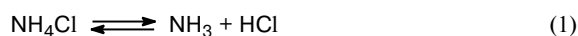
The so-called mild hydride synthesis procedure prevents the undesirable side disproportionation reaction; this procedure implies the delivery of hydrogen in small portions following its absorption or in a mixture with an inert gas into the autoclave at room temperature.^{8–9} Actually, treatment with ammonia is also an example of mild synthesis: heating (≤ 250 °C) a mixture of powders in a reactor filled with ammonia induces an equilibrium reaction of ammonia decomposition into hydrogen and nitrogen. In this case, the reaction occurs at a low hydrogen concentration and, hence, hydrogenolysis does not take place.

This review collates and analyzes the results of studies of hydronitriding of intermetallics (Ti_2Ni , Zr_2Ni , Zr_3Al_2 , and ZrV_2) and alloys ($\text{Ti}_{90}\text{Mg}_{10}$, $\text{Y}_{67}\text{Fe}_{33}$, and $\text{Ti}_{67}\text{Fe}_{33}$), promising for reversible hydrogen storage.

Alloys and intermetallics were prepared by fusing a batch consisting of appropriate metals of $>99.9\%$ purity in a furnace with a tungsten electrode under high-purity argon followed by annealing of the alloy beads at 800 °C for 14 days. The alloys were mechanically cleaned from the oxide film, then ground in a titanium mortar, and sieved to separate the <100 μm fraction of the powder (except for the experiments where the particle size of the alloy is specially indicated). The specific surface area of the product was ~ 0.04 m^2 g^{-1} .

The reaction of the obtained powders with ammonia was studied in the temperature range of 100–500 °C at an initial ammonia pressure of 0.6–0.8 MPa, in the presence of NH_4Cl as the activating agent (10 wt.% relative to the alloy weight).

The activating action of ammonium chloride is caused by its reversible decomposition taking place on heating:



The hydrogen chloride thus formed reacts with the surface metal oxide, thus breaking the oxide film, to give the chloride; this facilitates hydrogenation of the metallic phase. Since dissociation and recombination according to reaction (1) are very fast in an NH_3 atmosphere, metal chloride is formed in small amounts.

The metal hydronitriding products contained chemisorbed ammonia, which prevented oxidation and dehydrogenation, thus making it possible to handle the resulting powders in air. According to differential thermal analysis, the chemisorbed ammonia was removed at 80–120 °C.

The compositions of the initial alloys and the ammonia treatment products were determined using chemical analysis and powder X-ray diffraction, and the relative particle size for the powder was calculated from the specific surface area (S_{sp}) with the assumption of spherical particle shape. The experimental procedures, analytical methods, and determination accuracies were reported previously.¹⁰ The chemical and phase transformations of intermetallics and alloys under NH_3 atmosphere at a 1.5 MPa pressure at various temperatures are summarized in Tables 1 and 2.

Study of intermetallic compound—ammonia systems

Hydride-forming intermetallic compounds can reversibly absorb hydrogen under relatively mild conditions, which is important for the development of safe and compact systems for hydrogen storage. The data on hydronitriding of these intermetallics (Ti_2Ni and Zr_2Ni) are summarized in Table 1.

Table 1. Chemical and phase transformations of intermetallics depending on temperature in an NH₃ atmosphere at 1.5 MPa

Compound	T/°C	Reaction products
Ti ₂ Ni	150–200	Ti ₂ NiH _{3.3}
	350–400	Ti ₂ NiH _x N _y + TiNiH _x N _y + TiH ₋₂
	450–500	TiN + Ni
Zr ₂ Ni	250	Zr ₂ NiH _{4.7}
	400–450	ZrNiH _x N _y + ZrH ₂ + ZrN + Ni
	500	ZrH ₂ + ZrN + Ni
Zr ₃ Al ₂	150	Zr ₃ Al ₂ H _{0.4}
	250	Zr ₃ Al ₂ H _{1.1}
	300–350	Zr ₃ Al ₂ H _x N _y
	400–450	Zr ₃ Al ₂ H _x N _y + ZrH _{1.2} + ZrH ₂ + ZrN
	500	Zr ₃ Al ₂ H _x N _y + ZrH ₂ + ZrN + ZrAl ₂
ZrV ₂	150	ZrV ₂ H ₋₁
	250	ZrV ₂ H _{2.2}
	300	ZrV ₂ H _{0.7} N _{1.0}
	500	VN + ZrN

Table 2. Chemical and phase transformations of alloys depending on temperature in an NH₃ atmosphere at 1.5 MPa

Alloy	T/°C	Reaction products
Ti ₉₀ Mg ₁₀	350	TiH ₂ (cub.) + TiH ₂ (tetr.) + MgH ₂
	400–450	TiH ₂ (cub.) + TiH ₂ (tetr.) + Mg ₃ N ₂ + TiN
	500	Mg ₃ N ₂ + TiN
Y ₆₇ Fe ₃₃	100	YFe ₂ H _{3.6}
	150	YFe ₂ H _{3.6} + YH ₂ + YH ₃
	200–300	YFe ₂ H _x amorph. + YH ₃
	400–450	YN + Fe ₄ N
	500	YN + Fe ₃ N + α-Fe
Ti ₆₇ Fe ₃₃	150	β-Ti + TiFeH ₋₂
	200	β-Ti + TiFeH ₋₂ N _{0.1}
	250	β-Ti + TiH ₋₂ + TiFeH ₋₂ N _{0.1}
	350–400	TiN ₋₁ + TiFeH ₋₂ N _x
	500	TiN ₋₁ + Fe ₄ N + α-Fe + TiFe ₂

The only product formed in the reaction of Ti₂Ni with ammonia is the hydride Ti₂NiH_{3.3} ($a = 11.91 \text{ \AA}$) with the hydrogen content of 2.1 wt.%, the temperature of hydronitriding (200 °C) being optimal for its synthesis.¹⁰ The initial crystal lattice of the intermetallic is retained after hydrogen absorption, but its volume increases. Hydrogenation is accompanied by metal phase disintegration with increase in S_{sp} of the product to $0.23 \text{ m}^2 \text{ g}^{-1}$, which corresponds to an average particle size of $\sim 5 \mu\text{m}$.

The composition of hydronitriding products (350–400 °C) is determined by the competing disproportionation of the intermetallic compound, which starts at 250 °C and gives rise to titanium dihydride TiH₋₂. At 400 °C, apart from hydrogenation and disproportionation

of the alloy, nitriding (insertion of some nitrogen atoms into the metallic lattice of the hydride phase) starts, resulting in the hydridonitride phases, Ti₂NiH_xN_y and TiNiH_xN_y; this was confirmed by chemical analysis and powder X-ray diffraction data.

The products of Ti₂Ni reaction with ammonia (450–500 °C) comprise titanium nitride TiN and nickel metal and no hydridonitride intermetallic phases. The specific surface area of the products ($25.5 \text{ m}^2 \text{ g}^{-1}$) attests to a high degree of dispersion.

Unlike Ti₂Ni, the intermetallic compound Zr₂Ni is hydrogenated with ammonia only at 250 °C up to the Zr₂NiH_{4.7} composition (1.9 wt.% hydrogen), which retains the initial crystal lattice with enlarged unit cell parameters ($a = 6.858 \text{ \AA}$, $c = 5.676 \text{ \AA}$).¹¹ Hydrogenation is accompanied by size reduction of the metallic phase particles with increase in the S_{sp} up to $0.6 \text{ m}^2 \text{ g}^{-1}$, which corresponds to an average particle size of $\sim 2 \mu\text{m}$.

The products of Zr₂Ni interaction with ammonia at 400–450 °C (besides the hydridonitride phase ZrNiH_xN_y, which was first detected at $T = 350 \text{ °C}$) contain stoichiometric zirconium hydride ZrH₂, zirconium nitride ZrN, and Ni. At these interaction temperatures, the hydridonitride Zr₂NiH_xN_y phase does not exist.

The hydronitriding of Zr₂Ni at 500 °C gives highly dispersed ZrH₂, ZrN, and Ni ($S_{sp} = 5.2 \text{ m}^2 \text{ g}^{-1}$).

Treatment of the Zr₃Al₂ intermetallic compound with ammonia at 150–250 °C is accompanied by hydrogenation with gradual increase in the hydrogen content of the product (up to 0.3 wt.% for Zr₃Al₂H_{1.1}) and additional sample disintegration¹² (see Table 1).

In the reaction of the intermetallic compound with ammonia at 300 and 350 °C, the initial metallic matrix is retained but the alloy is not only hydrogenated but also nitrated (a minor amount of N₂ is inserted into the hydride phase), thus forming hydridonitride phases, Zr₃Al₂H_{1.7}N_{0.1} and Zr₃Al₂H_{0.7}N_{0.3}, respectively. The particle size of hydronitriding products is $0.4 \mu\text{m}$.

The obtained data for the products of treatment of the intermetallic compound powder with ammonia at $T > 350 \text{ °C}$ are indicative of several chemical processes taking place under the given conditions. Noteworthy are not only partial retention of the hydridonitride phase of the initial Zr₃Al₂ (up to high treatment temperature) but also appearance of decomposition products of this phase, zirconium hydrides and nitride, which are stable at 400–500 °C. A new intermetallic compound, ZrAl₂, which does not form a hydride phase, was detected among the high-temperature hydronitriding (500 °C) products.

A distinctive feature of the ZrV₂ intermetallic compound is that the constituent metals are able to form hydride phases. Treatment of the intermetallic compound with ammonia with temperature rise from 150 to 250 °C entails gradual hydrogenation of ZrV₂ to ZrV₂H_{2.2} (the average particle size of the hydride is $0.3 \mu\text{m}$).¹³ At 300 °C,

nitrogen is inserted into the intermetallic compound lattice to give the $ZrV_2H_{0.7}N_{1.0}$ hydridonitride phase. This product has a highly extensive surface ($S_{sp} = 4.0 \text{ m}^2 \text{ g}^{-1}$) and is a highly dispersed powder with a particle size of $\sim 0.5 \mu\text{m}$. Further increase in the ammonia treatment temperature reduces the stability of the hydridonitride phase; at $500 \text{ }^\circ\text{C}$, hydronitriding affords a mixture of vanadium and zirconium nitrides.

Study of alloy—ammonia systems

Owing to their unique functional properties (high strength, thermal stability, relatively low specific gravity, and high oxidation resistance), titanium alloys with light metals are promising construction materials for industry, in particular, for aircraft and space equipment and instrument manufacture.¹⁴ The practical use of these alloys requires, in some cases, converting them to highly dispersed powders. The process for converting Ti to nanodispersed powder, in particular, using ammonia, is rather well known,¹⁵ but it is necessary to study the possibility of disintegration of Ti alloys containing small amounts of metals by the ammonia dispersion technique.

According to published data,¹⁶ no intermetallic compounds were found in the Mg—Ti system, which rules out the previously established catalytic effect of intermetallic compounds in an alloy on the hydrogenation of the alloy metals.¹⁷ This is a specific feature of the study¹⁸ of the $Ti_{90}Mg_{10}$ — NH_3 system.

According to the powder X-ray diffraction data, the titanium—magnesium alloy ($Ti_{90}Mg_{10}$) is composed of two phases, α -Ti ($a = 2.9410 \text{ \AA}$, $c = 4.6757 \text{ \AA}$) and magnesium. The presence of the latter in the alloy is confirmed by several characteristic powder X-ray diffraction peaks.

At a temperature below $350 \text{ }^\circ\text{C}$, the $Ti_{90}Mg_{10}$ alloy virtually does not interact with ammonia. Analysis of the products of ammonia treatment of the initial alloy powder at $350 \text{ }^\circ\text{C}$ attests to occurrence of several chemical processes. Among them, note the formation of cubic and tetragonal titanium dihydride phases, which coexist in the interaction products. Magnesium was found in the products as MgH_2 . On further temperature rise, titanium nitride is accumulated in the hydronitriding products and magnesium hydride is converted to nitride. These phases are the products of reaction carried out at $500 \text{ }^\circ\text{C}$. The obtained mixture of nitrides has a high specific surface area ($S_{sp} = 52.5 \text{ m}^2 \text{ g}^{-1}$).

It follows from comparison of the results of hydronitriding of α -Ti^{15,19} and the $Ti_{90}Mg_{10}$ alloy that the presence of magnesium does not have a noticeable influence on the temperature at which titanium hydrogenation and nitriding start.

According to powder X-ray diffraction data,²⁰ the yttrium and iron alloy Y_2Fe ($Y_{67}Fe_{33}$) contains yttrium

metal and the YFe_2 intermetallic in 3 : 1 ratio. This alloy was selected for the study because AB_2 type intermetallics are high-capacity hydrogen absorbing materials. For example, the Laves phases RFe_2 can absorb up to 5 H(D) atoms per formula unit of the metal phase.^{21,22}

The heat treatment of metallic materials in a hydrogen gas atmosphere often gives amorphous products; this is also typical of iron-containing intermetallic compounds,²³ The amorphization is closely associated with disproportionation; therefore, elucidation of the conditions and boundaries of disproportionation reaction taking place during hydrogenation of iron-containing intermetallics is significant not only for theoretical but for also practical reasons.

Treatment of the Y_2Fe ($Y_{67}Fe_{33}$) alloy with ammonia at $100 \text{ }^\circ\text{C}$ is accompanied by the formation of the $YFe_2H_{3.6}$ hydride phase of the intermetallic compound stable at room temperature. Increasing the hydronitriding temperature to $150 \text{ }^\circ\text{C}$ gives rise to additional components, namely, yttrium di- and trihydrides. The interaction of the $Y_{67}Fe_{33}$ alloy with ammonia induces amorphization of the intermetallic phase present in the alloy. At $T \geq 200 \text{ }^\circ\text{C}$, the intermetallic hydride formed is X-ray amorphous. The X-ray diffraction pattern of the products shows peaks corresponding to yttrium trihydride, while the dihydride is absent in the products of hydronitriding at 200 – $300 \text{ }^\circ\text{C}$. Above $350 \text{ }^\circ\text{C}$, the hydride phase of the intermetallic compound does not exist, because it fully decomposes to give nitrides of the metals forming the alloy, and at $500 \text{ }^\circ\text{C}$, iron tetranitride decomposes to give iron trinitride, Fe_3N , and α -Fe.

The $TiFe$ intermetallic compound is of practical interest as a working medium of hydrogen accumulators: it can reversibly absorb up to 1.92 wt.% hydrogen.^{24,25} However, the use of this material requires preactivation under drastic conditions before the first hydrogenation and very high-purity hydrogen (poisoning with O_2 , H_2O , and CO impurities) for cycling. As noted above, titanium dihydride is used as a source of hydrogen not only in industry but also in laboratory.

Thus, the two-phase Ti_2Fe alloy can be used as a high-temperature (Ti-based) and low-temperature (TiFe-based) hydrogen storage system.

According to powder X-ray diffraction, the two-phase Ti_2Fe alloy (composition $Ti_{67}Fe_{33}$) consists of the TiFe intermetallic phase ($a = 2.976 \text{ \AA}$) and an iron solid solution in β -titanium (iron solubility in β -Ti is $\sim 18 \text{ at.}\%$ at $800 \text{ }^\circ\text{C}$, $a = 3.174 \text{ \AA}$).

At $150 \text{ }^\circ\text{C}$, hydronitriding of the alloy starts; this is accompanied by increasing specific surface area of the product (from 0.04 to $0.35 \text{ m}^2 \text{ g}^{-1}$). Titanium metal is not hydrided at this temperature, while the intermetallic phase absorbs hydrogen to give $TiFeH_{-2}$ ($a = 6.6090 \text{ \AA}$). Starting with $T = 200 \text{ }^\circ\text{C}$, minor amounts of nitrogen are inserted into the metallic lattice of the intermetallic hydride, inducing a slight change in the lattice constant (for

TiFeH₂N_{0.1}, $a = 6.6890 \text{ \AA}$). At 250 °C, the titanium dihydride TiH₂ phase adds to the already known hydronitriding products.

The products of treatment of the two-phase alloy with ammonia at 350–400 °C consist of the titanium nitride phase, TiN₁ ($a = 4.2332 \text{ \AA}$), and the interstitial phase of nitrogen insertion into the lattice of the intermetallic hydride phase, TiFeH₂N_x ($a = 6.6884 \text{ \AA}$). It is noteworthy that TiFe-based hydride phases (of the composition indicated in Table 2) are formed during cooling of the reactor to room temperature.

At 500 °C, iron nitride, Fe₄N ($a = 3.8149 \text{ \AA}$), is formed quantitatively as a result of more extensive decomposition of the intermetallic compound. According to powder X-ray diffraction data, apart from iron and titanium nitrides, the hydronitriding products contain α -iron ($a = 2.8656 \text{ \AA}$) and another intermetallic compound, TiFe₂ (hexagonal system, $a = 4.7722 \text{ \AA}$, $c = 7.8012 \text{ \AA}$), which does not interact with hydrogen under these conditions.

Ammonia has a passivating effect on the metal hydride phases; therefore, hydrogenation products can be studied by powder X-ray diffraction with retention of phase composition (this is especially important for TiFeH₂N_x). The use of ammonia as hydrogenating agent makes it possible to avoid the labor-consuming and rather complicated preactivation of the two-phase alloy components.

For the use of this alloy as a working material for a hydrogen accumulator, it is necessary, after removal of NH₄Cl, to perform additional after-hydrogenation of the product with pure hydrogen directly in the accumulator. This accumulator can be used both at room temperature owing to the evolution of hydrogen from the intermetallic hydride (~32% of the total amount of stored hydrogen) and at 550–660 °C owing to hydrogen evolution upon decomposition of titanium dihydride. A metal hydride storage device based on the two-phase Ti₂Fe alloy can operate in the range from room temperature to 600 °C.

Conclusion

The interaction of polymetallic systems with ammonia in the presence of ammonium chloride at various temperatures giving hydride, hydridonitride, and nitride phases has a number of specific features.

At relatively low temperature, ammonia is a hydrogenating agent suitable for the preparation of intermetallic hydride phases, and the use of ammonia as a source of active hydrogen decreases the temperature at which hydrogenation of the intermetallic compound starts (*e.g.*, by ~100 °C for Zr₃Al₂) and can provide hydrogenation of those intermetallics that are destroyed when high-pressure hydrogen is used.

As compared with the hydride dispersion, the ammonia dispersion of alloys does not require prolonged or cumbersome procedure for alloy or intermetallic compound

preactivation and does not impose high requirements on the initial gas purity; this allows the preparation of highly dispersed powders with the particle size in the nanometer range.

At certain temperatures, hydronitriding is accompanied by insertion of a slight amount of nitrogen into the metal lattice to give hydridonitride phases, which retain the hydrogen capacity and facilitate the hydrogenation process.

The hydronitriding of intermetallics at relatively high temperature may give a new intermetallic phase. The hydronitriding of alloys can serve for the manufacture of the working media of reusable hydrogen storage systems.

In some cases, ammonia treatment induces amorphization of the intermetallic compound (*e.g.*, formation of the amorphous YFe₂H_x hydride).

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