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BRIEF COMMUNICATIONS

Synthesis of Intermetallic Compounds $LaNi_5$ and $NdNi_5$ from Mixed Basic Carbonates of Lanthanum or Neodymium and Nickel

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Abstract—The possibility of obtaining powdered $LaNi_5$ and $NdNi_5$ intermetallic compounds by reaction of mixed basic carbonates $La_2Ni_{10}(CO_3)_8(OH)_{10} \cdot 54H_2O$ and $Nd_2Ni_{10}(CO_3)_8(OH)_{10} \cdot 14H_2O$ with calcium hydride in a hydrogen flow at 1073 K and 10^5 Pa was studied.

Powdered intermetallic compounds of rare-earth and 3*d*-transition metals are used as hydrogen-sorbing materials [1] and materials for fabrication of magnets with high magnetic characteristics [2]. The production of such materials includes the stage of alloying of appropriate metals in electric-arc or vacuum induction furnaces with the subsequent grinding of the alloys under the action of hydrogen [1, 3, 4] or under exernal mechanic action in various ball-type activating mills [5, 6].

Presently, attention is attracted in laboratory and industrial practice to reduction-diffusion methods for obtaining intermetallic compounds containing rare-earth and 3*d*-transition elements. These techniques include reduction of mixtures of metal oxides, hyroxides, chlorides, carbonates with various reducing agents in hydrogen or an inert medium [2, 7, 8]. The advantage of this method is that it yields powdered intermetallic compounds with narrow fraction distribution and controlled chemical composition without stages of alloying and mechanic grinding of the alloys.

This communication describes synthesis of basic carbonates $La_2Ni_{10}(CO_3)_8(OH)_{10} \cdot (H_2O)_x$ and $Nd_2Ni_{10}(CO_3)_8(OH)_{10} \cdot (H_2O)_y$ and their reduction with calcium hydride in hydrogen with the aim of obtaining the intermetallic compounds $LaNi_5$ and $NdNi_5$.

To prepare mixed basic carbonates of lanthanum(III) [or neodymium(III)] and nickel(II), we dissolved starting $Ni(OH)_2$ in a solution of $LnCl_3 + 10HCl$ (Ln–La, Nd) in the ratio Ln : Ni = 1 : 5 under heating without boiling. Then we filtered the solution, added a solution of Na_2CO_3 to the filtrate in the ratio $Ln^{3+} : CO_3^{2-} = 1 : 4$, and added, in the course of 0.5 h under conditions of vigorous stirring, a 1.2 N solution of NaOH in the amount corresponding to the ratio $Ln^{3+} : OH^- = 1 : 5$. The suspension was allowed to settle for 15–20 h, then filtered, and the precipitate was dried in air at room temperature for 20–30 h. The powders obtained were X-ray-amorphous. According to IR spectral and chemical analysis data, their empirical composition corresponded to the formulas: $La_2Ni_{10}(CO_3)_8(OH)_{10} \cdot (H_2O)_x$ ($x \approx 54$) and $Nd_2Ni_{10}(CO_3)_8(OH)_{10} \cdot (H_2O)_y$ ($y \approx 14$).

To elucidate the role of molecular hydrogen and calcium hydride in reduction of mixed basic carbonates of La(III) [or Nd(III)] and Ni(II) with the above-mentioned composition, we carried out the reaction in two stages. In the first stage, we placed a molybdenum container with a weighed portion of a mixed basic carbonate in a quartz reactor 20 mm in diameter and 600 mm in length, the reactor was purged with argon, the temperature in the hot zone of the reactor was raised to 1023 K for La(III) and Ni(II) basic carbonate and to 873 K for Nd(III) and Ni(II) basic carbonate, and the reactor was kept at these temperatures with flowing hydrogen for 2.5–3 h. The completion of the reaction was judged from termination of water drop formation in the cold part of the reactor. Thereafter the heating was switched off and the reaction mixture was cooled to room temperature in flowing hydrogen, then the reactor was purged with argon for 0.25 h, and the reaction products were discharged in an inert atmosphere. According to the results of X-ray phase analysis, the powders obtained were mix-

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tures of nickel with lattice constant $a_0 = 0.3521$ nm and hexagonal modifications of La_2O_3 with $a_0 = 0.4000$, $c_0 = 0.6340$ or Nd_2O_3 with $a_0 = 0.3963$, $c_0 = 0.6301$ nm, which is in good agreement with published data and points to the absence of reaction between these compounds in the solid phase.

In the second stage, powders of Ni and La_2O_3 or Ni and Nd_2O_3 were mixed with CaH_2, placed in the same reactor, and kept in flowing hydrogen for 2.5–3 h at 1273 K. After cooling the reaction mass first in flowing hydrogen and then in argon, the reactor was discharged. In the case of lanthanum, the powder was washed first with distilled water cooled to 273 K, and then with ethanol and diethyl ether. The resulting dried powder was composed of the intermetallic compound $LaNi_5$. According to the results of chemical analysis:

Found (wt %): La 31.95, Ni 68.00.
$LaNi_5$.
Calculated (wt %): La 32.12, Ni 67.88.

An X-ray phase analysis of the powder indicated that only a single phase is present, which corresponds to the intermetallic compound $LaNi_5$ crystallizing to give hexagonal crystals with lattice constants $a_0 = 0.5010$ and $c_0 = 0.3970$ nm.

According to the results of reaction gas chromatography, the content of oxygen in the sample obtained was 0.2 wt %; a chemical analysis demonstrated that the content of calcium and chlorine did not exceed 0.1 wt %.

Since neodymium salts are more susceptible to hydrolysis than lanthanum salts, the desired compound was isolated from the reaction mixture using magnetic separation [9]. According to the results of chemical analysis:

Found (wt %): Nd 32.87, Ni 66.96.
$NdNi_5$.
Calculated (wt %): Nd 32.95, Ni 67.05.

As indicated by reaction gas chromatography, the content of oxygen in the sample obtained was about 0.2 wt %. The compound $NdNi_5$ crystallizes to give hexagonal crystals with lattice constants $a_0 = 0.4963$ and $c_0 = 0.3974$ nm, which is in reasonable agreement with published data for the reference intermetallic compound $NdNi_5$ obtained in an electric arc furnace ($a_0 = 0.4926$ and $c_0 = 0.3957$ nm) [10].

The size of powder particles, calculated in the approximation of their spherical shape, is about 220 nm for $LaNi_5$ and 400 nm for $NdNi_5$.

The powders of intermetallic compounds, obtained by the above procedure absorb about 6 mol of hydrogen per 1 mol of intermetallic compound in the reaction with hydrogen. The enthalpies of hydrogenation of the samples under study in the region of the $\beta \rightarrow \alpha$ transition, calculated from the experimental dependence of $\log(P[H_2])$ on inverse temperature, are (kJ mol^{-1} H_2): $\Delta H = -33.0$ for $LaNi_5$ ($\Delta H = -32.9$ for a molten alloy) and $\Delta H = -30$ for $NdNi_5$ ($\Delta H = 30.1$ for a molten alloy).

Thus, the reactions of mixed basic carbonates of composition $La_2Ni_{10}(CO_3)_8(OH)_{10} \cdot 54H_2O$ and $Nd_2Ni_{10}(CO_3)_8(OH)_{10} \cdot 14H_2O$ with calcium hydride in flowing hydrogen yield $LaNi_5$ and $NdNi_5$ powders without stages of alloying of the corresponding metals or their mechanic grinding.

EXPERIMENTAL

In this study, we used commercial pure-grade $Ni(OH)_2 \cdot 0.25H_2O$, basic nickel carbonate containing 47.6% nickel(II), chemically pure-grade Na_2CO_3, NaOH, hydrochloric acid, metallic lanthanum of 99.9% purity, 99.85% pure neodymium, 99.99% pure nickel, and calcium hydride of purity 99.9% with respect to H_2. Hydrogen-sorption characteristics of $LaNi_5$ and $NdNi_5$ powders were studied on a high-pressure installation by plotting isotherms of hydrogen pressure against the composition of the hydride phase at various temperatures [11].

We used a metal-hydride battery [12] as a source of high-purity hydrogen. The composition of the hydride phases formed in the reactions of intermetallic compounds with hydrogen, calculated from pressure changes in a calibrated system, was refined by a standard procedure of sample combustion in flowing oxygen. The thermodynamic characteristics of hydride formation were determined from the dependence of the equilibrium pressure of H_2 in the regions of the $\beta \rightarrow \alpha$ transition on inverse temperature.

We prepared the reference intermetallic compounds $LaNi_5$ and $NdNi_5$ by alloying calculated amounts of La or Nd with Ni in an electric arc furnace with a permanent tungsten electrode in the atmosphere of high-purity argon. The alloy samples were subjected to threefold remelting and then to homogenizing annealing at 950–1000 K for 500 h with the subsequent quenching in water at 273 K. The X-ray studies were carried out using the powder technique on an ADP-1 diffractometer (Cu_{K_α} radiation) equipped with a microcomputer controller. The error in determining the lattice constants did not exceed 0.0004 nm. The elemental chemical analysis of mixed basic carbonates of La(III) or Nd(III) with Ni(II) and analysis of the final products of their reactions with CaH_2 and H_2 were carried out by the standard procedures.

All the operations involving loading and discharging of reactors, including sampling for analysis, were carried out in the atmosphere of argon.

CONCLUSION

Powders of the intermetallic compounds $LaNi_5$ and $NdNi_5$ were obtained without stages of high-temperature alloying and mechanic grinding of alloys. The compounds crystallize to give hexagonal crystals with lattice constants a_0 = 0.5010, c_0 = 0.3970 and a_0 = 0.4963, c_0 = 0.3974 nm, respectively.

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