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Chemical methods of dispergation of metallic phases

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The results of a cycle of works on the chemical dispergation of intermetallic compounds and alloys were summarized and analyzed. The chemical dispergation occurs in a hydrogen or ammonia atmosphere in the temperature range from 20 to 500 °C and a pressure of 0.5—2.0 MPa. The phase transformations were studied. The conditions suitable for the production of polymetallic phase powders of various degrees of dispersity were determined.

Key words: intermetallic compound, alloy, hydrogen, ammonia, dispergation, metallic powders.

Introduction

Powders of intermetallic compounds and alloys with varying dispersion are needed, as a rule, in many areas of modern industry dealing with the use of polymetallic systems. Among the latter are materials for permanent magnets and metallohydride electrodes, catalysts, absorbents for storage of hydrogen in the bound state, *etc*. Therefore, the develoment of preparative procedures useful to manufacture these powders by mechanical, physical, and chemical methods becomes very significant.[1] Chemical methods[1—3] have a number of advantages over other methods due to which they are especially attractive and demanded. These include: simple technical accomplishment; a low energy capacity; a possibility to control the process of particle formation; and the preparation of powders with the non-oxidized surface, without plastic deformation, and with the particle shape optimum for further use.

A chemical method for the synthesis of intermetallic compound powders is, for example, the method of the preparation of mixed basic carbonate $La_2Ni_{10}(CO_3)_8(OH)_{10} \cdot (H_2O)_x$ followed by its reduction with hydrogen and calcium hydride at 1000 °C.[4] Thus prepared powder of $LaNi_5$ with an average particle size of ~220 nm has a uniform chemical and phase composition and its properties of hydrogen adsorption are nearly indistinguishable from the properties of the intermetallic compound prepared by smelting.

The study of the chemical reaction of the compact metal with hydrogen of various purity and activity showed[5] that the insertion of hydrogen atoms in the crystalline lattice of the material changed its volume by 10—25%. Internal strains developed in this case reach values considerably exceeding the breaking point of the material, due to which it disintegrates to particular particles. Once absorbed hydrogen is removed, the starting material transfers into the dispersed state. This process is conventionally named the method of hydride dispergation.[6,7] This dispergation method is also accompanied by the reduction of surface oxides, which increases the purity of the material and, hence, improves its characteristics.

Another chemical method of dispergation (ammonia method) is based on the chemical interaction of metals and alloys with gaseous ammonia as a source of hydrogen and nitrogen formed at elevated temperatures.[8] As compared to the hydride method, the method of ammonia dispergation makes it possible to produce metallic powders with a smaller particle size, which achieves, in several cases, the nanometer range.

In this work, an attempt is made to summarize the results of studies on the production of polymetallic powders by the methods of hydride and ammonia dispergation and compare possibilities and features of these methods.

Experimental

Alloys and intermetallic compounds were prepared by smelting the charge composed of the corresponding metals with the purity >99.9% in a furnace with an inexpensive tungsten electrode in high-purity argon followed by annealing treatment of alloy prills at 800 °C for 2 weeks.

Alloys were purified from the oxide film by the mechanical method and hydrogenated in the compact or coarse-crystalline form at temperatures from 20 to 350 °C with high-purity hydrogen at the initial pressure 0.5—2 MPa.

For the ammonia treatment, the alloy prills purified from the oxide film were disintegrated in a titanium mortar and the powder fraction with the particle size smaller than 100 μm was used in experiments (except for experiments, where the particle size of the alloy is specially indicated). The specific surface area of this fraction was 0.04 $m^2 g^{-1}$.

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The interaction of the prepared powders with ammonia (the so-called hydronitriding process) was carried out in the presence of activator NH_4Cl, which was added in an amount of 10 wt.% of the weight of the alloy introduced in the reaction, in the temperature range 100—500 °C at the initial ammonia pressure 0.5—0.8 MPa.

The multiple repetition of procedures of hydrogenation or hydronitriding of the alloys and the subsequent dehydrogenation of the hydride or hydridonitride phases formed made it possible to obtain polymetallic powders with the required particle size.

The products of hydronitriding of metals contained chemisorbed ammonia preventing their oxidation and dehydrogenation, which allowed one to work with the prepared powders in air. According to the date of differential thermal analysis, chemisorbed ammonia is removed at 80—120 °C.

The composition of the starting alloys and products of the ammonia treatment was monitored by chemical and X-ray phase analyses. For all substances, the calculated parameters of the crystalline lattices coincided with those presented in the ASTM database.

The experimental procedures, analytical methods, and accuracy of determination of physical magnitudes are described in detail.[9,10] Magnetization curves of the studied samples were measured with a PARC M-4500 vibrational magnetometer.

Method of hydride dispergation of metallic phases

The possibility of wide use of the method of hydride dispergation appeared after high-purity hydrogen accumulators were put in practice.[9,11]

The interaction of hydrogen with intermetallic compounds AB_n can proceed *via* the reversible reaction

$$AB_n\,(c) + x\,H_2 \underset{P_2,\,T_2}{\overset{P_1,\,T_1}{\rightleftharpoons}} AB_nH_{2x}\,(d), \tag{1}$$

where c and d are the compact and dispergated samples, respectively; $P_1 > P_2$; and $T_2 > T_1$. However, in several cases, the reactions of complete (2) or partial decomposition (3) of the intermetallic compound with hydrogen are thermodynamically more favorable

$$AB_n\,(c) + m\,H_2 \xrightleftharpoons{P,\,T} (AH_{2m} + n\,B)\,(d), \tag{2}$$

$$2\,AB_n\,(c) + (m + x)\,H_2 \xrightleftharpoons{P,\,T} (AH_{2m} + AB_yH_{2x} + (2n - y)\,B)\,(d), \tag{3}$$

where $y > n$, and $x << m$.[12]

Understandably, only reaction (1), which is reversible and spontaneous at the direct contact of the reactants, is used for the low-temperature dispergation of the intermetallic compounds and alloys, and reactions (2) and (3) can be used for the preparation of the corresponding homogeneous mixtures ($A + B$ and $A + AB_y + B$).

We successfully used the method of hydride dispergation for the disintegration of the intermetallic compounds formed by scandium, yttrium, and rare-earth and transition 3d-metals ($ScFe_2$, $CeNi_3$, $CeCo_3$, $LaNi_5$, $SmCo_5$, *etc.*),[7] for the dispergation or embrittlement of the magnetic materials based on the alloys from the systems Sm—Co ($SmCo_5$ and Sm_2Co_{17} with additives of Gd, Zr, Cu, and Fe) and Nd—Fe—B [9] and of the procatalysts for synthesis of carbon nanostructures (La—Ni, Mg—Ni, Y—Ni, ...).[13,14]

Based on results of X-ray phase and granulometric analyses, measurement of specific surface area, optical and electron microscopy, various variants of the mechanism were considered and established, and optimum modes for dispersion of intermetallic compounds were determined.

The specific surface area (S_{sp}) of powders of selected intermetallic compounds after five cycles hydrogenation—dehydrogenation is given below.

Alloy	$S_{sp}/m^2\ g^{-1}$	Alloy	$S_{sp}/m^2\ g^{-1}$
YFe_2	0.15	$CeCo_3$	0.31
$ScFe_2$	0.75	$LaNi_5$	0.29
$ScCo_2$	0.46	YCo_5	0.36
$ScNi_2$	0.24	$NdCo_5$	0.27
$CeNi_3$	0.33	$SmCo_5$	0.27
YCo_3	0.27	Sm_2Co_{17}	0.05

The multiple repetition of procedures on the hydrogenation of intermetallic compounds followed by the dehydrogenation of the hydride phases formed makes it possible to obtain powders with various particle sizes. The disperse analysis of the powder of $SmCo_5$ subjected to one cycle of hydrogen treatment showed that the particle size of the obtained product did not exceed 40 μm and decreases to 10 μm after 8—10 cycles.[9] The results of X-ray phase analysis and electron probe X-ray microanalysis indicate that the formed powders are single-phase. As can be seen from the above-presented data, the specific surface of the intermetallic powders obtained after five hydrogenation—dehydrogenation cycles increases by an order of magnitude, being 0.2—0.5 $m^2\ g^{-1}$.

The alloys based on Sm_2Co_{17} of compositions $Sm(Co_{0.671}Cu_{0.080}Fe_{0.222}Zr_{0.025})_{8.92}$ or $Sm_{0.68}Gd_{0.17}Zr_{0.15}$-$(Co_{0.7}Cu_{0.07}Fe_{0.23})_{6.6}$ absorb hydrogen at 20—200 °C for several hours, and the second cycle ends already within ~30 min. The hydrogenation products contain less than 0.5 wt.% hydrogen and are embrittled, but the powders in the finely dispersed state cannot be obtained even after 20 hydrogenation—dehydrogenation cycles. Therefore, for the further use of materials based on R_2Co_{17} and subjected to the treatment with hydrogen, the embrittled samples should additionally be disintegrated in an inert or hydrogen atmosphere using other methods.

The ingots of the alloys $Nd_{19}Fe_{13}B_8$, $TbNd_{17}Co_{20}Fe_{55}B_8$, and several other (system Nd—Fe—B), preliminarily degassed by heating for 1 h in a vacuum of ~1 Pa at 300 °C, are hydrogenated without an induction period to form the hydride phase containing 0.4—0.7 wt.% hydrogen. Their cell volume increases by 2—5%, which induces a significant embrittlement of the samples. After discharging an excessive pressure, these samples, as a rule, contain 0.2—0.3 wt.% hydrogen that, according to the gravimetric analysis data, is evolved in one stage at 100—160 °C.

Thus, unlike mechanical milling, the method of hydride dispergation makes it possible to obtain metallic powders with the non-oxidized surface, without cold-hardenings and traces of plastic deformation, and with the particle shape optimum for further operation. However, the particle size of the compounds and alloys dispergated by this method is 1—10 μm, which restricts, in several cases, the application of some of them for the production of materials with specified properties. Even after tens of hydride dispergation cycles, the specific surface area of the products ranges from 0.1 to 0.7 $m^2 g^{-1}$.[7]

Method of ammonia dispergation of metallic phases

In our recent experiments extensive data on the relationships between the temperature, size of the initial particles, cycling (multiple repetition of hydrogenation—dehydrogenation procedures), and duration of the treatment in the chemical transformation of individual metals in ammonia have been accumulated. The study was primarily aimed at establishing the possibility of preparation of metal hydrides and nitrides in the ultradispersed state. This work resulted in metal hydrides and nitrides and their mixtures with a specified particle size (from microcrystalline to ultradispersed) and revealed some specific features of the processes that occur in the systems $M—NH_3$.[15] The conditions for the preparation of binary compounds of some metals are presented in Table 1.

The treatment of the metallic powders with ammonia under the conditions indicated in Table 1 gives metal hydrides of a certain composition, as a rule, with a developed specific surface. The metal hydrides are further transformed into nanosized powders of the corresponding metals by dehydrogenation *in vacuo* (down to ~10^{-3} Torr) at temperatures ~100 °C lower than the decomposition temperatures (to prevent or minimize metal caking on heating). The estimation of the average particle size performed in the approximation of the particles to a ball shape gave the following values: 85 nm for ZrH_2, 60 nm for ZrN, and 30—50 nm for VN.

Table 1. Conditions for the synthesis of metal hydrides and nitrides with ammonia

Metal	Metallic particle size/μm	Conditions for synthesis		Reaction product	
		T/°C	t/h	Composition	$S_{sp}/m^2 g^{-1}$
Ti	10	250	50	TiH_2	28.9
	50	250	55	TiH_2	57.4
	50	400	55	TiN	53.5
Zr	50	350	36	$ZrH_{1,2}$	1.8
	50	400	36	ZrH_2	12.9
	100	450	34	ZrH_2	2.5
	50	550	36	ZrN	3.8
V	100	350	60	VH_x	19.6
	50	500	50	VN	10.7
	100	500	60	VN	9.1
Mg	100—200	450	30	Mg_3N_2	5.4

The scientific data obtained at the first stage of investigation were used for the study of the possibility of using ammonia for dispergation of polymetallic phases, *viz.*, intermetallic compounds and alloys.

Ammonia dispergation of intermetallic compounds

The interaction of ammonia with the intermetallic compounds of various structural types at 100—150 °C affords the corresponding hydride phases, whose composition and some properties are listed in Table 2.[16—24] The obtained hydride phases are most frequently solid solutions of hydrogen in the crystalline lattice, whereas with the temperature increase to 200 °C and higher, in particular cases, insignificant amounts of nitrogen are inserted in the metallic lattice (<0.1 at. N/AB_n) to form hydridonitride phases.

The products of ammonia treatment carried out at 100—200 °C are highly dispersed powders with a developed specific surface, which exceeds by several orders of magnitude the specific surface of the starting polymetallic phases.

The behavior of intermetallic compounds CeT_2 (T is a metal of the iron triad) is anomalous compared to other intermetallic compounds of the AB_2 type: at 150 °C in an ammonia atmosphere compounds $CeFe_2$, $CeCo_2$, and $CeNi_2$ undergo disproportionation with the formation of the hydride phase of the new intermetallic compound $Ce_2T_{17}H_x$ and cerium hydride and nitride.[25] As will be shown below, the disproportionation also occurs in other $AB_n—NH_3$ systems but at higher temperatures.

The treatment of the intermetallic compounds with ammonia at 450—500 °C results in the complete decomposition of matrices of the starting intermetallic compounds and in the formation of homogeneous highly dispersed compositions consisting of the hydride and nitride phases of metal A and the phase of 3d-transition metal B. In these compositions, the particle size is tenths fractions of μm, as a rule. It should be mentioned that the formation of metal nitrides AN_x is preceded by the reaction of the metal with hydrogen to form hydride of the corresponding metal AH_x.[15] This fact explained the particularly observed coexistence of hydride and nitride phases of metals in the products of ammonia treatment.

The experimental results of the hydronitriding of the intermetallic compounds leading to various chemical and phase transformations are summarized in Table 3.

Table 2. Characteristics of the products of the interaction of intermetallic compounds with ammonia at 100—250 °C

Starting intermetallic compound	T/°C	Phase composition	S_{sp} /m^2 g^{-1}	Particle size /μm	Reference
Ti_3Al	100	$Ti_3AlH_{2.8}$	0.1	14.1	16
	150	$Ti_3AlH_{3.0}$	0.1	14.1	
	200	$Ti_3AlH_{3.0}N_{<0.1}$	0.2	7.1	
Mg_2Ni	100	Mg_2NiH_x	14.7	0.12	17
	150	$Mg_2NiH_x + MgH_2$	25.5	0.07	
TiFe	200	$TiFeH_{0.1} + TiFeH_2N_x$	4.5	0.22	18
	250	$TiFeH_{0.1} + TiFeH_2N_x$	4.3	0.25	
TiAl	100	$TiAlH_{0.7}$	0.5	3.1	16
	150	$TiAlH_{1.5}$	0.4	3.9	
	200	$TiAlH_{1.9}N_{<0.1}$	0.4	3.9	
$ScFe_2$	150	$ScFe_2H_{1.5}$	7.4	0.15	19
$ScNi_2$	150	$ScNi_2H_{1.0}$	6.8	0.15	19
$SmCo_5$	150	$SmCo_5H_{0.3}$	0.3	4.0	20, 21
	200	$SmCo_5H_{0.3}N_y$	1.4	0.86	
$LaNi_5$	150	$LaNi_5H_{0.5}$	1.3	0.56	20
Sm_2Co_{17}	150	$Sm_2Co_{17}H_xN_y$	3.4	0.20	21
	200	$Sm_2Co_{17}H_xN_y$	2.5	0.27	
Sm_2Fe_{17}	150	$Sm_2Fe_{17}H_xN_y$	1.9	0.40	22
	200	$Sm_2Fe_{17}H_xN_y$	7.8	0.11	
	250	$Sm_2Fe_{17}H_xN_y$	4.3	0.20	
$SmFe_{11}Ti$	150	$SmFe_{11}TiH_xN_y$	19.0	0.04	23
$Nd_2Fe_{14}B$	150	$Nd_2Fe_{14}BH_xN_y$	3.4	0.25	24
	200	$Nd_2Fe_{14}BH_xN_y$	2.8	0.28	
	250	$Nd_2Fe_{14}BH_xN_y$	4.2	0.20	

It turned out that intermetallic compound Ti_3Al is stable in an ammonia atmosphere at all temperatures of the studied temperature range.[16] As can be seen from the results of hydronitriding of Ti_3Al given in Table 4, the reaction with ammonia begins at 100 °C (sample **1**) and continues with the further temperature increase to 150 °C (sample **2**) to form hydride phases containing no nitrogen. As the temperature of ammonia treatment further increases, the hydride phase begins to accumulate certain amounts of nitrogen, which results in an increase in the specific surface of the obtained phases and, accordingly, in a decrease in the particle size. According to the thermal analysis data, from the samples obtained at 100—250 °C hydrogen is completely evolved with the exothermic effect at 270—280 °C.

The determination of the temperature dependence of the hydronitriding products of the intermetallic compounds (see Table 3) allows one to describe the processes occurring in the AB_n—NH_3 systems by reactions (4)—(6).

$$AB_n + NH_3 \xrightarrow[NH_4Cl]{100\text{—}150\ ^\circ C} AB_nH_x \tag{4}$$

$$AB_n + NH_3 \xrightarrow[NH_4Cl]{200\text{—}400\ ^\circ C} AB_nH_xN_y \tag{5}$$

$$AB_n + NH_3 \xrightarrow[NH_4Cl]{450\text{—}500\ ^\circ C} AN + n\ B\ (AB_2) \tag{6}$$

Reactions (4)—(6) make it possible to distinctly monitor how increasing temperature affects the process of the stage-by-stage chemical and/or phase transformation of the starting intermetallic compound AB_n into products of its complete or partial decomposition (AN, B, AB_2). In addition, a specific role of ammonia in these processes, which lies in the degradation of the metallic matrix, can be stressed. Certainly, the reactions presented do not describe all processes that occur during the treatment of the intermetallic compound with ammonia in the presence of a promoter. For example, as already mentioned, the formation of metal nitrides is accompanied by, or saying more exactly, preceded by the appearance of metal hydrides. The corresponding peaks in the diffraction patterns of the reaction products are often overlap each other and, therefore, it is not always possible to conclude unambiguously about the presence of the hydride phase in the products. In some cases, the starting intermetallic compound is resistant to ammonia (for example, Ti_3Al) or disproportionates to form a new intermetallic compound. Finally, it should specially be noted that in some intermetallic compounds metal A is chemically active. As mentioned above, these are intermetallic compounds CeT_2, but the compounds based on samarium (discussed below) and magnesium, Mg_2Ni, are of special interest.

The chemical activity of magnesium favors an enhanced reactivity shown by the intermetallic compound.

Table 3. Chemical and phase transformations of the intermetallic compounds in NH_3 at a pressure of 1.5 MPa at various temperatures

Intermetallic compound	*T*/°C	Reaction products
Ti_3Al	100—150	Ti_3AlH_x
	200—500	$Ti_3AlH_xN_y$
Mg_2Ni	100	Mg_2NiH_x
	150	$Mg_2NiH_x + MgH_2$
	200—300	$Mg(NH_2)_2$ + Ni
	350—500	Mg_3N_2 + Ni
TiFe	200—250	$TiFeH_{0.1} + TiFeH_2N_y$
	350—400	$TiFeH_2N_y$ + TiN + γ-Fe_4N
	500	$TiFe_2$ + TiN + α-Fe + Fe_3N
TiAl	100—150	$TiAlH_x$
	200—350	$TiAlH_xN_y$
	400—500	$TiAl_2 + TiN_y$
$ScFe_2$	150	$ScFe_2H_{1.5}$
	200—350	Amorphous to X-rays
	500	α-Fe + $ScN_{0.87} + ScH_2$
$ScNi_2$	200	$ScNi_2H_{1.0}$
	300—350	Amorphous to X-rays
	500	Ni + $ScN_x + ScH_2$
CeT_2 (T – Fe, Co, Ni)	150	$Ce_2T_{17}H_x + CeH_x$ + CeN
$CeFe_2$	300—500	CeH_x + CeN + α-Fe + Fe_4N
$CeNi_2$	250—500	CeH_x + CeN + Ni
$CeCo_2$	300—400	$CeH_x + Ce_2Co_{17}H_x$ + + CeN + α-Co + Co_{cube}
$LaNi_5$	150	$LaNi_5H_{0.5}$
	200—350	$LaNi_5H_x$ + X phase + Ni
	400—450	LaN + X phase + Ni
$SmCo_5$	150	$SmCo_5H_{0,3}$
	200	$SmCo_5H_xN_y$
	250—350	$SmCo_5H_xN_y$ + + $Sm_2Co_7H_xN_y$ + α-Co
	450—500	SmN + Co_{cube}
Sm_2Co_{17}	200	$Sm_2Co_{17}H_xN_y$
	250	$Sm_2Co_{17}H_xN_y + SmCo_3H_xN_y$
	300	$SmCo_3H_xN_y$ + + $Sm_2Co_{17}H_xN_y + Co_{cube}$
	500	SmN + Co_{cube}
Sm_2Fe_{17}	150	$Sm_2Fe_{17}H_x$
	200—250	$Sm_2Fe_{17}H_xN_y$
	350—400	$Sm_2Fe_{17}H_xN_y + SmFe_3H_x$ + + α-Fe + γ-Fe_4N
	500	α-Fe + SmN
$SmFe_{11}Ti$	150	$SmFe_{11}TiH_xN_y$
	200—250	$SmFe_{11}TiH_xN_y + SmFe_2H_x$ + + $TiFe_2$ + α-Fe
	300—350	$SmFe_2H_x + SmH_x + TiFe_2$ + + α-Fe + γ-Fe_4N
	400—450	SmN + $TiFe_2$ + α-Fe + + γ-$Fe_4N + TiH_2$
$Nd_2Fe_{14}B$	150—250	$Nd_2Fe_{14}BH_xN_y$
	300	$Nd_2Fe_{14}BH_xN_y$ + + γ-Fe_4N + α-Fe
	400—500	$Nd_2Fe_{14}BH_xN_y$ + γ-Fe_4N + + α-Fe + NdN + $BFe_2 + BFe_3$

For instance, a series of compounds with different structures and, in particular, magnesium amide $Mg(NH_2)_2$, which is far from polymetallic and metallic phases, is observed in the products of Mg_2Ni hydronitriding with the nature of the product changing with temperature.[17] The formation of amide is due to the decomposition of tetrahydride Mg_2NiH_4, which was formed at 150—200 °C, with the further temperature increase. However, the tetrahydride is involved not only in the decomposition but also in the competitive disproportionation reaction to form the new intermetallic compound $MgNi_2$. Nickel and magnesium nitride Mg_3N_2 are the final decomposition products at 500 °C.

Table 4. Conditions and results of hydronitriding of the intermetallic compound Ti_3Al

Sample	Treatment conditions		Composition of product	Particle size/μm
	T/°C	*t*/h		
1	100	30	$Ti_3AlH_{2.8}$	14.1
2	150	32	$Ti_3AlH_{3.0}$	14.1
3	200	30	$Ti_3AlH_{3.0}N_{<0.1}$	7.1
4	250	30	$Ti_3AlH_{2.0}N_{<0.1}$	2.8
5	300	28	$Ti_3AlH_{0.3}N_{0.10}$	1.1
6	350	28	$Ti_3AlH_{0.5}N_{0.15}$	0.8
7	400	30	$Ti_3AlH_{0.6}N_{0.25}$	0.4
8	450	30	$Ti_3AlH_{0.7}N_{0.25}$	0.25
9	500	30	$Ti_3AlH_{2.8}N_{0.35}$	0.2

Ammonia dispergation of alloys

It is well known that alloys of the system Ti—Al are promising as light structural materials with high strength, thermal stability, and resistance to oxidation. However, alloys with a high titanium content are considerably plastic, which is a reason for the appearance of cold-hardenings and amorphization and oxidation of the particle surface upon mechanical disintegration of the cast material. Therefore, it is reasonable to use chemical methods of disintegration for trituration of alloys of the Ti—Al system to form nanocrystalline materials. Since the interaction of the intermetallic compounds from this system of compositions TiAl and Ti_3Al with ammonia was studied,[16] it

Table 5. Specific surface areas of the products resulted from the interaction of alloys with ammonia at various temperatures

T/°C	Specific surface area/m^2 g^{-1}						
	Ti[28]	$Ti_{94}Al_6$ ($Ti_{15.7}Al$)	$Ti_{91}Al_9$ ($Ti_{10.1}Al$)	$Ti_{75}Al_{25}$ (Ti_3Al)	$Ti_{67}Al_{33}$ (Ti_2Al)	$Ti_{60}Al_{40}$ ($Ti_{1.5}Al$)	$Ti_{50}Al_{50}$ (TiAl)
100	—	—	—	0.1	0.1	0.4	0.5
150	—	5.8	0.4	0.1	0.2	0.2	0.4
200	—	8.5	0.8	0.2	0.2	0.2	0.4
250	28.8	8.7	1.2	0.5	0.5	0.6	0.5
300	60.7	11.3	1.5	0.8	0.7	0.9	5.7
350	49.5	35.6	1.7	1.8	1.2	1.4	3.1
400	50.1	52.0	48.9	3.6	3.3	1.3	2.8
450	—	78.8	50.5	5.7	5.4	3.9	3.7
500	—	50.5	60.0	8.8	7.3	17.8	1.5

seemed interesting to obtain and compare the data on dispergation and possible transformations of other alloys from this system in ammonia at 100—500 °C.

Powders of the titanium alloys with aluminum $Ti_{94}Al_6$ and $Ti_{91}Al_9$ (formula units $Ti_{15.7}Al$ and $Ti_{10.1}Al$, respectively),[10] $Ti_{67}Al_{33}$ and $Ti_{60}Al_{40}$ (Ti_2Al and $Ti_{1.5}Al$)[26] were chosen as objects of the study.

The alloys $Ti_{15.7}Al$ and $Ti_{10.1}Al$ are solid solutions with an aluminum content in α-titanium of 6 and 9 at.%. It should be mentioned that processes associated with the transformations of aluminum itself or aluminum-containing compounds were not identified because of the low content of aluminum in the alloys $Ti_{15.7}Al$ and $Ti_{10.1}Al$. Therefore, in case of these alloys we practically studied only the behavior of α-Ti in ammonia at various temperatures but taking into account some specific features related to the presence of the aluminum-containing phase in the alloys. The hydrogenation of α-Ti with ammonia commences at 250—300 °C to form titanium hydride, and with the further temperature increase to 400—500 °C it transforms into titanium nitride. The processes that occur in the systems $Ti_{15.7}Al—NH_3$ and $Ti_{10.1}Al—NH_3$ are different and, hence, the compositions of the formed products vary (the specific surface area of the products is given in Table 5, and the compositions and particle sizes are listed in Table 6). This difference is the result of the influence of different amounts of aluminum that is present in the alloys.[10]

Note the formation and coexistence of different phases of titanium dihydride, cubic and tetragonal, in the products of hydronitriding of the $Ti_{15.7}Al$ alloy at 300—450 °C.

No aluminum-containing compounds appear in the reaction products of the $Ti_{10.1}Al—NH_3$ system in the whole temperature range, but the diffraction patterns of the hydronitriding products of the alloy $Ti_{15.7}Al$, obtained at 450—500 °C, show the signals characteristic of aluminum nitride AlN.

It turned out that the presence of small amounts of aluminum is not favorable for the hydrogenation and nitriding of titanium and moreover it inhibits these processes. For example, a comparison of the results of hydronitriding of α-Ti and solid solutions of aluminum in titanium shows that an additive of 6—9 at.% Al to titanium increases the temperatures needed for the hydrogenation of titanium (by 100 °C) and for the formation of titanium nitride whereby the products formed show nearly the same particle size.

According to the X-ray phase analysis data, the melted alloys Ti_2Al and $Ti_{1.5}Al$ were two-phase and consisted of the intermetallic compounds Ti_3Al and TiAl in various

Table 6. Composition and dispersity of the hydronitriding products of alloys Ti—Al

Starting alloy	Composition after hydronitriding	Hydronitriding temperature/°C	Particle size /μm
$Ti_{50}Al_{50}$ (TiAl)	$TiAlH_{0.4}N_{0.2}$	300	0.3
$Ti_{75}Al_{25}$ (Ti_3Al)	$Ti_3AlH_{0.45}N_{0.35}$	450—500	0.25—0.15
$Ti_{60}Al_{40}$ ($Ti_{1.5}Al$)	$Ti_3AlH_xN_y + TiAlH_xN_y$	350—400	0.3—0.6
$Ti_{67}Al_{33}$ (Ti_2Al)	$Ti_3AlH_xN_y + TiAlH_xN_y$	350—400	0.3—0.6
$Ti_{91}Al_9$ ($Ti_{10.1}Al$)	TiH_2	350—400	$(35—45) \cdot 10^{-3}$
$Ti_{94}Al_6$ ($Ti_{15.7}Al$)	TiH_2	350—400	$(35—45) \cdot 10^{-3}$
$Ti_{91}Al_9$ ($Ti_{10.1}Al$)	TiN	450—500	$(15—20) \cdot 10^{-3}$
$Ti_{94}Al_6$ ($Ti_{15.7}Al$)	TiN	450—500	$(15—20) \cdot 10^{-3}$

ratios.[26] Therefore, the hydronitriding "Ti_2Al" and "$Ti_{1.5}Al$" in the temperature range 100—400 °C turned out to be similar to the interaction of intermetallic compounds with ammonia. In addition, intermetallic compound TiAl suffers amorphization as the heating temperature increases from 100 to 400 °C.[27] The treatment of the studied alloys with ammonia at 450—500 °C results in the partial destruction of crystalline lattices of the intermetallic compounds that compose the alloys. Titanium, which is formed due to the destruction of the crystalline matrix at these temperatures, reacts with hydrogen evolved upon ammonia decomposition or with ammonia to form titanium dihydride, the amount of which increases with an increase in the reaction temperature from 450 to 500 °C. Titanium hydride is simultaneously transformed into titanium nitride. This transformation is accompanied by the formation of intermediate hydridonitride phases of varying compositions. In addition, the reaction products include intermetallic compounds $TiAl_3$ and $TiAl_2$, which do not react with hydrogen. These compounds are the products of destruction of the metallic lattice of intermetallic phases composing the initial alloys. As a result, the complicated composition of the reaction products of the alloys with ammonia at 450—500 °C can be explained. It should be mentioned that, according to the chemical analysis data, the products of hydronitriding performed at 450—500 °C contain a considerable amount of nitrogen: up to 8.6 and 3.9 wt.% for the systems $Ti_{1.5}Al—NH_3$ and $Ti_2Al—NH_3$, respectively. These data confirm the results of X-ray phase studies of the formation and accumulation of the nitride phases in the reaction products.

The values of the specific surface area of the hydronitriding products for all alloys of the Ti—Al systems studied at 150—500 °C and (for comparison) for titanium according to the published data[28] are listed in Table 6. They indicate the monotonic growth and a significant increase (by orders of magnitude) in the specific surface area of the products with an increase in the hydronitriding temperature. The increase in the specific surface area corresponds to a further disintegration of the particles during the hydronitriding of the alloy powder due to the chemical transformations of the particles with the formation of products with a higher dispersity. In fact, the estimation of the average particle size assuming their spherical shape showed high dispersity of the powders (for the corresponding data, see Table 6).

As should be expected, the presented values of specific surface for the products of treatment of titanium and alloy $Ti_{15.7}Al$ containing a small amount of aluminum with ammonia at 350—400 °C coincide (see Table 5).

It can be seen that the products of hydronitriding of the alloys $Ti_{1.5}Al$ and Ti_2Al obtained on heating to 250 °C have a low specific surface area indicating the embrittlement of the particle surface only. An additional high-energy treatment, for example, in planetary-type ball mills in ammonia, is necessary for the preparation of highly dispersed or nanosized powders of the alloys $Ti_{1.5}Al$ and Ti_2Al. The powders obtained at a hydronitriding temperature of 350—400 °C are highly dispersed (particle size 0.3—0.6 μm). The powders formed at 500 °C, especially those of $Ti_{1.5}Al$, have a developed specific surface area exceeding that of the starting alloys by two—three orders of magnitude, but they represent a mixture of various substances.

Ammonia dispergation of magnetic materials

It is especially important for the manufacturing of permanent magnets to find easily preparative methods of disintegration of cast materials that are also suitable for industrial applications. The initial materials for the production of the permanent magnets are alloys based on samarium and iron and especially alloys of the system RE —Fe—B (RE is a rare-earth element) characterized by a high plasticity. These alloys are based on the corresponding intermetallic compounds. Therefore, for the preparation of highly dispersed powders, we studies possibilities of using the method of ammonia dispergation at various temperatures for intermetallic compounds $SmCo_5$,[20,21] Sm_2Co_{17},[21] Sm_2Fe_{17},[22] $SmFe_{11}Ti$,[23] and $Nd_2Fe_{14}B$.[24] In addition, the treatment of polymetallic compositions with ammonia results in the insertion of 3.0—3.5 nitrogen atoms per unit cell of the crystalline lattice of intermetallic compounds. This insertion increases the interatomic distances Fe—Fe and thus improves the characteristics of the exchange interaction of "magnetic" iron atoms.[29] Accordingly, the process of insertion makes it possible to obtain a materials with improved magnetic properties. Some of the relevant results are summarized in Tables 2 and 3.

The reaction of intermetallic compound $SmCo_5$ with ammonia at 150—200 °C affords solid solutions of hydrogen and nitrogen in the metallic matrix of the intermetallic compound.[21] At 250 °C during the hydronitriding of $SmCo_5$, the intermetallic compound begins to decompose within 26 h to evolve metallic cobalt and form the hydridonitride phase with a smaller content of cobalt of the composition $Sm_2Co_7H_xN_y$. The specific surface area of the reaction products achieves a value of 6.5 $m^2 g^{-1}$, which is several tens of times higher than the specific surface area of the products obtained by the method of hydride dispergation. The estimation of the average particle size (~110 nm) confirmed the formation of a highly dispersed material. A similar process is characteristic of the hydronitriding of Sm_2Co_{17} under the same conditions.[21] The particle size of the powder is ~0.3 μm. In addition, according to the X-ray phase analysis data, the reaction products of both intermetallic compounds, $SmCo_5$ and Sm_2Co_{17}, with ammonia contain trace amounts of hydridonitride phases. These phases are based on new intermetallic compounds Sm_2Co_7 and $SmCo_3$, respectively, and they are the products of decomposition of the starting intermetallic compounds caused by the combined insertion of small amounts of nitrogen and hydrogen in the metallic matrix.

It is known that in the range of particle sizes lower than micrometers intermetallic compound $SmCo_5$ shows a correlation between two variables: the coercive force of the intermetallic compound increases with a decrease in the particle size. The measurement of the magnetic characteristics did not show the presence of the initial phase in the products of reaction of $SmCo_5$ with ammonia at a temperature of 250 °C corresponding, as already indicated, to the maximum dispergation (S_{sp} = 6.5 $m^2 g^{-1}$). Indeed, the presence of strong peaks related to the phases $SmCo_5H_xN_y$ and $Sm_2Co_7H_xN_y$ in the diffraction patterns yet doesn´t indicate that the sample contains no small particles of $SmCo_5$ amorphous to X-rays. However, the samples of $SmCo_5$ amorphous to X-rays, which were obtained by milling in an inert atmosphere, retain a high coercive force ($H \geq 0.4$ T).[30] The values of H for the products of the reaction of $SmCo_5$ with ammonia at 250 °C are 0.006—0.007 T.

The hydronitriding of compound Sm_2Fe_{17} at 200—250 °C for 24 h yielded hydridonitride containing 1.0—2.5 wt.% nitrogen with a developed specific surface area and a particle size of 0.1—0.2 μm. The composition of the products obtained by the treatment of this compound with ammonia at other temperatures is presented in Table 3.

According to the published data,[31] correct measurements of the coercive force H and saturation magnetization σ for the samples Sm_2Fe_{17} can be performed only in fairly high fields. Our measurements of the hysteresis loop at -1 T $\leq H \leq 1$ T made it possible to emphasize this specific feature of intermetallic compound Sm_2Fe_{17} and to show the character of changes in its magnetic properties upon the ammonia treatment.

As for the system $SmFe_{11}Ti—NH_3$ (see Table 3), it should be mentioned that the specific surface area of the nitriding products $SmFe_{11}Ti$ obtained at 150—200 °C (S_{sp} = = 19—25 $m^2 g^{-1}$, particle size 40—50 nm) is higher than that of the hydrogenation product of the same compound (S_{sp} = 0.4 $m^2 g^{-1}$ for $SmFe_{11}TiH_1$).

The measurements of the coercive force showed that the treatment of $SmFe_{11}Ti$ with ammonia afforded the nanosized powder $SmFe_{11}TiN_xH_y$ with the value H(1T) = = 0.0212 T, which makes it a more convenient object for technological procedures than the starting powder $SmFe_{11}Ti$.

The interaction of $Nd_2Fe_{14}B$ with NH_3 (see Table 3) already at 150 °C (24 h) produces the crystalline and a highly dispersed hydridonitride phase $Nd_2Fe_{14}BH_xN_y$ (a = 8.905 Å, c = 12.36 Å, nitrogen content 2.3 wt.%, average particle size 0.25 μm), which starts to decompose at 250 °C in ammonia to form trace amounts of metallic α-iron. The nitrogen content increases to 5.6 wt.%, and the particle size is 0.25 μm, which is sufficient for the preparation of permanent magnets.

Note that an indirect evidence of the incorporation of nitrogen atoms in the intermetallic compound lattice is an appreciable increase in the ratio c/a compared to this value for the starting sample. As known, hydrogen and nitrogen atoms occupy different sites in the lattice of intermetallic compound $Nd_2Fe_{14}B$. Hydrogenation results in a decrease in the c/a ratio. The effect from the insertion of nitrogen in the lattice is stronger and, hence, the c/a ratio for samples **12** and **13** (Table 7) is higher than that for the starting intermetallic compound.

The magnetic properties of intermetallic compound $Nd_2Fe_{14}B$, its hydride phase, and the reaction products with ammonia at 150 and 200 °C are characterized in Table 7. It was found that the magnetic properties of samples **12** and **13** are different from analogous characteristics of both the initial intermetallic compound and its hydride phase. The measurements were performed in the fields -1 T $\leq H \leq$ 1 T far from the saturation fields. Nevertheless, it can be noted that the insertion of hydrogen atoms results in an increase in the magnetization value in an external field of 1 T (σ_1), whereas the insertion of nitrogen atoms decreases this value. In the case of sample **12**, the effect from the insertion of hydrogen atoms is stronger, which resulted in an increased value of σ_1. On the contrary, in the case of sample **13**, the effect from inserted nitrogen atoms is stronger and the value of σ_1 was found to be lower than that for the starting intermetallic compound. These data confirm the known fact that the introduction of nitrogen increases the magnetic characteristics of intermetallic compounds.[29]

No clear explanation can be so far suggested for the presented values of magnetic characteristics of the substances, the starting materials for the production of permanent magnets. However, these values clearly indicate the retention and improvement of the magnetic properties of the substances subjected to the ammonia treatment (see, *e.g.*, the data in Table 7). Since it was established that the use of ammonia for the dispergation of magnetic materials makes it possible to produce highly dispersed powders or powders with the nanometer particle size (see Table 2), the conclusion can be made that they can be used for the production of permanent magnets. The works in this direction are in progress, and testing of pilot samples are currently under way.

Table 7. Ratio c/a, its change (Δ), saturation magnetization in an external field of 1 T (σ_1), and coercive force (H) for the studied samples $Nd_2Fe_{14}B$

Sample	c/a	Δ	σ_1 /emu g^{-1}	$H \cdot 10^4$ /T
$Nd_2Fe_{14}B$ (**10**)	1.3838	0	77.6	131
$Nd_2Fe_{14}BH_x$ (**11**)	1.3798	−0.0040	113.5	117
$Nd_2Fe_{14}BH_xN_y$ (150 °C) (**12**)	1.3880	+0.0042	91.5	139
$Nd_2Fe_{14}BH_xN_y$ (200 °C) (**13**)	1.3911	+0.0073	66.4	123

Conclusion

The hydride dispergation based on the reversible interaction of polymetallic systems with hydrogen is a promising method for the preparation of highly dispersed powders of metallic phases or their hydrides.

Depending on the treatment temperature, the reaction of polymetallic systems with ammonia, *viz.*, ammonia dispergation, can easily be used to prepare nanodispersed powders of metallic phases, hydrides, hydronitrides, and nitrides of metals and metallic phases, whereas highly dispersed powders of the metallic phases are obtained after the removal of hydrogen from hydrides.

The use of ammonia instead of hydrogen for the dispergation of metallic phases makes it possible to obtain highly dispersed powders or powders with the nanometer particle size without using preliminary activation, without adherence to strict requirements imposed on the purity of hydrogen used, and to rigid restrictions on the composition of the alloy during its melting. The prepared powders containing some amounts of hydrogen and nitrogen are suitable as the starting materials for the production of pressed items, which is well known from the literature (see, *e.g.*, Ref. 29). Mixtures of powders obtained at high temperatures of hydronitriding are utilizable for the production of diverse composite materials.

References

1. R. A. Andrievskii, *Usp. Khim.*, 1994, **63**, 431 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1994, **63**].
2. I. V. Tananaev, V. B. Fedorov, E. G. Kalashnikov, *Usp. Khim.*, 1987, **56**, 193 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1987, **56**].
3. I. I. Kornilov, *Titan* [*Titanium*], Moscow, Nauka, 1963, 123 pp. (in Russian).
4. B. P. Tarasov, A. G. Burlakova, L. S. Volkova, N. G. Mozgina, Z. A. Rumynskaya, Yu. M. Shul´ga, S. P. Shilkin, *Zh. Neorg. Khim.*, 1997, **42**, 209 [*Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1997, **42**].
5. K. N. Semenenko, V. V. Burnasheva, *Vest. Mos. Gos. Univ., Ser. 2. Khimiya*, 1977, **18**, 618 [*Vestn. Mosk. Univ., Ser. Khim.* (*Engl. Transl.*), 1977, **18**].
6. V. N. Verbetskii, A. A. Salamova, K. N. Semenenko, *Izv. Akad. Nauk SSSR, Ser. Metally* [*Bull. Acad. Sci. USSR, Ser. Met.*], 1989, 196 (in Russian).
7. V. N. Fokin, B. P. Tarasov, I. I. Korobov, S. P. Shilkin, *Koord. Khim.*, 1992, **18**, 526 [*Russ. J. Coord. Chem.* (*Engl. Transl.*), 1992, **18**].
8. V. N. Fokin, S. P. Shilkin, E. E. Fokina, B. P. Tarasov, I. I. Korobov, *Zh. Neorg. Khim.*, 1999, **44**, 885 [*Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1999, **44**, 823].
9. V. N. Fokin, E. E. Fokina, S. P. Shilkin, *Zh. Prikl. Khim.*, 1994, **67**, 1372 [*Russ. J. Appl. Chem.* (*Engl. Transl.*), 1994, **67**, 1207].
10. V. N. Fokin, E. E. Fokina, B. P. Tarasov, *Neorg. Mater.*, 2010, **46**, 1438 [*Inorgan. Materials* (*Engl. Transl.*), 2010, **46**, 1304].
11. V. N. Fokin, S. L. Troitskaya, E. E. Fokina, S. P. Shilkin, *Zh. Neorg. Khim.*, 1991, **36**, 299 [*Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1991, **36**].
12. V. A. Yartys´, V. V. Burnasheva, K. N. Semenenko, *Usp. Khim.*, 1983, **52**, 529 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1983, **52**].
13. B. P. Tarasov, V. E. Muradyan, Y. M. Shul´ga, E. P. Krinichnaya, N. S. Kuyunko, O. N. Efimov, E. D. Obraztsova, D. V. Schur, J. P. Maehlen, V. A. Yartys, H.-J. Lai, *Carbon*, 2003, **41**, 1357.
14. A. A. Volodin, P. V. Fursikov, Yu. A. Kasumov, I. I. Khodos, B. P. Tarasov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2005, 2210 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2281].
15. V. N. Fokin, E. E. Fokina, B. P. Tarasov, *Zh. Neorg. Khim.*, 2010, **55**, 1628 [*Russ. J. Inorg. Chem.* (*Engl. Transl.*), 2010, **55**, 1536].
16. V. N. Fokin, E. E. Fokina, B. P. Tarasov, *Zh. Obshch. Khim.*, 2008, **78**, 888 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2008, **78**, 1118].
17. V. N. Fokin, E. E. Fokina, B. P. Tarasov, *Neorg. Mater.*, 2009, **45**, 926 [*Inorgan. Materials* (*Engl. Transl.*), 2009, **45**, 859].
18. V. N. Fokin, E. E. Fokina, I. I. Korobov, B. P. Tarasov, *Neorg. Mater.*, 2008, **44**, 184 [*Inorgan. Materials* (*Engl. Transl.*), 2008, **44**, 142].
19. S. P. Shilkin, V. N. Fokin, E. E. Fokina, B. P. Tarasov, I. I. Korobov, *Zh. Obshch. Khim.*, 2000, **70**, 399 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2000, **70**, 371].
20. V. N. Fokin, Yu. M. Shul´ga, B. P. Tarasov, E. E. Fokina, I. I. Korobov, A. G. Burlakova, S. P. Shilkin, *Zh. Obshch. Khim.*, 2004, **74**, 1765 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2004, **74**, 1641].
21. V. N. Fokin, S. P. Shilkin, B. P. Tarasov, E. E. Fokina, I. I. Korobov, A. G. Burlakova, Yu. M. Shul´ga, *Zh. Neorg. Khim.*, 2004, **49**, 17 [*Russ. J. Inorg. Chem.* (*Engl. Transl.*), 2004, **49**, 13].
22. V. N. Fokin, Yu. M. Shul´ga, B. P. Tarasov, E. E. Fokina, I. I. Korobov, A. G. Burlakova, S. P. Shilkin, *Neorg. Mater.*, 2004, **40**, 580 [*Inorgan. Materials* (*Engl. Transl.*), 2004, **40**, 497].
23. V. N. Fokin, Yu. M. Shul´ga, B. P. Tarasov, E. E. Fokina, I. I. Korobov, A. G. Burlakova, S. P. Shilkin, *Zh. Obshch. Khim.*, 2005, **75**, 881 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2005, **75**, 831].
24. V. N. Fokin, Yu. M. Shul´ga, B. P. Tarasov, E. E. Fokina, I. I. Korobov, A. G. Burlakova, S. P. Shilkin, *Zh. Neorg. Khim.*, 2005, **50**, 1061 [*Russ. J. Inorg. Chem.* (*Engl. Transl.*), 2005, **50**, 975].
25. V. N. Fokin, E. E. Fokina, I. I. Korobov, B. P. Tarasov, S. P. Shilkin, *Zh. Neorg. Khim.*, 2001, **46**, 587 [*Russ. J. Inorg. Chem.* (*Engl. Transl.*), 2001, **46**, 511].
26. V. N. Fokin, E. E. Fokina, I. I. Korobov, B. P. Tarasov, *Int. J. Hydrogen Energy*, 2011, **36**, 1217.
27. K. Hashi, K. Ishikawa, K. Suzuki, K. Aoki, *J. Alloys Comp.*, 2002, **330—332**, 547.
28. V. N. Fokin, S. P. Shilkin, E. E. Fokina, N. G. Mozgina, *Zh. Obshch. Khim.*, 1997, **87**, 705 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 1997, **87**].
29. O. V. Kravchenko, V. V. Burnasheva, A. D. Terekhov, K. N. Semenenko, *Zh. Obshch. Khim.*, 1998, **68**, 705 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 1998, **68**].
30. M. L. Kahn, J.-L. Bobet, F. Weill, B. Chevalier, *J. Alloys Comp.*, 2002, **334**, 285.
31. J. M. D. Coey, H. Sun, D. P. F. Hurley, *J. Magn. Magn. Mat.*, 1991, **101**, 310.

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