Russian Journal of General Chemistry, Vol. 75, No. 6, 2005, pp. 831–834. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 6, 2005, pp. 881–885.

Reaction of the Intermetallic Compound $SmFe_{11}Ti$ with Gaseous Ammonia

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Received January 15, 2004

Abstract — The reaction of the intermetallic compound $SmFe_{11}Ti$ with ammonia at the initial NH_3 pressure of 0.6–0.8 MPa in the temperature range 150–450°C in the presence of 10 wt % NH_4Cl as activator was studied. Depending on the reaction temperature, $SmFe_{11}Ti$ undergoes both hydrogenation to form a hydride phase of the starting intermetallic compound and disproportionation to form a hydride phase of a new intermetallic compound. The reaction products are finely dispersed powders. The magnetic properties of the products were studied.

Intercalation of hydrogen or nitrogen atoms into the crystal lattice of $SmFe_{11}Ti$ appreciably affects the magnetic properties of the compound [1–3]. Formation of the hydride $SmFe_{11}TiH$ or nitride $SmFe_{11}TiN$ is not accompanied by structural changes of the matrix, but the unit cell volume increases by 1 [3] or 3% [2], respectively. Whereas hydrogen is intercalated into the $SmFe_{11}Ti$ matrix at room temperature or on slight heating, the nitriding occurs only at 400–500°C [2].

$SmFe_{11}Ti$ has a tetragonal structure of the $ThMn_{12}$ type with the parameters *a* 8.558(1), *c* 4.789(1) Å [3]. The unit cell parameters of the hydride phase $SmFe_{11}TiH$ are *a* 8.573(1), *c* 4.808(1) Å [3], and those of the nitride phase $SmFe_{11}TiN$, *a* 8.646, *c* 4.816 Å [4].

The saturation magnetization of the hydride and nitride derived from $SmFe_{11}Ti$ is, on the average, 5 and 10% higher, respectively, than that of $SmFe_{11}Ti$ proper [5].

This work continues a series of studies on preparation of high-melting metal and intermetallic compounds as finely dispersed or nanometer-size powders by the reaction with ammonia [6, 7]. Here we report on the transformations of $SmFe_{11}Ti$ in ammonia at various temperatures in the presence of ammonium chloride as reaction activator.

According to X-ray phase analysis, the annealed sample of $SmFe_{11}Ti$ is single-phase. The diffraction pattern of the powder of this substance contains only the reflections corresponding to the tetragonal structure of the $ThMn_{12}$ type with the unit cell parameters *a* 8.566, *c* 4.799 Å, well consistent with the published data [3].

The results of experiments on reaction of $SmFe_{11}Ti$ with ammonia in the presence of NH_4Cl are listed in the table. It is seen that heating of the reaction mixture at 150°C for 26 h (sample no. 1) yields a crystalline hydride–nitride phase of the composition $SmFe_{11}Ti \cdot H_xN_y$ in the finely dispersed state with the unit cell parameters *a* 8.587, *c* 4.822 Å. The specific surface area of the product is 19 $m^2 g^{-1}$, which considerably exceeds the specific surface area of the powder of the initial intermetallic compound (0.05 $m^2 g^{-1}$, particle size 100 μm) and corresponds to the powder particle size of about 50 nm. The dispersing effect is due to intercalation of the hydrogen and nitrogen atoms into the metallic matrix. The mean particle size is estimated assuming the spherical particle shape. After twofold washing of the reaction product with ethanol, the nitrogen content in the sample decreased from 5 to 2 wt %; that of hydrogen, from 1.3 to 0.4 wt %; and that of chlorine, from 5.0 to 0.2 wt %.

According to X-ray phase analysis, the reaction of $SmFe_{11}Ti$ with ammonia at 200°C for 26 h (sample no. 2) yields, along with the hydride–nitride phase based on the starting intermetallic compound, also α-Fe, a hydride phase based on a new intermetallic compound $SmFe_2$, and a second intermetallic compound $TiFe_2$ resistant to both hydrogen (even nascent) and nitrogen in the entire temperature range examined. The formation of the new phases is due to decomposition of $SmFe_{11}Ti$ under the influence of the combined intercalation of the nitrogen and hydrogen atoms; as a result, the specific surface area of the sample increases

1070-3632/05/7506-0831

Conditions and products of reaction of $SmFe_{11}Ti$ with ammonia

Sample no.	Reaction conditions			Reaction products		
	T, °C	τ, h	$p(NH_3)$, MPa	phase composition	unit cell parameters, Å	specific surface area, $m^2\ g^{-1}$
1	150	26	0.64	$SmFe_{11}TiH_xN_y$	*a* 8.587, *c* 4.822	19.0
2	200	26	0.68	$SmFe_{11}TiH_xN_y$ + α-Fe + $TiFe_2$ + + $SmFe_2H_x$ traces	*a* 8.582, *c* 4.821 *a* 2.869 *a* 4.784, *c* 7.791	24.7
3	250	24	0.76	α-Fe + + $TiFe_2$ + + $SmFe_2H_x$ + $SmFe_{11}TiH_xN_y$ traces	*a* 2.869 *a* 4.787, *c* 7.791 *a* 7.478	14.2
4	300	24	0.70	$SmFe_2H_x$ + + α-Fe + + α-Fe_4N + + iFe_2 + + SmH_x traces	*a* 7.478 *a* 2.872 *a* 3.792 *a* 4.783, *c* 7.797	12.7
5	350	24	0.68	α-Fe + + α-Fe_4N + + $TiFe_2$ + + $SmFe_2H_x$ traces + +SmH_x traces	*a* 2.866 *a* 3.800 *a* 4.787, *c* 7.797	9.3
6	400	24	0.68	α-Fe + + SmN + + α-Fe_4N + + $TiFe_2$ + + TiH_2	*a* 2.864 *a* 5.035 *a* 3.802 *a* 4.785, *c* 7.799 *a* 4.444	6.9
7	450	26	0.74	α-Fe + + SmN + + α-Fe_4N + + $TiFe_2$ + + TiH_2	*a* 2.867 *a* 5.031 *a* 3.801 *a* 4.783, *c* 7.796 *a* 4.448	1.3

to 24.7 $m^2\ g^{-1}$, which corresponds to the particle size of 40 nm. After washing with alcohol and water to remove chlorine compounds, the content of nitrogen in the sample decreased from 7.8 to 3.2 wt %; that of hydrogen, from 2.0 to 0.5 wt %; and that of chlorine, from 5.0 to 0.5 wt %.

As shown by X-ray phase analysis, the reaction of $SmFe_{11}Ti$ with ammonia at 250°C for 24 h (sample no. 2) results in a virtually complete disappearance of the hydride–nitride phase based on the initial intermetallic compound. The major reaction products are α-Fe (*a* 2.869 Å), $TiFe_2$ (*a* 4.787, *c* 7.791 Å), and *a* hydride phase based on $SmFe_2$ (*a* 7.478 Å). The resulting finely dispersed mixture of a uniform appearance has a developed surface: specific surface area 14.2 $m^2\ g^{-1}$. After washing with alcohol and water to remove chlorine compounds, the content of nitrogen in the sample decreased from 6.8 to 5.4 wt %; that of hydrogen, from 1.0 to 0.4 wt %; and that of chlorine, from 3.7 to 1.0 wt %.

An increase in the reaction temperature to 300–350°C (sample nos. 4, 5) is accompanied by decomposition of the hydride phase $SmFe_2H_x$ with the formation of Fe metal (*a* 2.872 Å) and trace amounts of samarium hydride. The reflections of the cubic phase of the iron nitride γ-Fe_4N (*a* 3.800 Å) also appear in the diffraction patterns of the reaction products. This phase is formed by the reaction of ammonia with iron released in the decomposition of the intermetallic compound. The $TiFe_2$ phase is present in all the reaction products. The specific surface area of the samples obtained at 300 and 350°C is 12.7 and 9.2 $m^2\ g^{-1}$, respectively.

The reaction at 400°C for 24 h (sample no. 6)

results in complete decomposition of the new hydride phase based on $SmFe_2$. The major reaction products at this temperature are α-Fe (*a* 2.864 Å), samarium and iron nitrides (SmN, *a* 5.035 Å; γ-Fe_4N, *a* 3.802 Å), and the nonreactive phase $TiFe_2$ (*a* 4.785, *c* 7.799 Å). The $TiFe_2$ phase starts to decompose at this temperature to α-Fe and titanium dihydride crystallizing in the cubic system with the unit cell parameter a 4.444 Å. The finely dispersed mixture has a fairly large specific surface area (6.9 $m^2 g^{-1}$).

The reaction at 450°C for 26 h (sample no. 7) gave similar products. The results of the X-ray diffraction analysis of the reaction products are listed in the table. It should be noted that the specific surface area of the products drastically decreases (to 1.3 $m^2 g^{-1}$).

Thus, the reaction of $SmFe_{11}Ti$ with NH_3 in the presence of NH_4Cl in the range 150–450°C involves the following transformations:

$$SmFe_{11}Ti + NH_3 \xrightarrow[NH_4Cl]{150°C} SmFe_{11}TiH_xN_y, \quad (1)$$

$$SmFe_{11}Ti + NH_3 \xrightarrow[NH_4Cl]{200–250°C} SmFe_{11}TiH_xN_y + SmFe_2H_x + TiFe_2 + \alpha\text{-Fe}, \quad (2)$$

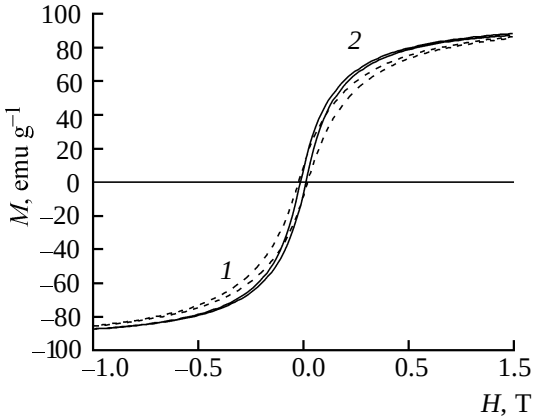
$$SmFe_{11}Ti + NH_3 \xrightarrow[NH_4Cl]{300–350°C} SmFe_2H_x + SmH_x + TiFe_2 + \alpha\text{-Fe} + \gamma\text{-}Fe_4N, \quad (3)$$

$$SmFe_{11}Ti + NH_3 \xrightarrow[NH_4Cl]{400–450°C} SmN + TiFe_2 + \alpha\text{-Fe} + \gamma\text{-}Fe_4N + TiH_2. \quad (4)$$

Schemes (1)–(4) clearly illustrate the stepwise transformation of the initial intermetallic compound $SmFe_{11}Ti$ into products of its complete decomposition ($TiFe_2$, SmN, γ-Fe_4N, α-Fe, TiH_2) with an increase in the temperature from ~20 to 450°C. A particular role of ammonia in the process is seen.

It should be noted that the specific surface area of the product formed in the reaction of $SmFe_{11}Ti$ with ammonia (nitriding) is larger than that of the hydrogenation product. Whereas the specific surface area of $SmFe_{11}TiH_1$ is 0.4 $m^2 g^{-1}$, that of the nitriding products formed at 150–200°C is as large as 19–25 $m^2 g^{-1}$, which corresponds to a particle size of 40–50 nm. This process is favored by accumulation of a certain amount of nitrogen in the lattice of the intermetallic compound.

For the two samples prepared at 150 and 200°C, which are the most interesting, we measured the magnetization curves. The figure shows the specific magnetization *M* (emu g^{-1}) of the products of the reaction of $SmFe_{11}Ti$ with ammonia at 150 (curve *1*) and 200°C (curve *2*) as a function of the external field *H* (T). With $SmFe_{11}Ti$, the saturation magnetization σ_s



Magnetization curves for the products of the reaction of $SmFe_{11}Ti$ with ammonia at (*1*) 150 and (*2*) 200°C.

(126 G $cm^3 g^{-1}$ [1]) is reached at very high external fields (the magnetic anisotropy field H_A is 102 kOe at 300 K [1]). The intercalation of hydrogen atoms increases both σ_s and H_A. As for the intercalation of the nitrogen atoms into the $SmFe_{11}Ti$ lattice, it increases σ_s to a still greater extent than does the intercalation of hydrogen but alters the anisotropy: whereas the initial compound had a easy magnetization axis, $SmFe_{11}TiN$ has an easy magnetization plane [1, 4]. The data shown in the figure give certain ideas of the magnetic properties of compounds $SmFe_{11}TiN_xH_y$ with unknown *x* and *y*. The lower σ (1 T) of the single-phase sample prepared at 150°C (86.4 G $cm^3 g^{-1}$), compared to σ_s, is caused by several factors: (1) $H_c \gg$ 1 T; (2) the contribution of the surface oxide film in the case of nanometer-size powders may be significant; and (3) the sample contains residual ammonium chloride.

The quantity H_c, which may be a nonlinear function of the particle size in the nanometer range [8], in the case of $SmFe_{11}M$ samples depends also on the maximal external magnetic field used in the experiment [2]. The measurmenets showed that treatment of $SmFe_{11}Ti$ with ammonia yielded a nanometer-size $SmFe_{11}TiN_xH_y$ powder with *H* (1 T) 212 Oe, which makes it more convenient for applications compared to the starting $SmFe_{11}Ti$ powder.

EXPERIMENTAL

The starting $SmFe_{11}Ti$ samples were prepared by fusion of Sm, Fe, and Ti (≥99.7% purity) in a vacuum induction oven under argon. The alloy was annealed in a vacuum oven at 950°C for 240 h.

Powders of the intermetallic compound were prepared by mechanical crushing of an alloy regulus,

followed by treatment in a vibration mill at room temperature in an inert atmosphere for 15 min and sieving with isolation of the required fraction. The specific surface area of the resulting powder was 0.05 $m^2 g^{-1}$.

The hydride $SmFe_{11}TiH_1$ was prepared by treatment of the powder of the intermetallic compound (200 μm) with high-purity hydrogen under a pressure of 2 MPa after degassing for 1 h at 200°C. The specific surface area of the resulting powder was 0.4 $m^2 g^{-1}$; unit cell parameters *a* 8.596, *c* 4.823 Å.

Ammonium chloride was dried in a vacuum at 150°C for 9 h. Ammonia (99.99% purity) was dried over sodium metal.

Experiments on nitriding of the intermetallic compound were performed at the initial ammonia pressure of 0.6–0.8 MPa; ammonium chloride (10 wt % relative to the amount of the intermetallic compound) was used as activator.

A mixture of $SmFe_{11}Ti$ and NH_4Cl powders was subjected to vibration milling at ~20°C for 30 min. The reaction of the resulting mixture with ammonia was performed in a 60-ml high-pressure laboratory installation. The required amount of the starting mixture (1.0–1.5 g) was placed in a stainless steel container and charged to the pressure vessel; the vessel was evacuated to a residual pressure of ~1 Pa for 30 min at ~20°C, after which NH_3 was pumped in to a pressure of 0.6–0.8 MPa, and the vessel was allowed to stand for 30 min at ~20°C. Then the vessel was kept at various preset temperatures for 3 h, cooled to ~20°C, and heated again. Since, in so doing, the pressure in the vessel increased owing to the release of hydrogen and nitrogen, the reaction was considered to be complete when the pressure ceased to change. After performing the required number of heating–cooling cycles, the ammonia was transferred into a buffer tank, and the products were unloaded in an inert atmosphere and analyzed.

To wash the reaction products to remove NH_4Cl and other possible chlorine-containing impurities, we developed the following procedure. A ~0.5-g sample was stirred with 10 ml of absolute ethanol for 3 h. The washing, as a rule, was repeated. If the chlorine content in the sample, determined by chemical analysis, remained at a level of 1–2 wt %, the sample was additionally washed with distilled water. In some cases, the mixture was boiled. Traces of water were removed from the sample by treatment with absolute diethyl ether for 10 min with stirring. The products were analyzed for the content of H, N, and Cl.

X-ray diffraction studies were performed on an automatic complex consisting of an ADP-1 diffractometer (CuK_α or CrK_a radiation) and a controlling computer. The interplanar spacings were determined to within 0.005 Å.

The specific surface area of the samples was determined from the low-temperature adsorption of krypton after removal of volatiles from the solid phase (1.3×10^{-3} Pa, 300°C, 15 h) and was calculated by the BET method [9]. The determination accuracy was ±10%.

The hydrogen content in the reaction products was determined by the standard procedure (combustion in an oxygen flow); the nitrogen content, by the Kjeldahl method; and the chlorine content, turbidimetrically.

The magnetization curves were recorded with a PARC M-4500 vibration magnetometer.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 01-03-33241).

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