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Preparation of Hydrides of Intermetallic Compounds

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Abstract—Interaction of a series of intermetallic compounds with ammonia at 100–250°C and 1.5 MPa in the presence of promoter NH_4Cl was studied. The optimal conditions of preparations of hydride phases have been determined. Properties of hydronitrogenation products of intermetallic compounds have been compared with those of direct hydrogenation products.

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Reducing solid materials to particle of desired redefined size is one of the most important technological operations in processing metals and multimetallic phases used as material of permanent magnets, metal hydride electrodes, catalysts, and absorbents for bound hydrogen storage. Highly dispersed materials are more easily processed and often possess functional properties different from those of the bulky material. In view of this, development and optimization of dispergation methods is a topical issue.

Dispergation methods can be roughly divided into physical and chemical ones [1]. The special interest to chemical methods [1–3] is due to their easy practical implementation, possibility to produce powders with non-oxidized surface and the shape of particles optimized for sub-sequent processing as well as to low power expenditure.

It has been shown that interaction of metal alloys and compounds with hydrogen results in metal powders of varied dispersity. Therefore, it has been suggested to dispergate or embrittle metals and multimetallic compositions under the action of internal stresses developed in the course of reaction with hydrogen as alternative to external mechanical impact of grinding equipment. Upon incorporation of hydrogen atoms into metal crystal lattice the volume of the latter is increased by 10–25% [4]. Simultaneously, the internal stresses are developed exceeding the material strength; therefore, it disintegrates into separate particles. After elimination of the absorbed hydrogen the dispersed form of initial material is obtained. The approach is known as hydride dispergation [5, 6] and is widely applied in practice [6, 7]. Multiple repetition of hydrogenation–dehydrogenation cycles allows to regulate the particle size of the produced powder. Hydride dispergation is accompanied by partial (about 50%) reduction of surface oxides, this improving the material purity and some utilitarian properties.

In the course of hydride dispergation powders with particle of 1–10 μm are usually formed. Such particles are relatively large which may somewhat limit their application. Even after tens of hydride dispergation cycles the specific surface area of the material S_{sp} is 0.1–0.7 m^2/g [6].

Ammonia-induced dispergation is a different method of metal chemical grinding due to internal stressed developed in the course of interaction with ammonia at relatively low temperature [8, 9]. As compared with hydride dispergation, the ammoniac dispergation method yields metal powders of much smaller particles (in certain cases, the particle size can be of nanometer range) and, therefore, of higher specific surface area.

In the experiments, influence of temperature, initial particle size, treatment duration, and number of heating–cooling cycles on the direction of the reaction of metal with ammonia in the presence of promoter NH_4Cl has been studied in [10]. Conditions of preparations of hydrides and nitrides of certain metals (Zr, Ti, and V) as well as their mixtures have been elaborated to give particle of certain size (from microcrystalline to superdispergated). The reactions proceeding at rise in temperature in M–NH_3 systems are represented by Eqs. (1)–(3).

$$M + NH_3 \xrightarrow{\Delta,\ NH_4Cl} MH_x + N_2, \qquad (1)$$

$$M + NH_3 \xrightarrow{\Delta,\ NH_4Cl} MH_x + MN_y, \qquad (2)$$

$$M + NH_3 \xrightarrow{\Delta,\ NH_4Cl} MN_x + H_2. \qquad (3)$$

The promoting effect of ammonium chloride in reactions (1)–(3) is due to the reversible reaction: $NH_4Cl \rightleftarrows NH_3 + HCl$ occurring at heating. Apparently the emerging hydrogen chloride interacts with metal oxides on the surface facilitating the hydrogenation. Metal chlorides are formed in negligible quantity and are not detected by X-ray diffraction analysis.

Evidently, only reaction (1), not yielding any nitride, can be used for low-temperature dispergation of metal phases. On the other hand, this reaction allows metal hydride formation under relatively mild conditions [9, 10]. It was interestingly and usefully from the practical point of view to consider the application of the reaction (1) for the synthesis of hydrides of intermetallic compounds, especially those with decomposition temperature below the direct hydrogenation temperature.

In this work we established the possibility to produce hydride phases of selected intermetallic compounds by their interaction with ammonia and determined the optimal conditions of hydronitrogenation. Furthermore, for some of the intermetallides we compared the results of ammonia treatment with those of direct hydrogenation.

First of all, we focused on the investigation of the possibility of formation of hydride phases of intermetallides at the interaction of structurally different intermetallic compounds (AB, AB_2, AB_5, A_2B_{17}, and others) with ammonia under varied conditions. The features of the occuring processes were elucidated, and at 100–250°C multimetallic hydride phases were obtained. Their composition and properties are collected in Table 1.

Hydrogen content in the prepared hydride phases was increasing with the process temperature. However, at elevated temperatures minor amounts of nitrogen atoms (<0.1 N/AB_n) were incorporated into metal lattice forming the corresponding hydride-nitride phases and preservating of metal matrix.

Table 1. Characteristics of hydride phases formed upon interaction of intermetallic compounds with ammonia at 100–250°C

Initial intermetallic compound	*T*, °C	Phase composition	S_{sp}, m^2/g	Particles size, μm
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
Mg_2Ni	150	$Mg_2NiH_x + MgH_2$	25.5	0.1
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
TiFe	200	$TiFeH_{0.1} + TiFeH_2N_x$	4.5	0.2
	250	$TiFeH_{0.1} + TiFeH_2N_x$	4.3	0.3
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
$ScFe_2$	150	$ScFe_2H_{1.5}$	7.4	0.2
$ScNi_2$	150	$ScNi_2H_{1.0}$	6.8	0.2
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
$SmCo_5$	150	$SmCo_5H_{0.3}$	0.3	4.0
	200	$SmCo_5H_{0.3}N_y$	1.4	0.9
$LaNi_5$	150	$LaNi_5H_{0.5}$	1.3	0.6
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
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
$SmFe_{11}Ti$	150	$SmFe_{11}TiH_xN_y$	19.0	0.04
$Nd_2Fe_{14}B$	150	$Nd_2Fe_{14}BH_xN_y$	3.4	0.2
	200	$Nd_2Fe_{14}BH_xN_y$	2.8	0.3

Specific surface area of the prepared hydride and hydride-nitride phases exceeded that of the initial multimetallic phases by several orders of magnitude. Thus, hydronitrogenation was proved to be an efficient approach to dispergation of the intermetallic compounds. Below we will describe the individual features of hydrogenation in each of the studied intermetallic compound – ammonia systems.

Reaction of the intermetallide Ti_3Al with ammonia started at 100°C (Table 2, sample no. 1); up to 150°C (Table 2, sample no. 2) it yielded hydride phases containing no nitrogen. At still higher hydronitrogenation temperature, the forming hydride phase

Table 2. Conditions and products of hydronitrogenation of intermetallic compound Ti_3Al

Sample no.	Treatment conditions		Product composition	Particles size, μm
	T, °C	time, 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

incorporated certain experimentally detectable amount of nitrogen. Simultaneously, the particle size decreased, and the specific surface area increased. According to the thermal analysis data, the products obtained at 100–150°C completely released the absorbed hydrogen at 270–280°C, the desorption being endothermic.

Hydronitrogenation of intermetallic compounds containing reactive metal A (that is, easily hydrogenated) is of particular interest. The examples studied in this work were intermetallic compounds CeT_2 (T being a metal of iron triad) and compounds of samarium and magnesium.

As compared with other AB_2-type intermetallic compounds, $CeFe_2$, $CeCo_2$, and $CeNi_2$ disproportionated at 150°C in ammonia atmosphere to give hydride phase of another intermetallic compound ($Ce_2T_{17}H_x$) along with cerium hydride and nitride. Note that disproportionation in the presence of ammonia was observed in the cases of other intermetallic compounds as well, but at higher temperature.

Hydronitrogenation of the intermetallic compounds in the systems Sm–Co, Sm–Fe, and rare-earth metal–Fe–B is of special practical interest, as such compounds are used for production of permanent magnets. Treatment of Sm_2Fe_{17}, $SmFe_{11}Ti$, and $Nd_2Fe_{14}B$ with ammonia even at relatively low temperature (≤200°C) led to incorporation of nitrogen into the crystal lattice of compounds (3.0–3.5 N atoms per unit cell). According to [11], that resulted in increase in the Fe–Fe distance and therefore enhanced the exchange interaction between "magnetic" iron atoms. Therefore, hydronitrogenation could improve the material magnetic properties.

In the case of the $SmFe_{11}Ti–NH_3$ system, specific surface area of the hydronitrogenation products produced at 150–200°C (S_{sp} 19–25 m^2/g, particle size of 40–50 nm) was significantly higher as compared with that of the product of direct hydrogenation of the same compound (S_{sp} = 0.4 m^2/g in the case of $SmFe_{11}TiH_{\sim 1}$). Moreover, the measurement of coercive force showed that the $SmFe_{11}TiN_xH_y$ nanopowder produced by hydronitrogenation was easier processed as compared with the initial $SmFe_{11}Ti$ powder [12].

The special behavior of the intermetallic compound Mg_2Ni was due to high reactivity of magnesium. Depending on the treatment temperature, Mg_2Ni hydronitrogenation resulted in a variety of products including magnesium amide $Mg(NH_2)_2$. At 100°C, the intermetallic compound did not react with ammonia, however, the processing led to significant increase of specific surface area (from 0.04 to 14.7 m^2/g, by several orders of magnitude); according to X-ray diffraction studies, it was accompanied by the moderate change in the crystal lattice period. Upon further increase to 150°C, Mg_2Ni absorbed hydrogen to give a mixture of hydrides of magnesium and the intermetallic compound.

Using ammonia instead of hydrogen decreased the onset of the hydride phase formation by about 100°C in the case of intermetallic compound Zr_3Al_2. As was noted above, that could be of practical importance for hydrogenation of intermetallides requiring elevated processing temperature for the first hydrogenation but unstable in hydrogen atmosphere.

In certain cases, the interaction of intermetallic compounds with ammonia resulted in X-ray-amorphous products even at relatively low temperature. In particular, $ScFe_2$ and $ScNi_2$ (Table 1) gave crystalline hydride phases at 150°C in ammonia atmosphere; however, further heating up to 200–300°C yielded X-ray-amorphous products.

Crystal lattice periods of all the prepared hydride phases coincided with the known reference data.

EXPERIMENTAL

Intermetallic compounds were prepared by fusion of metal blend (purity >99.9%, furnace with non-consumable tungsten electrode, highly pure argon atmosphere) followed by two weeks annealing at 800°C.

The alloy was washed with ethanol and diethyl ether to get rid of the storage oil traces and then cleaned of the oxide film. For further studies, the intermetallic compound specimens were prepared by grinding of the metal regulus in metal mortar, the fraction of particles with 100 μm size was used. Specific surface area of the powder was of 0.04–0.06 m^2/g. Composition of the prepared alloys was determined by X-ray phase analysis.

Ammonium chloride (chemically pure grade) was dried in a vacuum at 150°C during 9 h. Ammonium dried with metal sodium was of 99.99% purity.

Interaction of the intermetallic compound powder with ammonia was studied in the presence of NH_4Cl (10 wt % with respect to the intermetallic compound) at initial ammonia pressure of 0.6–0.8 MPa.

Mixture of the powders (0.8–1.0 g) was ground in agate mortar at room temperature and then put into the high-pressure reactor. The reactor was evacuated during 0.5 h to ~1 Pa at room temperature, filled with ammonia, and incubated during 0.5 h. Then the reactor was heated up to predefined temperature, incubated during 3 h, cooled to room temperature, and heated up again. Pressure in the reactor did not exceed 1.5 MPa. After certain number of the heating–cooling cycles, the excess of ammonia was released to a buffer reservoir, the solid products were discharged under inert atmosphere and analyzed.

Ammonium chloride was removed by one of the two procedures: ~0.1 g of the sample was twice placed in 10 mL of anhydrous ethanol and mechanically stirred during 1 h at room temperature, or the mixture of products was evacuated to ~1 Pa at 300°C during 3 h.

Characterization of products. X-ray diffraction studies were performed with ADP-1 diffractometer (CuK_α radiation). Error of the interlayer distance determina-tion was below 0.0005 nm.

Specific surface area of the specimens was determined by low-temperature krypton adsorption after removal of the volatile products in a vacuum (1.3×10^{-3} Pa, 300°C, 15 h) and calculated following the Brenauer-Emmett-Teller method. Accuracy of the determined values was within 10%.

Hydrogen pressure was measured with manometers of the 0.4 accuracy class.

Composition of all prepared phases was determined by elemental analysis. Hydrogen and nitrogen content was determined with CHNS/O Vario MICRO cube Elementar GmbH analyzer (accuracy ±5%). Chlorine content was determined by turbidimetry (±1%).

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