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## HIGH-COERCIVITY Nd-Fe-B POWDERS OBTAINED BY HIGH-TEMPERATURE MILLING

### WYSOKOKOERCYJNE PROSZKI Nd-Fe-B OTRZYMYWANE PRZEZ MIELENIE W WYSOKIEJ TEMPERATURZE

The possibility of employing high temperature milling (600°C) for the production of highly coercive Nd-Fe-B powders was examined. The materials were the Nd<sub>12</sub>Fe<sub>82</sub>B<sub>6</sub> alloy which was subjected to mechanical milling and the powders of the constituent elements of this alloy which were processed by mechanical alloying. The processes were conducted in the two variants: the first variant consisted of mechanical milling performed at a high temperature which was maintained during the entire process, and the other variant included preliminary milling carried out at room temperature and then the milling temperature was increased. All the processes gave nanocrystalline powders with hard magnetic properties. The powders produced by mechanical milling had better properties than those produced by mechanical alloying as they were more homogeneous and contained smaller amounts of the  $\alpha$ -Fe phase.

*Keywords:* Hard magnetic materials, Nd-Fe-B, mechanical alloying, mechanical milling

W pracy badano możliwości zastosowania procesu mielenia w wysokiej temperaturze (600°C) do otrzymywania wysokokoercyjnych proszków Nd-Fe-B. Mieleniu poddano stop Nd<sub>12</sub>Fe<sub>82</sub>B<sub>6</sub>, a także zastosowano metodę mechanicznej syntezy stopów tzn. mielono proszki pierwiastków składników stopu. Procesy prowadzono w dwóch wariantach: cały proces odbywał się w podwyższonej temperaturze lub stosowano wstępne mielenie w temperaturze pokojowej, a następnie mielenie w wysokiej temperaturze. We wszystkich procesach uzyskano nanokrystaliczne proszki o właściwościach magnetycznie twardych. Proszki uzyskane w procesie mielenia stopu miały właściwości lepsze od proszków otrzymanych w procesie mechanicznej syntezy stopów, ponieważ były bardziej jednorodne i posiadały mniejszy udział fazy  $\alpha$ -Fe.

## 1. Introduction

High-coercivity Nd-Fe-B powders may be produced using the melt spinning method [1, 2], HDDR (hydrogenation, disproportionation, desorption, recombination) method, and obtained by milling the Nd-Fe-B alloy (mechanical milling) or the individual elements which are alloying components of this alloy (mechanical alloying). The milling process yields a mixture of an amorphous phase with nanocrystalline Fe precipitates. In order to improve its magnetic properties, the powder thus obtained must be additionally subjected to annealing.

This paper presents the results of experiments with the use of high-temperature milling (600°C) for producing high-coercivity Nd-Fe-B powders, a technique which permits the entire process to be realized during a single operation without the need for additional annealing.

Besides our earlier publications [3, 4], no reports concerning hot-milling of magnetically hard alloys are available in the literature. Among the papers describing, but only in general terms, milling and mechanical alloying of powders, we can find publications concerned with milling at low temperatures, and a few studies devoted to milling at elevated temperatures [5-7]. A research group at the University of Wol-

longong describes a method in which the milling operation is assisted with electric discharges ignited between a ball and the surface of the container [8]. This experiment gave very interesting results. Depending on the treated material and the milling parameters, the rate of refinement of the powders could be increased, the powders agglomerated or new phases were formed, other than those occurring under the equilibrium conditions. The decisive factor was here the electric discharge, but the increase of the temperature due to this discharge was not analyzed.

Our experiments were the first to examine and describe the high-temperature mechanical alloying of the Nd-Fe-B materials.

## 2. Experimental

The material subjected to high-temperature milling was an alloy with the chemical composition Nd<sub>12</sub>Fe<sub>82</sub>B<sub>6</sub>, cast in the form of plates (about 20 mm thick) or Nd, Fe and Fe-B alloy powders. The milling process was conducted in a vibration ball mill using an argon protective atmosphere.

Four versions of the process were examined. In the first version, a cast alloy with the composition Nd<sub>12</sub>Fe<sub>82</sub>B<sub>6</sub> was

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milled at a temperature of 600°C for various times (further referred to as Process 1). The second version consisted of preliminary milling the same alloy at room temperature for 18 hours, then, while still milling, the container with the powder inside was heated to 600°C and the milling process was continued for 0.5h (Process 2). In the third and fourth versions, the  $\text{Nd}_{12}\text{Fe}_{82}\text{B}_6$  powder was obtained by mechanical alloying i.e. by milling the constituent elements of the alloy (Nd, Fe, and an FeB alloy). In version 3 the elements were milled at a temperature of 600°C for various times (Process 3) whereas in version 4 they were initially milled at room temperature for 18h and then, with the container heated to 600°C, the milling operation was continued for various times (Process 4). The milling time of 18h was chosen for the experiments since in our earlier studies we had found that after this time the mixture contained an amorphous phase and nanocrystalline Fe precipitates. In each of the processes the powder was removed from the container by additional milling in toluene, conducted at room temperature for 20min. The container was made of steel with 0.4% of C and 13% of Cr. The temperature was measured outside the container.

The magnetic properties of the powders thus produced were examined in a Lake Shore vibrating sample magnetometer. The powders were also examined by XRD using the  $\text{CuK}\alpha$  radiation. The size of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  crystallites was determined using the Scherrer method for the (202) peak.

### 3. Result

Figure 1 and 2 show the dependence of the coercivity and remanence, respectively, of the powders on the milling time. We can see that in the powders obtained by process 1 (mechanical milling), the coercivity and remanence increase with increasing milling time, but never achieve the high values obtained with process 2 in which the milling was initially conducted at room temperature for 18h when the powder acquired an amorphous form, and then the milling was continued at a temperature of 600°C for 0.5h.

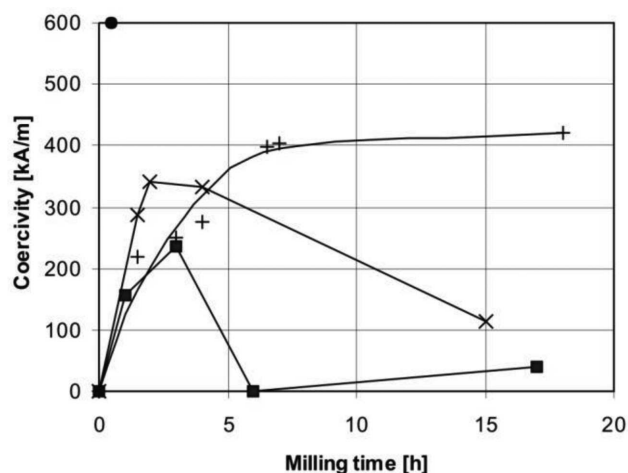


Fig. 1. Coercivity versus milling time in the powders produced by process 1 (x), process 2 (●), process 3 (+), and process 4 (■)

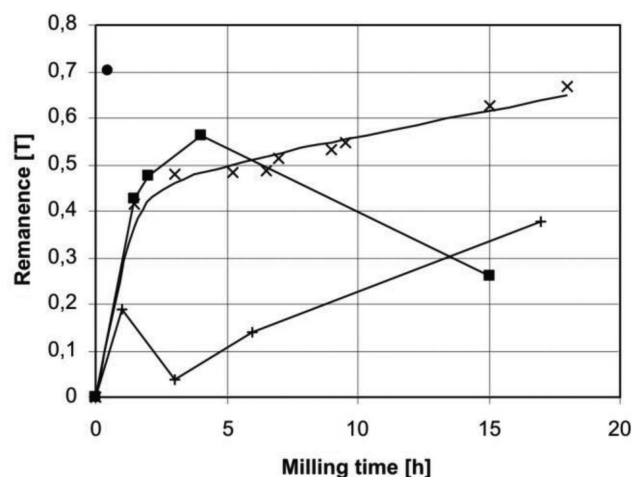


Fig. 2. Remanence versus milling time in the powders produced by process 1 (x), process 2 (●), process 3 (+), and process 4 (■)

Examinations of the phase structure of the powders have shown significant differences between the structures of the powders produced by mechanical alloying at room temperature and at 600°C (Fig. 3). It is known that mechanical alloying conducted at room temperature yields a mixture of the starting elements, whereas when conducted at 600°C the powder contains the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase and shows certain magnetic properties. However even after longer milling times, above 3h, its magnetic properties are very poor. The observation that the magnetic properties of the powder after mechanical alloying are lower than those achieved by mechanical milling can be explained in terms of the difference in the behavior, during the milling process, between the Nd-Fe-B powder and the mixture

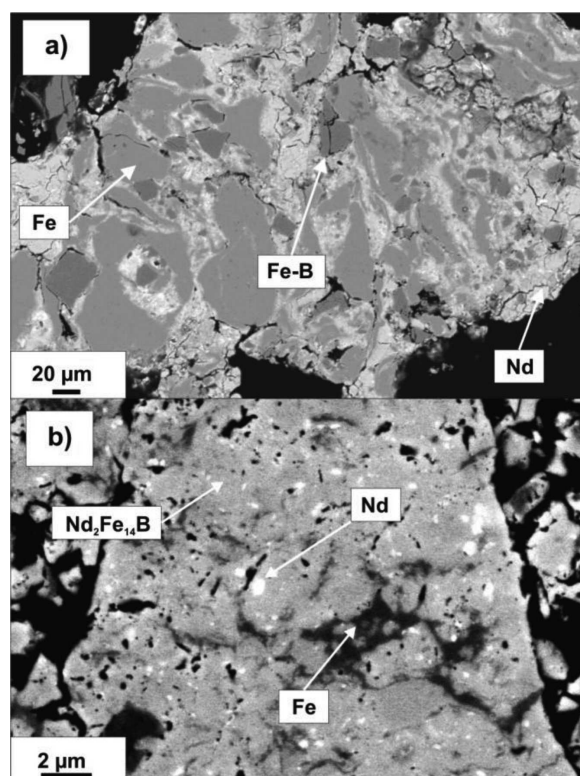


Fig. 3. SEM image of the microstructure of the powder milled for 1.5h at room temperature (a) and at a temperature of 600°C (b)

of the Nd, Fe, and Fe-B powders. The powder of the Nd-Fe-B alloy is a brittle material and shows little tendency to adhesive sticking to the walls of the container and the balls, contrary to the Nd and Fe powders which at a temperature of 600°C show high plasticity and tend to stick to the container and balls.

Fig. 4 shows a cross-section of the powder container wall after mechanical alloying conducted at 600°C for 10 hours. It can be seen that the powder sticks to the container walls. The reactions that proceed there lead to the formation of brittle  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase which, when milling is continued, falls off the container walls. The chemical composition of the powder thus obtained, especially when it is milled for a short time, may differ from that expected. This is the reason why the powders milled for the time as short as a few hours have very poor magnetic properties. We can also infer from Fig. 4 that Nd reacts with the elements present in the material of the container and probably also with those present in the ball material.

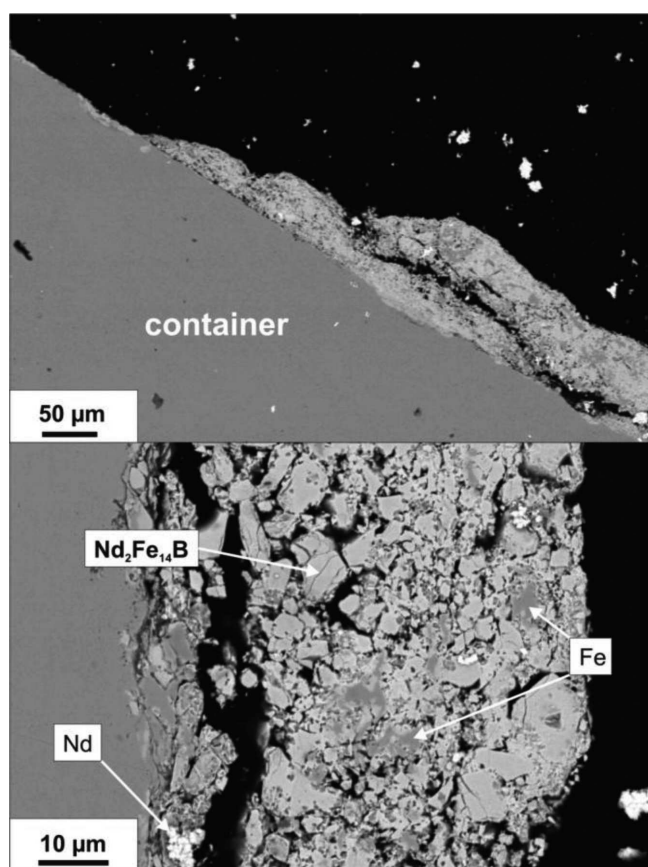


Fig. 4. SEM image of a cross-section through the wall of the container after a mechanical alloying process (process 3) conducted in it for 10h, showing the powder stuck to the container wall. Before the cross-section was made, the container wall was protected with epoxy resin poured to the container

These observations also explain why the mixture of the Nd, Fe and Fe-B powders subjected to preliminary milling for 18h and then to milling at a temperature of 600°C has substantially better magnetic properties than the mixture milled at the high temperature from the very beginning of the process. This is so since, at room temperature, the powder deforms plastically and undergoes strengthening, as a result of which its susceptibility to stick to the mill walls decreases. After the powder is heated to 600°C, the reaction that leads to the formation

of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  proceeds very quickly, since it takes place in a mixture of amorphous and nanocrystalline phases. Hence the contact between Nd, which at 600°C is strongly reactive, and the container walls is very much limited. In mechanical milling, on the other hand, the Nd atoms take part in the formation of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase or the amorphous phase and are even less able to diffuse into the container and ball materials. In effect the powders produced by mechanical milling have much better magnetic properties than those produced by mechanical alloying. In mechanical milling it is advantageous to possibly reduce the time for which the powder, being at a high temperature, is in contact with the container and the balls. The properties of the powder produced by Process 2 (amorphized prior to heating) are significantly better than the properties of the powder processed by Process 1.

The superiority of mechanical milling to mechanical alloying also lies in that the latter, within the milling time range examined in the present experiments, does not give homogeneous material. The microstructure of the powder obtained by Process 3 carried out for 18h contained non-dissolved inclusions of the Fe-B alloy and regions with increased Fe concentration (Fig. 5).

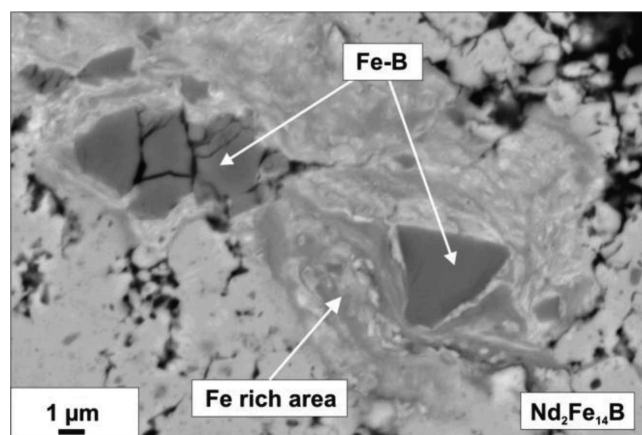


Fig. 5. SEM image of a cross-section through a particle of the powder produced by process 3 (mechanical alloying) conducted for 18h

Examinations of the phase composition confirm the presence of phases other than  $\text{Nd}_2\text{Fe}_{14}\text{B}$ . Fig. 6 shows diffractograms of the powders produced by Processes 1, 3, and 4 after long milling times. We can infer from these diffractograms that the  $\alpha$ -Fe content is the lower in the powder produced by Process 1, since the intensity of the Fe peak is here relatively low (comparable with that of the neighboring peak due to the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase). The Fe peaks in the diffractograms of the powders produced by mechanical alloying (Processes 3 and 4) are much more intensive. Therefore the degree of reaction of the constituents to form the hard magnetic phase is considerably smaller. This is especially visible in the powders subjected to Process 3 in the diffractograms of which, additionally, Nd peaks appear. Examinations also included measurements of the crystallite sizes in all the powders produced using such process parameters that ensured the best magnetic properties. The results are given in Table 1.



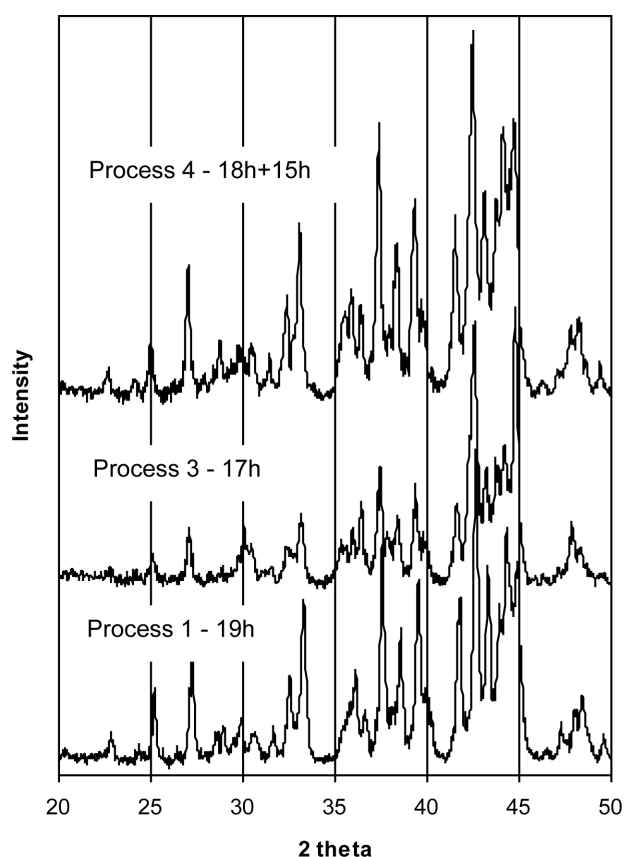


Fig. 6. Diffraction phase analysis of the powders produced by Process 1 (milling time – 19h temperature – 600°C), Process 3 (milling time – 17h, temperature – 600°C), and Process 4 (milling time – 18h at room temperature and then 15h at 600°C)

TABLE 1

Crystallite sizes in the powders produced at the optimum process parameters

Process	Time of preliminary milling [h]	Milling time at 600°C	Crystallite size [nm]
1	-	19	31
2	18	0,5	25
3	-	4	50
4	18	15	30

The crystallites were the smallest in the powder produced by Process 2 and only slightly greater in the powders produced by Processes 1 and 4. Process 2 (mechanical milling) gave however markedly better magnetic properties than Process 4 (mechanical alloying) in which the factor deciding about degrading the properties is the higher  $\alpha$ -Fe content.

Our experiments have shown that all the variants of high temperature milling permit producing nanocrystalline materials. Mechanical milling (Processes 1 and 2) ensure however much better homogeneity of the chemical composition of

the material and also results in a more advantageous phase composition. The materials produced by mechanical alloying (within the milling time range examined here) are inhomogeneous and have a high content of the  $\alpha$ -Fe phase. Comparing the properties of the powders milled at a high temperature during the entire process (Processes 1 and 3) with those of the powders subjected to preliminary milling (amorphisation) at room temperature (Process 2 and Process 3) we can state that finer grains and better properties can be obtained in the latter case. Crystallization conducted in a mixture of an amorphous phase and nanocrystalline precipitates appears to be more advantageous than crystallization that proceeds in the powders with a stable phase structure.

#### 4. Summary

Milling carried out at high temperatures is a very interesting method which has not been investigated yet. It permits producing high-coercivity Nd-Fe-B powders during a single operation. The greatest obstacle is here the diffusion of the components of the powder being milled into the walls of the container and the balls. This is however only a technical problem which can be solved by using a container and balls made of e.g. ceramic in place of steel. Mechanical milling at high temperatures is an effective method of refining powders which, when subjected to a long-lasting high-energy milling, become amorphous. We have also found that, by using the milling process, it is possible to refine a microcrystalline powder so as to obtain a nanometric grain size.

#### Acknowledgements

This work was supported by the Polish Ministry of Science and Higher Education, project no. N N507 475537.

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