Research into processes of production of hydrides of materials containing rare-earth metals and their corrosion

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Abstract. Production of permanent magnets on basis of rare earth elements (REE) is implemented by means of powder metallurgy, therefore a technologically important operation is the multistage mechanical crushing of materials to the extent of domains. The promising technique of crushing of magnetic materials is their consistent hydrogenation-dehydrogenation that allows obtaining nano-dispersed powders which are stable enough in air. Hydrogenation apparatuses, as opposed to conventional grinding machines, do not comprise motion works and their producing capacity is much higher. Hydrogenation process does not require any additional preparation of materials and it excludes undermilling and overmilling as well as material oxidation. The paper presents the results of investigation on the temperature effect on the hydrogenation process of Nd-Fe alloys. The study results on the corrosion stability of ligature hydrides under various conditions are also given. Kinetic parameters of the hydrogenation process of ligatures are determined. The phase composition of corrosion products is detected. Guidelines on hydride powder storage are given.

1. Introduction
One of the methods of improving the quality of Nd-Fe-B alloys, used for the production of rare earth permanent magnets, is the solid-phase alloying technique based on the combined grinding of magnetic alloys with alloying additions. At the same time, there is the optimal allocation of constituents by volume and the particles surface activation which improves the growth of the master magnetic phase of Nd$_2$Fe$_{14}$B, with the subsequent compression and agglomeration of powders taking place.

The base material, used for the correction of the composition of magnetic alloys, is the Nd-Fe ligature. However, this material has an essential fault, i.e. high strength. It results in impossibility of its usage for the combined grinding with the fragile Nd-Fe-B alloy [1].

Separate ligature grinding with subsequent adding into the composition of magnetic alloys is technologically difficult, as the powders are pyrophoric and easy-to- oxidize in air. To solve the problems described, we suggest using the hydrogen destruction method which is used for the grinding of magnetic alloys [2].

The process of the hydride grinding of Nd-Fe-B alloys is carried out by means of crushing a magnetic alloy ingot into pieces of 10-20 mm and their processing with hydrogen. This process is known as the hydrogen decrepitation (HD) [3]. It results in the hydrogenation of intergranular high-neodymium phase and its destruction. The hydrogenation being done, the material is easily destructed into the powder having domains of 1-3 micrometers. During the process the oxidation of the...
hydrogenated product does not occur, the grinding taking place generally along the grain boundaries of the Nd$_2$Fe$_{14}$B magnetic phase.

The paper presents the results of investigation of both the temperature effect on the hydrogenation process of Nd-Fe alloy and the corrosion stability of hydrogenation products of magnetic materials containing a rare-earth component (40 – 80 % wt) under various conditions.

2. Research into the temperature effect on the Nd-Fe alloy hydrogenation process

2.1. The scheme of the experimental device

The subject of inquiry was the Nd-Fe alloy produced by means of out-of-furnace calcium-thermal reduction of neodymium and iron fluorides.

The research into the hydrogenation process was conducted with the help of the apparatus presented in Fig. 1.

![Diagram of experimental apparatus](image)

1, 2 – hydrogen and helium cylinders; 3 – column with dehumidifier; 4 - container with lanthanum nickelid (hydrogen accumulator); 5, 7 - shaft furnaces; 6 - hydrogenation reactor; 8 - thermocouple vacuum gauge; 9 – fore pump BH-1; 10 - diffusion pump; 11 - hydrogen afterburner; T1, T3 - furnace temperature sensors; T2 - sample temperature sensor; P1, P2 - pressure-and-vacuum gages; P3 – pressure gauge “Sapfir”; P4 – manometer; B1 – B15 valves

Figure 1. The scheme of the experimental apparatus.

The apparatus consists of a vacuum post which provides the system degassing to the residual pressure of 10 Pa, a hydrogenation reactor and a reactor with a hydrogen accumulator (lanthanum nickelid). The usage of lanthanum nickelid allowed purifying technical hydrogen from traces of water and other impurities.

The rate of the hydrogenation process was controlled via pressure changes in the reactor with the help of an automatic manometer “Sapfir” accurate within (±1)%, and the general pressure in the supply pipeline was controlled by means of precision pointer-type combined pressure-and-vacuum gages.

2.2. Procedure of the experiment

Hydrogen treatment. The system was vacuumized to the residual pressure of 10 Pa with the help of a fore pump. Hydrogen from the cylinder ran through the column with silica gel and filled the container with lanthanum nickelid. After that hydrogen pressure was increased up to 1 MPa. Supervision was being carried out to monitor hydrogen absorption by lanthanum nickelid. Pressure decrease having been stopped, the container with lanthanum nickelid was ready for operation.

Alloy treatment. Alloy ingots were chipped with the help of a hydraulic press. Then they were ground into pieces of 5-10 mm by means of a jaw breaker.

Experiments. The required quantity of the alloy was taken and put into the pan, made of stainless steel. Then it was weighed on the high-accuracy weighing machine. In a number of cases,
metallographic samples of the alloy were used for the subsequent metallographic study. The pan was put into the reactor. Then the reactor was vacuumized to the residual pressure of 100-1000 Pa. In a number of experiments higher vacuum was used, but it had almost no impact on the results of the experiments.

Further, the retort was filled with pretreated hydrogen and the recording of pressure changes was started. The effect of the process temperature on the hydrogenation rate was studied.

Based on the results of the conducted experiments there have been designed the diagrams of dependence of the hydrogenation degree on the duration at various temperatures of the process. Then mathematical treatment of the diagrams was done.

To investigate structural changes, taking place in the material, the X-ray phase analysis was used (Dron 4.0 with a copper cathode).

The specific area of samples was estimated with the help of BET technology using thermal argon desorption as consistent with the internal standard. Before the beginning of measuring operations all samples were heated in Ar and He current at the temperature of 120 °C for 30 minutes.

2.3. Consideration of results

Based on the experimental data there have been designed the diagrams of dependence of the hydrogenation degree changes on temperature for samples having different masses. The diagrams are presented in Figure 2.

The charge is: 1 – 3-5 g; 2 – 150-200 g

**Figure 2.** Dependence of the alloy hydrogenation degree on temperature.

*Dependence of the alloy hydrogenation degree on the duration of the process at different temperatures.* The diagrams presented in fig. 2 show that temperature has a material effect on the duration of the induction period and does not on the rate of the process in whole. It is particularly detected when the hydrogenation of small alloy charges (3-5 g) is taking place (fig. 2.1).

The maximum induction period (longer than 6 min) is observed at the temperature of 50 °C. The charge being enlarged to 200 g (fig. 2.2), the induction period almost disappears.

From our point of view, such influence of temperature on the duration of the induction period is conditioned by the rate of hydrogen intrusion deep into the material along the grain boundaries.

At cold temperatures the rate of hydrogen intrusion into the material is low; therefore, the reaction surface is negligible. The hydrogenation rate races up only after forming the sufficient number of transporting fractures which provide unimpeded hydrogen penetration to the reaction surface. Metallographic examinations confirm that.

Calculations, carried out with the help of formal kinetic equation for heterogeneous reactions of the type “solid + gas = solid”, show that in the range of 25-250°C the temperature does not have any
material effect on the hydrogenation rate and the process is controlled by the hydrogen diffusion to the reaction surface.

The apparent activation energy of the process is \((7.0\pm0.5)\) kJ/mol.

The formal equation of contractive sphere \(1-(1-\alpha)^{1/3} = k\tau\) describes the experimental data of the Nd-Fe alloy hydrogenation process particularly precise (correlation coefficient is 0.8-0.9).

3. Research into the corrosion stability of hydrides under different atmospheric humidity

The subjects of inquiry were nano-disperse hydrides of Nd-Fe alloys, having different compositions, as well as hydrides of Dy-Fe alloys obtained in work [1], which were used in the solid-phase alloyage process in the sequel.

The research technique was the following: the polydisperse hydrogenation product, having the weight up to 60 g, was transferred to the boat with the size \(50\times30\times20\) mm and put into the temperature-controlled exiccator filled with water. Over all the time of the experiment the temperature in the exiccator was maintained in the range of \((20\pm1)\) °C. In this case the absolute humidity was 100%, the water vapor pressure was constant and equaled 3.2 kPa.

Periodically (once a day) the exiccator was opened, the changes which took place on the product surface during this time were registered, the boat was pulled out of the exiccator and weighed, the sample of the material was taken to carry out the X-ray phase analysis.

The conducted experiments showed the following: being put under such extreme conditions, the hydrogenation products have sufficiently high hygroscopicity. For three days the weight of the sample has increased by more than 10% (fig. 3, curve 1); then it almost stopped changing.

![Figure 3](image)

1 - damp atmosphere, 2 – flow air atmosphere

**Figure 3.** Dependence of changes of the sample weight on the duration of the corrosion process of Nd-Fe hydrides.

The diffraction pattern presented in figure 4 shows that a virtually complete surface amorphization of the sample takes place in twenty-four hours. In two days sufficiently well-defined Nd(OH)\(_3\) phase reflexes appear in the diffraction pattern.

In the course of further damp atmosphere storage the materials do not undergo changes in the phase composition. It should be mentioned, that owing to high amorphization of these hydride powders, X-ray phase analysis does not allow complete identification of the forming crystalline phases. To consider the details of this process a complex physicochemical analysis is required.

**Figure 5.** Presents the results of the derivatographic analysis of the alloy hydride.

**Figure 5** shows that adsorbed water extraction takes place at initial time. The temperature being raised up to 120 °C, the dehydrogenation process starts. The dehydrogenation process has several stages and it ends at temperatures of 350-400 °C. It means that the NdH\(_3\) dehydrogenation process proceeds according to the following probable scheme:

\[
\text{NdH}_3 \rightarrow \text{NdH}_2 \rightarrow \text{NdH}_{2-x} \rightarrow \text{Nd}.
\]
Figure 4. Phase composition of corrosion products of Nd-Fe hydrides (according to the X-ray fluorescence analysis).

Figure 5. Derivatogram of decomposition of the hydrogenation product of the high-neodymium alloy Nd-Fe.

The investigated sample being put in inert atmosphere, oxidation of the dehydrogenated product did not take place.

In the course of the research the physical properties of the sample have also undergone changes. Thus, the hydride which initially looked like black plates having different shapes turned into a grey powder (fig. 6) having high specific surface (about 15 m²/g).

The neodymium hydroxide production process is accompanied by increase in molar volume. Owing to this the volume of the charge increased visually one and a half or twice as much.
To investigate hydride storability and to detect optimal hydride storage conditions there have been conducted tests in flow air atmosphere, isolated air atmosphere, inert atmosphere and hydrogen atmosphere. The results of investigations on neodymium hydride in flow air atmosphere are presented in figure 3 (curve 2).

The diagram (2) presented in figure 3 shows that corrosion takes place in flow air atmosphere at room temperature and humidity fluctuations from 70% to 85% during the two-day initial period. In the sequel the corrosion rate goes down sharply, practically to zero. The mass increase of samples is 1.0-1.5% wt. In isolated air atmosphere (a covered plastic container) and inert helium and hydrogen atmospheres the corrosion process was not observed.

![Image showing a - source alloy; b - after hydrogenation; c - after damp atmosphere storage](attachment:image.png)

**Figure 6.** Exterior view of the products of hydrogenation and corrosion of Nd-Fe alloy.

4. Conclusions
The temperature effect on the alloy hydrogenation process has been studied. It has been determined that this process is limited by hydrogen diffusion to the reaction surface, apparent activation energy of the process in the temperature range 25-300 °C is $(7.0\pm0.5) \text{kJ/mol}$.

The research into corrosion stability of powders of Nd-Fe and Dy-Fe hydrides under different conditions shows the following:
- being in dry atmosphere of air, helium and hydrogen the materials are totally stable;
- with the atmosphere humidity being approximate to 100%, the metal hydrides undergo complete amorphization in 24 hours and turn into hydroxides in 48 hours.

Thus, storage and usage of powders of nano-disperse alloys of rare earth metals should be done in dry air or inert atmosphere.

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