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Boris P. Tarasov, Valentin N. Fokin, Evelina E. Fokina, Volodymyr A. Yartys

SYNTHESIS OF HYDRIDES BY INTERACTION OF INTERMETALLIC COMPOUNDS WITH AMMONIA

Boris P. Tarasov[a*], Valentin N. Fokin[a], Evelina E. Fokina[a], and Volodymyr A. Yartys[b, c*]

[a]*Institute of Problems of Chemical Physics of the Russian Academy of Sciences, Chernogolovka 142432, Russia*

[b]*Institute for Energy Technology, Kjeller, NO 2027, Norway*

[c]*Department of Materials Science and Engineering, Norwegian University of Science and Technology, Trondheim, NO 7491, Norway*

ABSTRACT

Interaction of intermetallic compounds with ammonia was studied as a processing route to synthesize hydrides and hydridonitrides of intermetallic compounds having various stoichiometries and types of crystal structures, including A_2B, AB, AB_2, AB_5 and A_2B_{17} (A = Mg, Ti, Zr, Sc, Nd, Sm; B = transition metals, including Fe, Co, Ni, Ti and nontransitition elements, Al and B). In presence of NH_4Cl used as an activator of the reaction between ammonia and intermetallic alloys, their interaction proceeds at rather mild P-T conditions, at temperatures 100–200 °C and at pressures of 0.6–0.8 MPa. The mechanism of interaction of the alloys with ammonia appears to be temperature-dependent and, following a rise of the interaction temperature, it leads to the formation of interstitial hydrides; interstitial hydridonitrides; disproportionation products (binary hydride; new intermetallic hydrides and binary nitrides) or new metal-nitrogen-hydrogen compounds like magnesium amide $Mg(NH_2)_2$. The interaction results in the synthesis of the nanopowders where hydrogen and nitrogen atoms become incorporated into the crystal lattices of the intermetallic alloys. The nitrogenated materials have the smallest particle size, down to 40 nm, and a specific surface area close to 20 m^2/g.

Keywords:

Intermetallic compounds; Metal hydrides; Ammonia; Hydrogen; Hydrogen decrepitation

* Corresponding authors:

B.P.Tarasov: Institute of Problems of Chemical Physics of the Russian Academy of Sciences, Chernogolovka 142432, Russia. Tel./fax: 8(496)5221743. *E-mail address*: tarasov@icp.ac.ru.

V.A. Yartys: Institute for Energy Technology, Kjeller, NO 2027, Norway. Tel. +47 454 22 065.

E-mail address: volodymyr.yartys@ife.no.

1. Introduction

Efficient powder metallurgy technologies are aimed at synthesis of the powders with controlled chemical composition and particle size by decrepitation of the initial bulk materials. Importantly, functional properties of the fine powders are frequently superior as compared to the characteristics of the corresponding bulk samples. Thus, development and optimization of the technologies of the powdering of the materials yielding the particles with required morphology and size is extremely important. Among such technologies, chemical processing has a special role [1–3], because it offers the advantages of simplicity of technical realization, low power consumption, while producing at the same time the powders with uniform shape and clean surfaces.
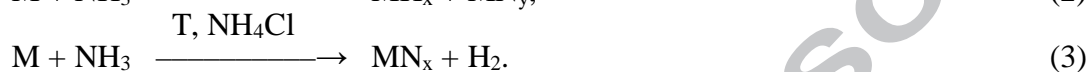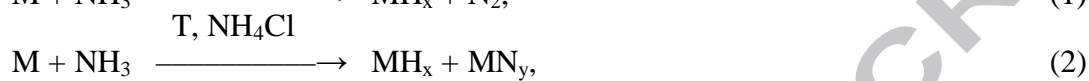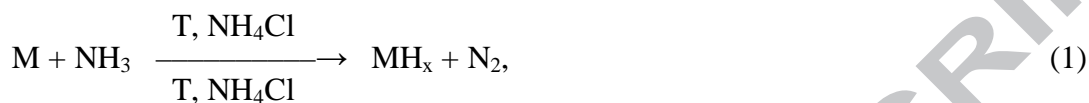
Formation of the metal hydrides leads to the accommodation of hydrogen atoms into the crystal lattice of the metals/alloys and is accompanied by a significant volume increase, on average 10–25% [4]. This expansion creates stresses and causes embrittlement of the initial materials leading to the formation of cracks in the bulk alloy. Reversible interaction of the alloys and metal compounds with hydrogen typically results in their powdering leading to the formation of the metal powders with a particle size depending upon: a) changes in the volume of the crystal structures during a transformation of the metal into the hydride; b) number of hydrogen absorption-desorption cycles; c) intrinsic properties of the materials.

After removal of hydrogen from the hydrides, the initial materials turn into a dispersed state. Such a method of chemical processing via application of a hydrogen absorption-desorption cycle is known as hydride decrepitation [5, 6] and has been successfully utilized in a number of applications [6–8]. The powders received by applying hydrogen decrepitation have a particle size of 1–10 μm with a corresponding specific surface area (S_{sp}) of 0.1–0.7 m^2/g [6].

Decrepitation process leads to the synthesis of the materials with clean surface layers and, hence, to the improvement of the properties of the functional materials.

An interaction of the alloys with ammonia is used as another chemical processing technology which allows to achieve powdering of the metals because of the ammonia-based decrepitation [3, 9]. As compared to the hydride decrepitation, the ammonia-based decrepitation technology allows to synthesize metal powders with smaller size of the particles reaching in some cases nanometer range, and, correspondingly, with a larger specific surface area.

2

During studies of the influence of the processing time, temperature, dimensions of the initial particles, temperature cycling of heating and cooling on the mechanism of the interaction of the metals with ammonia, we have demonstrated that, in presence of NH_4Cl acting as an activator of the interaction, depending from the conditions of interaction, the reaction proceeds via three possible mechanisms 1-3 leading to the synthesis of the metal hydrides (M = Zr, Ti, V), metal nitrides or their mixtures.

$$M + NH_3 \xrightarrow{\text{T, } NH_4Cl} MH_x + N_2, \tag{1}$$

$$M + NH_3 \xrightarrow{\text{T, } NH_4Cl} MH_x + MN_y, \tag{2}$$

$$M + NH_3 \xrightarrow{\text{T, } NH_4Cl} MN_x + H_2. \tag{3}$$

The activation effect of ammonium chloride in the processes (1)–(3) is related to the temperature-dependent reversible reaction (4):

$$NH_4Cl \leftrightarrow NH_3 + HCl \tag{4}$$

Following a temperature increase, hydrogen hydrochloride is released. HCl obviously interacts with surface oxides of the metals, opens nonoxidized surface and, thus, facilitates the hydrogenation.

During the interaction according to the reactions (1)-(3), chemical processing in all cases results in the powdering of the materials and yields particles with various sizes, from microcrystalline to the nanosized ones [3].

Obviously, only the reaction (1), which can be reversed by increasing the temperature to release the absorbed hydrogen, can be utilized for the low-temperature decrepitation of the metals. On the other hand, this reaction can be utilized as a synthesis route yielding metal hydrides at rather soft pressure-temperature conditions [3, 9]. It would be useful to apply reaction (1) to synthesize the hydrides of intermetallic compounds, if the interaction temperatures will be lower than the temperatures of the decomposition of the targeted hydrides. The benefit of such processing route will be in applying mild processing conditions to synthesize intermetallic hydrides.

We note that studies of interaction of the metals and their hydrides with ammonia attracted a lot of attention during the last years. The reason for the increasing interest to this topic is in a fact that such a process is a convenient chemical route to synthesize the metal nitrides and, also,

3

chemical derivatives of ammonia where hydrogen atoms in the ammonia molecule are partially substituted for the metal atoms – metal amides and imides. One example is an exothermic interaction between the lithium hydride and ammonia which proceeds already at room temperature leading to the release of hydrogen and a formation of lithium amide [10, 11]. Later it has been shown that interaction in the systems MH-NH$_3$ for M = Li, Na, K

$$MH + NH_3 \leftrightarrow MNH_2 + H_2 \qquad\qquad (5)$$

is reversible and, consequently, can be used for the chemical storage of hydrogen gas [12]. Hydrogen generation process was performed at room temperature, while a reverse process of a transformation of the metal amides into the corresponding hydrides was conducted at 50-300 $^{\circ}$C in a flow of hydrogen gas. Reactivity of the alkaline hydrides MH increases in a sequence Li < Na < K, while a partial (70 %) reversibility of the synthesis-decomposition process requires temperatures spanning from 300 (LiNH$_2$) to 100 $^{\circ}$C (KNH$_2$).

Metal nitrides, including Li$_3$N, Ca$_3$N$_2$, h-BN, Mg$_3$N$_2$, Si$_3$N$_4$, AlN, TiN, VN, ZrN, can also be utilised as potential hydrogen storage materials [13]. Their interaction with hydrogen takes place when applying mechanochemical process during the milling of the nitrides in a planetary mill in hydrogen gas at pressures of around 1 MPa and leads to the formation of the products containing 0.2-5.0 mass. % H. IR spectroscopy study of the formed products showed a presence of the N-H bonds; thus it was concluded that formation of the metal imides takes place.

Complex nitrogen-containing compounds formed in the systems M-N-H (M = Li, Ca, Mg) were proposed as hydrogen storage materials in [14]. Such compounds are not limited to the nitrides, amides and imides, but also include ternary complexes like Li$_2$MgN$_2$H$_2$ (containing 5.5 wt. % H) formation of which is associated with the release of hydrogen gas according to the following mechanism (6):

$$Mg(NH_2)_2 + 2LiH \rightarrow Li_2MgN_2H_2 + 2H_2 \qquad\qquad (6)$$

Hydrogen is released from the latter compound at 174 $^{\circ}$C. This is by nearly 100 $^{\circ}$C lower as compared to the temperature of hydrogen desorption from Li$_2$NH (270 $^{\circ}$C).

In a number of cases, the mechanism of chemical interaction in the M-N-H systems is rather complex and includes a formation of not only N-containing hydrides, but also of the binary hydrides of the corresponding metals, thus leading to the increase in the values of the accumulated hydrogen content in the materials. One example is a Ca-containing system, where the interaction is taking place as follows [15]:

$$Ca_2NH + H_2 \rightarrow CaNH + CaH_2 \tag{7}$$

A list of such interesting and useful for hydrogen storage interactions could be extended further. However, the reference data do not sufficiently describe the processes of interaction of the metals, alloys and intermetallic compounds with ammonia at mild interaction conditions, yielding metal hydrides or hydridonitrides containing small amounts of nitrogen.

Insertion elements, H and N, influence magnetism of the metal lattices. Earlier the effect of hydrogen and nitrogen on the magnetic properties has been studied for the R_2Fe_{17}, $R_2Fe_{17}H_{max}$ and $R_2Fe_{17}N_{max}$, compounds [16]. The Curie temperatures increase by 40% for the hydrides and by 120% for the nitrides as compared to the alloys. A greater expansion of the unit cells for the nitrides as compared to the hydrides is caused by the increase of the size of the interstitial nonmetals ($r_N > r_H$); thus, N more significantly increases Fe-Fe and R-Fe distances as compared to H. For the light rare earth metals (R=Ce, Pr and Nd) and Sm, T_c increases from ~225-390 °C for the alloys to ~440-570 °C for the hydrides and to the ~730-760 °C for the nitrides.

Alloys formed in the Sm-Co, Sm-Fe и Rare Earth Metal-Fe-B systems are known as materials for the permanent magnets with energy product. Introduction of nitrogen into a composition of the Sm_2Fe_{17} alloy and achieving a uniform distribution of nitrogen in the crystal lattice to form $Sm_2Fe_{17}N_3$ allowed to significantly improve the magnetic properties [17, 18].

In the present work we have determined optimum conditions for the synthesis of a number of intermetallic hydrides and characterized properties of the formed hydrogenated alloys. Furthermore, for some intermetallic hydrides we have compared properties of the hydrides synthesized via interaction of the alloys with ammonia (route 1) with those for the hydrides obtained via interaction of the alloys with gaseous hydrogen.

2. Experimental details

2.1. Initial compounds

The intermetallic compounds were prepared by arc-melting a mixture of individual metals with purity >99.9% under a purified argon gas. The obtained alloys were annealed at 800 °C for 250 h. Prior to the studies, the surface oxide films were removed from the alloys; they were washed in ethanol and diethyl ether to clean their surface after that. The intermetallic samples were prepared as the powders by grinding pieces of the bulk alloys in a metallic mortar, followed by sieving to a particle size of below 100 μm. Specific surface area of such powders was 0.04–0.06 m^2/g. The composition of the received alloys was examined by X-ray analysis.

Ammonium chloride (reagent grade) was dried in vacuum at 150 °C for 9 h. The purity of ammonia after drying over the sodium metal was 99.99 %.

2.2. Experiment procedure

Interaction of the powders of intermetallic alloys with ammonia was studied at initial pressure of ammonia of 0.6–0.8 MPa in presence of NH_4Cl; the latter was added to form a mixture of 10 wt. % NH_4Cl + 90 wt. % of the intermetallic alloy.

The powders (0.8–1.0 g) were mixed and ground in an agate mortar and placed into a high pressure autoclave. The autoclave was vacuumed for 0.5 h at room temperature to a pressure of ~1 Pa, filled with ammonia and maintained during 0.5 h. Consequently, the autoclave was heated during 3 h to the various processing temperatures, cooled to the room temperature and heated up again. The pressure in the system during the processing did not exceed 1.5 MPa. After performing a certain number of the heating-cooling cycles, the excess ammonia was dumped into a buffer volume, and the reaction autoclave was disconnected from the system. After that, the solid products of interaction were removed from the autoclave in inert atmosphere and analysed.

The NH_4Cl was removed from the reaction products by using two procedures;

(a) by a double washing of the reaction products with absolute ethanol for 1 h while stirring the mixture at room temperature, and by

(b) vacuuming the reaction products at ~1 Pa and 300 °C over a period of 3 h.

2.3. Analysis techniques

X-ray diffraction patterns were collected on an ADP-1 diffractometer (CuK_α-radiation).

6

Interplanar spacings were determined with an accuracy lot less than 0.0005 nm.

The specific surface area of the samples was evaluated by BET analysis (accuracy ±10%) using the low temperature krypton adsorption measurements; prior to the BST analysis, the solid phase was degassed in vacuum (1.3×10^{-3} Pa) at 300 °C for 5 h.

The hydrogen pressure was monitored using calibrated manometers (accuracy class 0.4). The composition of the received products was determined by chemical analysis. The hydrogen and nitrogen contents of the reaction products were determined using a Vario Micro Cube CHNS/O elemental analyser (accuracy ±5%), while the amount if chlorine-ions was quantified by chemical analysis (accuracy ±1%).

The thermal stability of the reaction products was studied with a Netzsch STA 409 Luxx simultaneous thermal analyser (TG–DTA/DSC) in an argon atmosphere using a heating rate of 10 deg./min.

3. RESULTS

The main focus was on the establishment of the possibilities to synthesize hydrides of the intermetallic compounds with various stoichiometric compositions, A_2B, AB, AB_2, AB_5 and A_2B_{17}, during their interaction with ammonia.

3.1. General regularities

The studies revealed the main trends governing such interactions.

When the operating temperatures are limited to 100–250 °C, the synthesis of the insertion type hydride phases of the initial alloys takes place. The composition of the synthesized hydrides and selected properties of the hydrogenated materials are summarized in the Table 1. Insertion of small amount of nitrogen (<0.1 at. N/ f.u. AB_n), coexisting with hydrogen in the metal sublattice, does not affect the thermodynamic equilibria in the hydrogenated systems, as decomposition temperatures of the formed hydrides remain unaltered. The crystallographic characteristics for all synthesized hydrides well agree with the reference data.

Hydrogen content in the synthesized hydrides increases when higher processing temperatures are used. However, higher temperatures normally also cause a partial nitrogenation of the alloys, even though only trace amounts of nitrogen become bound to the alloys (<0.1 at. N/f.u. AB_n). Fortunately

7

and importantly, formation of the mixed hydridonitrides does not lead to the chemical degradation of the initial alloys as their crystal structures remain intact. The type of the atomic structure of the metal sublattices does not change, as indicated by X-Ray diffraction, but expansion of the unit cells takes place proportionally to the amount of hydrogen and nitrogen accommodated by the crystal lattice. A mixed occupancy of the larger in size octahedral sites by H and N takes place in these structures.

The formation of amorphous products was also occasionally observed during the interaction of intermetallics with ammonia even at low operating temperatures. As example, $ScFe_2$ and $ScNi_2$ form crystalline hydrides when interaction of the intermetallic compounds with NH_3 takes place at 150 ℃ (see Table 1), but at higher temperatures, 200–300 ℃, the formed mixed hydridonitrides become amorphous.

Hydrogenation, which in a number of cases is accompanied by a partial nitrogenation, leads to the significant chemical decrepitation of all studied materials. The lowest mean particle size, down to 40-200 nm, and, correspondingly, the highest specific surface area, from 3 to 19 m^2/g, was found for TiFe, and for Sc and Sm alloys with transition metals - Fe, Co and Ti. Interestingly, all compounds forming fine powders, even nanopowders, contain octahedral interstices in their crystal lattices capable of accommodating both H and N atoms. This is indeed the case for TiFe, A_2B_{17} and $AB´_{11}B´´$ compounds crystallizing, respectively, with CsCl, Th_2Zn_{17} and $ThMn_{12}$ types of crystal structures.

3.2. Titanium alloys

The temperature of interaction of the alloys with ammonia strongly affects the reaction mechanism. Initiation of the interaction leading to the hydrogenation does not take place at ambient temperature and requires heating of the samples to surpass a threshold temperature. As example, interaction of Ti_3Al with ammonia starts only at 100 ℃ and proceeds at 100-150 ℃ to yield a nitrogen-free hydride phase. According to the thermal analysis data, the samples synthesized at 100–150 ℃, completely release hydrogen in an endothermic decomposition at 270–280 ℃.

Further growth of the temperature of interaction of Ti_3Al with ammonia leads to the synthesis of

hydridonitrides containing a small, but experimentally detectable, amount of nitrogen. Partial nitrogenation leads to an increase in the specific surface area of the synthesized products and to a corresponding reduction of the particle size.

Interestingly, it appears that Ti_3Al intermetallic remains stable against a disproportionation into a mixture of TiH_2/TiN/Al even at such high interaction temperature as 500 ℃.

In the system Ti_2Ni–NH_3 formation of the hydride of the initial intermetallic alloy with maximum hydrogen content $Ti_2NiH_{3.3}$ takes place already at 100–150 °C; this hydride is in equilibrium with an H solid solution in the initial intermetallic compound, $Ti_2NiH_{0.X}$. Further rise of the temperature of interaction to 200 °C, yields the hydride with a maximum H content of 2.1 wt. % H which becomes a sole product of the hydrogenation. During the hydrogenation, the alloy crushes into a powder with an average particle size of around 5 μm.

3.3. Zirconium alloys

According to the data of the XRD and element analysis, at temperatures of 100 and 150 °C the intermetallic compound Zr_2Ni does not interact with ammonia. Only at 250 °C it absorbs hydrogen to form $Zr_2NiH_{4.7}$ hydride containing 1.9 wt.% H. The hydrogenation causes the volume exposition of 17.6 %, as it follows from the XRD data shown in Figures 1a and 1b, thus leading to a decrepitation of the metal alloy. This increases the specific surface area to 0.6 m^2/g, which corresponds to an average particle size of 1.6 μm.

For another intermetallic compound of zirconium, Zr_3Al_2, its interaction with ammonia instead of hydrogen reduces the temperature of the initiation of the hydrogenation for ~100℃. As mentioned earlier, such a decrease has an important practical consequence allowing synthesis of the hydrides in the first hydrogenation at mild operating conditions.

3.4. Alloys of rare earth metals

CeT_2 (T – Fe, Co, Ni) intermetallic compounds, disproportionate in ammonia already at 150 °C to yield the hydrides and depleted by Ce intermetallic compound Ce_2T_{17}, cerium hydride and cerium nitride. Disproportionation reaction takes place for the other intermetallic alloys also;

however, it takes place at higher processing temperatures.

The processing of the magnetic intermetallic compounds, Sm–Co, Sm–Fe, and REM–Fe–B (REM is a rare-earth metal), in ammonia is particularly important from the applied point of view, as such compounds belong to the permanent magnet materials. Interaction of Sm_2Fe_{17}, $SmFe_{11}Ti$ and $Nd_2Fe_{14}B$ with NH_3 even at relatively low temperatures (≤ 200 °C) leads to the insertion of nitrogen atoms into the crystal lattices of intermetallic alloys (3.0–3.5 at. N/unit cell). Nitrogen, when inserted at low temperatures, fills octahedral interstices and forms thermally stable nitrides. For the small content of nitrogen in the metal matrix, no significant changes in the properties of the metal hydrides take place. The temperature of hydrogen desorption remains unchanged; nitrogen does not form ammonia in the products of H desorption as it is strongly bound with the metal sublattice.   Figure 2 shows that for both hydride $Sm_2Fe_{17}H_{5.1}$ and nitride $Sm_2Fe_{17}N_3$ the magnetization curves reach saturation in a field of 1 T. In agreement with the work [21], formation of insertion type hydrides and nitrides increases interatomic distances Fe–Fe and, because of that, increases Curie temperatures and enhances magnetic exchange interaction between the iron atoms and the atoms of the rare earth metals. Consequently, hydridonitriding allows to improve magnetic properties of the materials.

A correlation between the elongation of the Fe-Fe interatomic distances and increase of the Curie temperatures in R-Fe compounds is in agreement with earlier observations [22].

For the system $SmFe_{11}Ti$–NH_3, a substantial growth of the specific surface area of the products of a combined hydrogenation and nitrogenation takes place for the materials synthesized at 150–200°C (S_{sp} = 19–25 m^2/g, particle size 40–50 nm for $SmFe_{11}TiH_1N_{0.1}$), in a sharp contrast with a rather course powder obtained during a direct hydrogenation of the same $SmFe_{11}Ti$ intermetallic alloy (S_{sp} = 0.4 m^2/g for $SmFe_{11}TiH_1$). Most importantly, the measurements of the coercivity showed that synthesized nanosized powders of $SmFe_{11}TiN_xH_y$ are more suitable as permanent magnet materials as compared to the initial $SmFe_{11}Ti$ intermetallic alloy [23].

3.5. Magnesium alloys
An interesting and complex mechanism of interaction with ammonia has been found for the

10

magnesium-containing Mg_2Ni intermetallic. Below 100 $^{\circ}C$ the intermetallic compound does not interact with ammonia. During the chemical interaction taking place between 100 and 150 $^{\circ}C$, Mg_2Ni absorbs hydrogen with a formation of the mixture of the ternary hydride Mg_2NiH_4 and a binary magnesium dihydride, the latter appearing because of the disproportionation of Mg_2Ni during its interaction with NH_3. By selecting appropriate P-T conditions, it was possible to synthesize also the magnesium amide $Mg(NH_2)_2$.

4. CONCLUSIONS

Chemical interaction of intermetallic compounds with various stoichiometries, A_2B, AB, AB_2, AB_5 and A_2B_{17}, (A = Mg, Ti, Zr, Sc, Nd, Sm; B = transition metals, including Fe, Co, Ni, Ti and nontransitition elements, Al and B) with ammonia appears to be a useful chemical route to synthesize interstitial type hydrides and hydridonitrides. Such an interaction results in the synthesis of the nanopowders where hydrogen and nitrogen atoms become incorporated into the crystal lattices of the intermetallic alloys. The nitrogenated materials have a particle size as small as 40 nm and the specific surface area close to 20 m^2/g. The mechanism of interaction of the alloys with ammonia appears to be temperature-dependent and, following a rise of the interaction temperature, such an interaction leads to the formation of interstitial hydrides; interstitial hydridonitrides; disproportionation products (binary hydride; new intermetallic hydrides and binary nitrides) or new metal-nitrogen-hydrogen compounds like magnesium amide $Mg(NH_2)_2$.

A possibility to use a combined hydrogenation and nitrogenation allows to increase Curie temperature and to enhance magnetic interaction between the rare earths and iron atoms. Such processing has a potential applied impact as allowing synthesis of the advanced materials for the bonded permanent magnets.

REFERENCES

[1] R.A. Andrievski, B.P. Tarasov, I.I. Korobov, N.G. Mozgina, S.P. Shilkin, Hydrogen absorption and electrocatalytic properties of ultrafine $LaNi_5$ powders, *Int. J. Hydrogen Energy* 21 (1996) 949–954.

[2] V.N. Fokin, E.E. Fokina, B.P. Tarasov, S.P. Shilkin, Synthesis of the tetragonal titanium dihydride in ultradispersed state, *Int. J. Hydrogen Energy* 24 (1999) 111–114.

[3] B.P. Tarasov, E.E. Fokina, V.N. Fokin, Chemical methods of dispergation of metallic phases,
Russ. Chem. Bull. 60 (2011) 1252–1260.

[4] V.A.Yartys, V.V.Burnasheva and K.N.Semenenko. Structural chemistry of hydrides of intermetallic compounds, *Sov.Advances in Chemistry* 52 (1983) 529-562.

[5] V.A.Yartys, A.I.Shtogryn. Production of fine powders of NdFeB alloys by hydrogen decrepitation technique, *Physicochemical Mechanics of Materials* 24 (1988) (4) 111-114.

[6] V.N. Fokin, B.P. Tarasov, I.I. Korobov, S.P. Shilkin, Some patterns of dispergation of the intermetallic compounds and alloys on their base formed of rare earth and 3d transition metals under the hydrogen action, *Koord. Khim.* 18 (1992) 526–534 (in Russian).

[7] V.N. Fokin, E.E. Fokina, The use of high purity hydrogen for dispergation or embrittlement of magnetic materials, *Zh. Prikl. Khim.* 67 (1994) 1372–1374 (in Russian).

[8] B.P. Tarasov, Metal-hydride accumulators and generators of hydrogen for feeding fuel cells, *Int. J. Hydrogen Energy* 36 (2011) 1196–1199.

[9] V.N. Fokin, E.E. Fokina, B.P. Tarasov, Hydride and ammonia dispersion of metals, *Russ. J. Inorg. Chem.* 55 (2010) 1536–1540.

[10] Y. Kojima, K. Tange, S. Hino, S. Isobe, M. Tsubota, K. Nakamura, Molecular hydrogen carrier with activated nanohydride and ammonia, *J. Mater. Res.* 24 (2009) 2185–90.

[11] S. Hino, N. Ogita, M. Udagawa, T. Ichikawa, Y. Kojima, Thermodynamic properties of lithium amide under hydrogen pressure determined by Raman spectroscopy, *J. Appl. Phys.* 105 (2009) 023527.

[12] H. Yamamoto, H. Miyaoka, S. Hino, H. Nakanishi, T. Ichikawa, Y. Kojima, Recyclable hydrogen storage system composed of ammonia and alkali metal hydride *Int. J. Hydrogen Energy* 34 (2009) 9760-9760.

[13] Y. Kojima Y., Kawai, N. Ohba, Hydrogen storage of metal nitrides by a mechanochemical reaction, *J. Power Sources* 159 (2006) 81–87.

[14] Z.T. Xiong, G.T. Wu, J.J. Hu, P. Chen, Ternary imides for hydrogen storage, *Adv. Mater.* 16 (2004) 1522-1525.

[15] P. Chen, Z. Xiong, J. Luo, J. Lin, K.L. Tan, Interaction of hydrogen with metal nitrides and imides, *Nature* 420 (2002) 302-304.

[16] J.L. Soubeyroux, D. Fruchart, O. Isnard, S. Miraglia, E. Tomey, Role of the (H,C,N) interstitial elements on the magnetic properties of iron-rare earth permanent magnet alloys, *J. All. Compds* 219 (1995) 16-24.

[17] T. Ishikawa, K. Yokosawa, K. Watanabe, K. Ohmori, Modified process for high-performance anisotropic $Sm_2Fe_{17}N_3$ magnet powder, *J. Physics: Conference Series* 266 (2011) 012033.

[18] C. Kuhrt, Processing of permanent magnet materials based on rare earth-transition metal intermetallics, *Intermetallics* 3 (1995) 255-263.

[19] F. Aubertin, S.J. Campbell, Phase separation in hydrides of Zr_2Ni, *Hyperfine Interactions* 54 (1990) 767-774.

[20] M.M. Elcomb, S.J. Campbell, C.J. Howard, H.G. Bittner, F. Aubertin, The crystal structure of Zr_2NiD_4, *J. All. Compds* 232 (1996) 174-179.

[21] O.V. Kravchenko, V.V. Burnasheva, A.D. Terekhov, K.N. Semenenko, Synthesis and scientific bases of manufacture of «supernitromag» $Sm_2Fe_{17}N_3$, *Zh. Obshch. Khim.* 68 (1998) 705–708 (in Russian).

[22] Hans R. Kirchmayr and Carl A. Poldy, Handbook on the Physics and Chemistry of Rare Earths, edited by K. A. Gshneidner, Jr. and L. Eyring. North Holland, Amsterdam, 1979; Chapter 14.

[23] V.N. Fokin, Yu.M. Shul'ga, B.P. Tarasov, E.E. Fokina, I.I. Korobov, A.G. Burlakova, S.P. Shilkin, Transformations of intermetallic compound $SmFe_{11}Ti$ in the ammonia environment, *Russ. J. Gen. Chem.* 75 (2005) 831–834.

13

Figure captions in the paper

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Figure 1. XRD pattern for Zr_2Ni (tetragonal; $CuAl_2$ type; a =6.479(7); c = 5.30(1) Å); V = 222.48 Å^3; (a) and $Zr_2NiH_{4.7}$ (a = 6.767(7); c = 6.76(1); c = 5.72(1); β = 89.4(2)°); V = 261.65 Å^3; (b). The unit cell parameters well agree with the reference data for the individual Zr_2Ni intermetallic alloy (a =6.49; c = 5.28 Å [19]) and its tetrahydride Zr_2NiH_4 (a = 6.79; b = 6.76; c = 5.67 Å; β = 91.0 °; [20]). For simplification indexing is given in the pseudotetragonal setting in the Fig. (b).

Figure 2. Magnetisation curves for the hydride $Sm_2Fe_{17}H_{5.1}$ (1) and nitrogenated by ammonia at 200 °C Sm_2Fe_{17} (2).
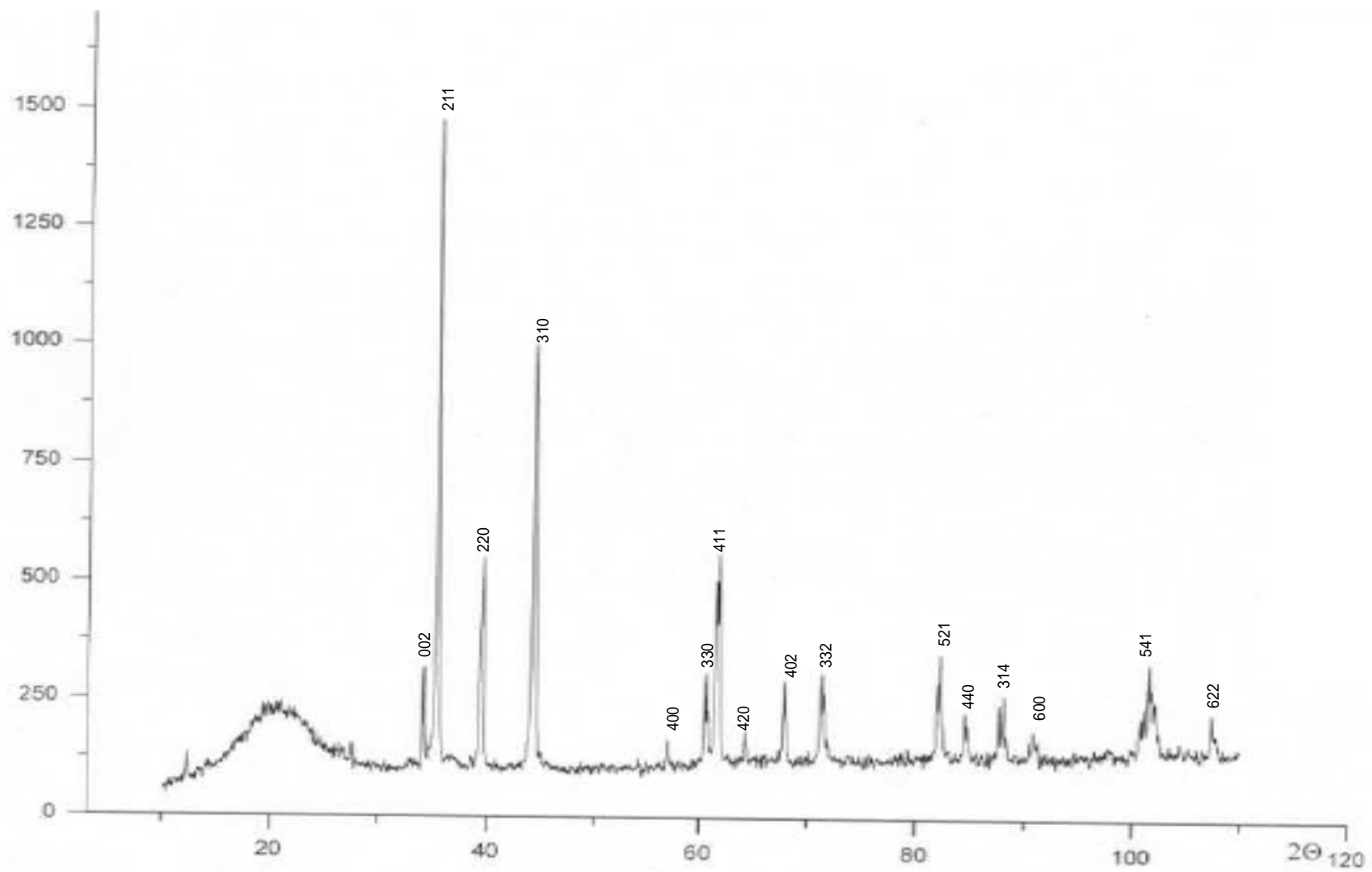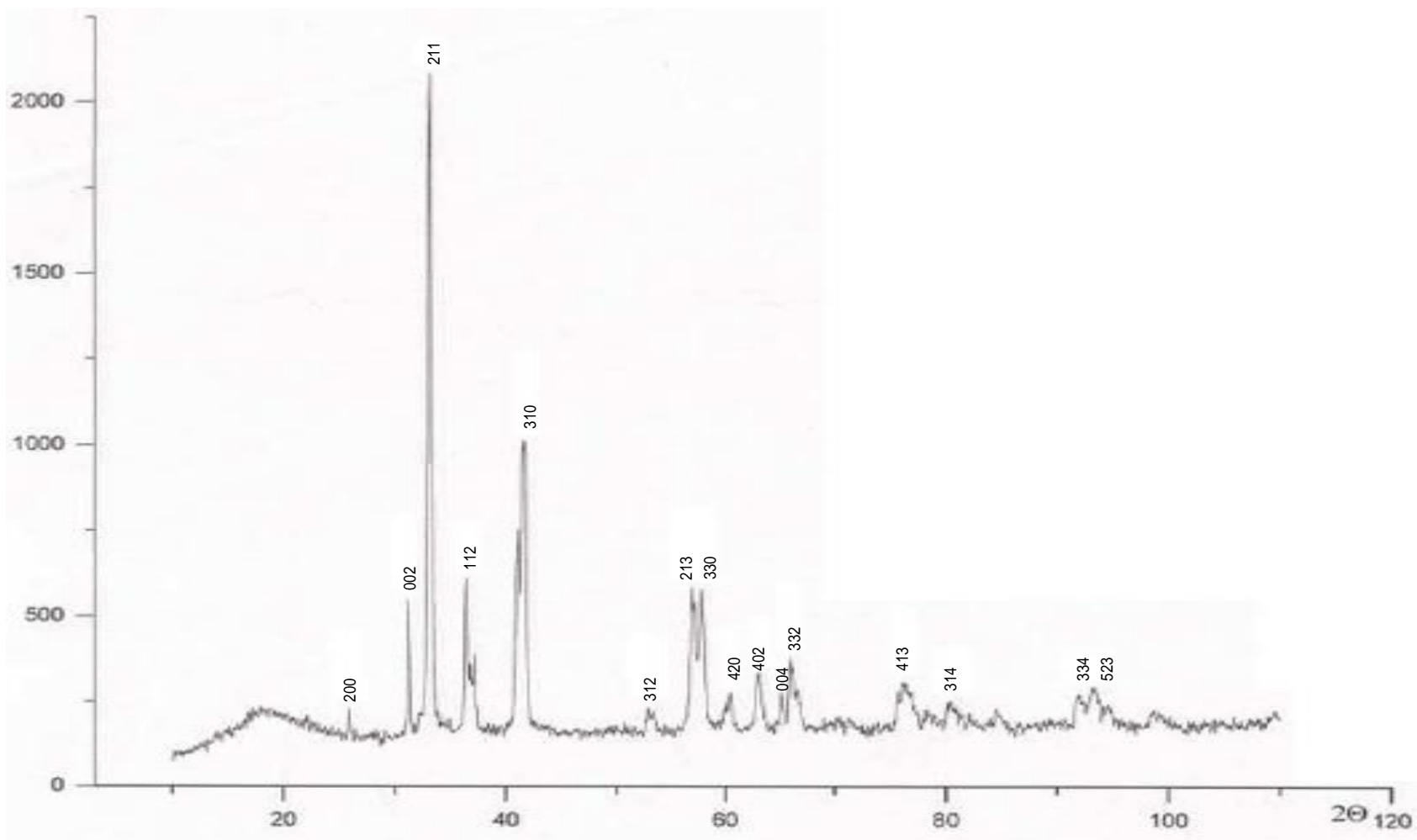
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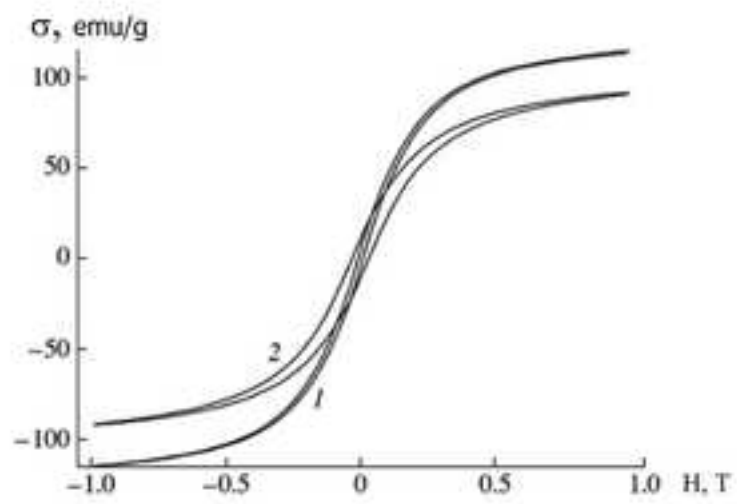**Figure 1a**

Figure 1b

Figure 2

Table 1

Characteristics of hydrogen- and nitrogen-containing materials formed during interaction of intermetallic compounds with ammonia at 100–250°C.

Initial intermetallic compound	T, °C	Phase composition	S_{sp}, m^2/g	Mean size of the particles, μm
Mg_2Ni	150	$Mg_2NiH_x + MgH_2$	25.5	0.1
Ti_3Al	100	$Ti_3AlH_{2.8}$	0.1	14.1
	150	$Ti_3AlH_{3.0}$	0.1	14.1
	200	$Ti_3AlH_{3.0}N_{<0.1}$	0.2	7.1
$TiAl$	100	$TiAlH_{0.7}$	0.5	3.1
	150	$TiAlH_{1.5}$	0.4	3.9
	200	$TiAlH_{1.9}N_{<0.1}$	0.4	3.9
Ti_2Ni	200	$Ti_2NiH_{3.3}$	0.2	5.0
$TiFe$	200	$TiFeH_{0.1} + TiFeH_2N_x$	4.5	0.2
	250	$TiFeH_{0.1} + TiFeH_2N_x$	4.3	0.3
Zr_3Al_2	150	$Zr_3Al_2H_{0.4}$	0.3	3.7
	200	$Zr_3Al_2H_{0.8}$	0.5	2.2
	250	$Zr_3Al_2H_{1.1}$	1.3	0.9
Zr_2Ni	250	$Zr_2NiH_{4.7}$	0.6	1.6
ZrV_2	150	$ZrV_2H_{\sim 1}$	1.0	0.9
	200	$ZrV_2H_{1.3}$	2.4	0.4
	250	$ZrV_2H_{2.2}$	2.6	0.3
$ScNi_2$	150	$ScNi_2H_{1.0}$	6.8	0.2
$ScFe_2$	150	$ScFe_2H_{1.5}$	7.4	0.2
$LaNi_5$	150	$LaNi_5H_{0.5}$	1.3	0. 6
$Nd_2Fe_{14}B$	150	$Nd_2Fe_{14}BH_xN_y$	3.4	0.2
	200	$Nd_2Fe_{14}BH_xN_y$	2.8	0.3
$SmCo_5$	150	$SmCo_5H_{0.3}$	0.3	4.0
	200	$SmCo_5H_{0.3}N_y$	1.4	0.9
Sm_2Co_{17}	150	$Sm_2Co_{17}H_xN_y$	3.4	0.2
	200	$Sm_2Co_{17}H_xN_y$	2.5	0.3
$SmFe_{11}Ti$	150	$SmFe_{11}TiH_xN_y$	19.0	0.04
Sm_2Fe_{17}	150	$Sm_2Fe_{17}H_xN_y$	1.9	0.4
	200	$Sm_2Fe_{17}H_xN_y$	7.8	0.1
	250	$Sm_2Fe_{17}H_xN_y$	4.3	0.2

Highlights

- Interaction of the intermetallics A_2B, AB, AB_2, AB_5 and A_2B_{17} with NH_3 was studied
- The mechanism of interaction of the alloys with ammonia is temperature-dependent
- Hydrides, hydridonitrides, disproportionation products of metal-N-H compounds are formed
- NH_4Cl was used as an activator of the reaction between ammonia and intermetallics
- Interaction with ammonia results in the synthesis of the nanopowders