Production of Nd-Fe-B magnets by the hydride technique

Y N Makaseev, A S Buinovskiy, E Y Kartashov, V I Sachkov, V L Sofronov
National Research Nuclear University «MEPhI», 115409, Russia, Moscow, Kashirskoe sh. 31
VLSofronov@mephi.ru

Annotation. Rare-earth permanent Nd-Fe-B magnets are the most promising ones because they have the highest magnetic and operating characteristics. These magnets are produced from alloys having the respective chemical composition principally by the powder metallurgy technology. The paper presents the results of study of the manufacturing process of high-quality permanent magnets by the method of solid-phase alloying of magnetic alloys obtained by means of the out-of-furnace fluoride technique. In the present work, metallic foundry alloys and alloy hydrides of Nd-Fe, Dy-Fe and Tb-Fe systems are considered as alloying additions.

1. Introduction

One of the ways to improve the quality of magnetic materials is the technique of solid-phase alloying (SPA) of magnetic materials. This technique is based on intergrinding of base Nd-Fe-B magnetic alloys and alloying additions. SPA makes it possible to correct both the chemical composition and the structure of base magnetic alloys.

Rare-earth foundry alloys are considered to be one of the most promising materials for alloying additions. However, these materials have serious disadvantages – high strength and ductility, making it practically impossible for them to be used during mechanical intergrinding with the brittle Nd-Fe-B alloy.

The promising method of grinding such materials is the hydrogenation-dehydrogenation technique [1, 2].

After hydrogenation the material is easily destructed. The main advantages of this method, which define its wide application for magnetic materials production, are high efficiency and simplicity of the process, the possibility of obtaining powder materials of stable quality, ease of grinding and short reaction time.

The paper considers the process of solid-phase alloying (SPA) of Nd-Fe-B magnetic alloys by metallic foundry alloys and alloy hydrides having the following composition: 75%Nd-Fe, 42Dy-Fe and 70Tb-Fe. Alloy hydrides were produced by hydrogenation of corresponding foundry alloys by means of gaseous hydrogen, using the technique mentioned in [3].

Alloys and foundry alloys, used for the research, were obtained by the technique of out-of-furnace calcium-thermic reduction smelting of metal fluorides [4].

The schematic diagram of production of Nd-Fe-B permanent magnets by the solid-phase alloying technique is presented in Fig. 1. We consider these stages in detail.

2. Reduction

To obtain alloys and foundry alloys we used the calcium-thermic technique. This technique has no expensive stages of production and refinement of rare-earth metals (REM). REM fluorides, transition
metal (Fe, Co, etc.) fluorides and alloying elements were reduced. It is an out-of-furnace process, i.e. the quantity of heat, released during the reduction reaction of REM compounds and transition metals, is enough to transform all reaction products into the molten state and to form compact metal ingots. Due to the high exothermicity of the reduction process of transition metal fluorides, it is possible to introduce a part of elements into the charge mixture in the form of metal powder, and boron - in the form of ferroboron. REM fluorides, used for this method, were obtained either by precipitation from solutions by means of the hydrofluoric acid and subsequent precipitate dehumidification and baking, or, like transition metal fluorides, by metal oxide processing with gaseous fluorine.

![Diagram](image-url)

**Figure 1.** The schematic diagram of Nd-Fe-B magnets production using solid-phase alloying.

### 3. Grinding of Nd-Fe-B alloys

Ingots grinding was performed in two steps: crushing and milling. Preliminary crushing to pieces ranging in size from 20.0 to 30.0 mm was done by the press; small fraction fines were periodically separated; crushing to pieces ranging in size from 1.0 to 2.0 mm was continued in jaw crushers. To prevent powder oxidation, milling was performed by a vibrating mill UB in a liquid medium or inert atmosphere at the ratio Solid : Liquid = 1:1.7 (by weight). Ethyl and isopropyl alcohols served as inert liquid. Used inert liquids were rectified for reutilization.
The duration of grinding was chosen experimentally for each type of material being ground and the mill, so as not less than 90.0% of weight of ground powder had particle size ranging from 2.0 to 5.0 micrometers.

4. Centrifugation and drying
The pulp from the vibrating mill was separated by a centrifuge. The liquid phase (alcohol) was sent to regeneration, wet powder was sent to vacuum drying and pressing.

5. Compaction in the magnetic field
The pressing operation was applied in the transverse magnetic field of 900 kA/m (11.2 kOe). The direction of the pressing force was orthogonally related with the direction of the texturing magnetic field.

Moulding blanks was performed on presses equipped with electromagnets. After the die, made of diamagnetic alloy, had been filled with alloy powder, it was put between the poles of the electromagnet. Imposition of vibration on the die during powder texturing in the constant magnetic field or substitution of the constant magnetic field by the pulsed magnetic field promoted more qualitative alignment of particles in the pressed powder and improved magnetic properties of future magnets.

6. Sintering blanks
This operation is necessary for the final texture consolidation, increase in density and mechanical strength of magnet blanks. To obtain sufficient density and strength of the sintered product, the following main parameters are of great importance: temperature and duration of sintering, gaseous medium, size of powder being moulded and degree of compaction during pressing and sintering.

Pressed blanks were packaged in boats, made of alloyed steel 12X18H10T, for loading into vacuum furnaces with tungsten heaters. They were sintered at temperature of 1060-1200 °C under residual pressure of about 0.1 Pa during 90-120 minutes.

7. Mechanical treatment
To obtain products of desired sizes, sintered and thermal treated (or annealed as appropriate) magnet blanks were cut by vulcanite wheels. Then they were ground by surface-grinding and circular grinding machines with corundum wheels having bakelite bond, with lubrication-cooling fluids being used. The cutting process was conducted very carefully to minimize overheating, oxidation and edge chipping.

8. Magnetizing and control
After the manufacturing was completed, the blanks required pulsed magnetization in the homogeneous magnetic field with intensity of 20-30 kOe. Finished magnets were 100% tested, with induction and magnetic linkage being measured.

Before hydrogenation, foundry alloys were treated the same way as alloys. Hydrogenation was performed by gaseous hydrogen under residual pressure of 100-1000 Pa at temperature of 50-100 °C. To obtain the desired structure of magnetic materials, foundry alloy hydride powder was sent to the stage of alloy grinding; then the mixture obtained was moulded and sintered at temperature of 1060-1200 °C. At this temperature, complete dehydrogenation takes place and hydrogen is eliminated from enclosed volume. Nd, Dy and Tb, obtained by dehydrogenation, complement the actual composition and they are involved in the recombination of Pr3Fe14B phase. It results in producing blanks of permanent magnets which have desired composition and structure.

9. Solid-phase alloying (SPA) of base magnetic alloys by metallic foundry alloys
The experiments were conducted using the technique described above. The only difference was the following: base magnetic alloys and foundry alloys, obtained by calcium-thermic reduction smelting, were subjected to two-step mechanical trituration. Then these powders were mixed for SPA; their
intergrinding continued during 30-40 minutes. It has been found experimentally that optimum amount of alloy additives for SPA is (5.0±1.0)%. Hysteresis characteristics for the second quarter (demagnetization curves) are presented in Fig. 2.

![Graph showing hysteresis characteristics](image)

Figure 2. Demagnetization curves of magnets obtained by SPA with metallic foundry alloys.

Magnet “0” was made of the base magnetic alloy 32Nd-Fe-1.1B; magnets “1-4” were made by the solid-phase alloying with foundry alloys 75%Nd-Fe, 42Dy-Fe, 40Tb-Fe and 70Tb-Fe, respectively.

The diagrams presented in Fig. 2 show that addition of metallic foundry alloy during the stage of fine grinding considerably increases the coercive force of magnets from 1.5 to 3 times. The value of residual magnetic induction either remains at the same level, or decreases insignificantly.

Most likely, it occurs owing to partial oxidation of the chemically active foundry alloy, its undermilling, causing it to fulfill a role of interphase ballast, rather than alloying material for the magnetic phase.

10. Solid-phase alloying (SPA) of base magnetic alloys by hydrides of foundry alloys

The research of the effect of solid-phase alloying on properties of magnets began with calibration of the crushing machine. Figure 3 presents the dependence of residual magnetic induction ($B_r$) and the magnet coercive force ($H_{cu}$) on the duration of intergrinding of the alloy and the alloying addition in the form of 75Nd-Fe and in the amount of 5% by weight.
Figure 3. Dependence of coercive force and residual magnetic induction on duration of grinding.

The diagrams presented in figure 3 show that the optimal duration of intergrinding of the base magnetic alloy and the alloying addition in the form of hydrides by a vibrating mill UB is 10 minutes.

Hysteresis characteristics of the magnets, obtained by solid-phase alloying of base alloys by means of hydrides of foundry alloys with the composition 75%Nd-Fe, 42Dy-Fe, 40Tb-Fe and 70Tb-Fe for the second quarter (demagnetization curves) are presented in Fig. 4.

Figure 4. Demagnetization curves of magnets obtained by SPA by mean of hydrides of foundry alloys.
The diagrams presented in Fig. 4 show that during solid-phase alloying by hydride powders, one can observe a considerable increase in both the coercive force of magnets (up to 3-5 times) and their residual induction (about 5–15%). Dy and Tb are the most efficient materials which allow increasing the coercive force of Nd-Fe-B permanent magnets.

Thus, in the course of the experimental research of production of magnets using solid-phase alloying of base magnetic Nd-Fe-B alloys by powders of REM-containing addition alloys obtained with the help of mechanical and hydride comminution, it has been ascertained:

- the process of solid-phase alloying by hydride powders is a quite effective technique of improving properties of Nd-Fe-B magnets;
- the use of mechanically comminuted metallic powders of foundry alloys for solid-phase alloying mainly results in increase of the coercive force of alloyed magnets; at the same time, the residual magnetic induction either remains the same or decreases insignificantly.

It is important that the process of work with powders of foundry alloys hydrides is simpler than that with metallic powders of foundry alloys, because the latter are highly active, pyrophoric and must be stored and used in the inert atmosphere only. Hydride powders do not have these disadvantages, and they can be stored in dry hermetically sealed containers.

11. Conclusion
There has been studied the production process of Nd-Fe-B magnets using solid-phase alloying by REM-containing foundry alloys in the form of metallic powders and their hydrides. The process of solid-phase alloying by hydride powders is the most effective technique of improving properties of Nd-Fe-B magnets.

Acknowledgments
This work was supported by the Federal Target Program “Research and development on priority directions of scientific-technological complex of Russia for 2014-2020” (RFMEFI57814X0002).

References
[1] Dolukhanyan S K, Aleksanyan A G, Shekhtman V Sh 2010 Synthesis of Transition Metal Hydrides and a New Process for Production of Refractory Metal Alloys An Autoreview International J. of Self-Propagating High-Temperature Synthesis 19 2 85–93
[2] Shatalov V V, Melnickov S A, Nickonov V I, Parshin A P 2007 Design of a safe technique of hydrogen processing of different functional materials Mining information analysis newsletter 12 232-244
[3] Buinovskiy A, Sofronov V, Kartashov E, Kalaev M 2016 Hydrogenation of Nd-Fe Alloys under Conditions of Different Pressure and Hydrogen Concentration Key Engineering Materials 683 44-52
[4] Bujnovskij A S, Sachkov V I, Sofronov V L, Anufrieva A V 2015 Basic stages of magnet production by fluoride technology Advanced Materials Research 1085 209-213