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High temperature milling – new method of processing Nd-Fe-B powders

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The present paper describes a method of processing Nd-Fe-B powders, in which the milling operation is carried out, entirely or only in the final stage, at high temperatures, so that the destruction of the $Nd_2Fe_{14}B$ phase and its recombination occur simultaneously. In this way a powder with good magnetic properties immediately after milling was obtained. In the present experiments, the $Nd_{14}Fe_{80}B_6$ powder was subjected to high-energy milling for 17h (until the material becomes amorphous) and, then, the milling was continued for 0.5h with the powder container being heated to an appropriate temperature. Diffraction examinations have shown that the powder thus processed contains the $Nd_2Fe_{14}B$ phase. Its magnetic properties appear to depend on the applied temperature. The best magnetic properties were achieved in the powder milled at a temperature between 520 and 540°C, but we found that even milling at a temperature of 455°C gave a material with a high coercivity. The powder milled at room temperature for 17h and then heated to 520°C in a separate furnace shows much worse magnetic properties than the powder subjected to heating at the same temperature but during the final stage of the milling. Therefore our experiments have proved that the milling and heating operations conducted simultaneously give better results than processes in which the two operations are performed separately.

Keywords: High temperature milling; Nd-Fe-B powders; Mechanical milling.

Los polvos con alta coercitividad Nd-Fe-B se obtienen por varios métodos (melt-spinning, HDDR, mechanical milling, mechanical alloying). Generalmente en los procesos utilizados podemos distinguir la etapa de destrucción de la fase de grano grueso $Nd_2Fe_{14}B$ y la etapa de su recombinación en estructuras con grano visiblemente menor. Esta secuencia de cambios se produce, por ejemplo, en el método de molienda mecánica, donde se provoca la amorfización de la aleación Nd-Fe-B y el recocido posterior da lugar a la nueva cristalización de la fase $Nd_2Fe_{14}B$ en forma nanocristalina. En el presente estudio se describe el método de molienda a altas temperaturas, donde ambas etapas, de destrucción y de recombinación, se superponen en el tiempo. Como resultado de tal proceso, tras la molienda, que en su totalidad o en su última etapa se realiza a alta temperatura, se obtiene un polvo de buenas propiedades magnéticas. El polvo de la aleación, de composición $Nd_{14}Fe_{80}B_6$, fue sometido a molienda de alta energía durante 17h (hasta la amorfización del material), luego el recipiente con el polvo fue calentado durante la molienda y se continuó este proceso a la temperatura deseada durante 0,5h más. Los ensayos por difracción de rayos X demostraron que el polvo al final de este proceso contenía la fase $Nd_2Fe_{14}B$. Las propiedades magnéticas de los polvos obtenidos dependieron de la temperatura aplicada. Las mejores propiedades correspondieron a los polvos molidos a temperaturas del orden de 520-540°C, pero incluso moliendo a una temperatura de 455°C se obtuvo un material de alta coercitividad. El polvo molido a temperatura ambiente durante 17h, y recocido al horno en un proceso aparte a 520°C de temperatura, alcanza claramente peores propiedades magnéticas en comparación con la molienda realizada en la etapa final a esta temperatura. Se ha realizado también un experimento en que toda la molienda se realizaba a una temperatura elevada (520°C). En este caso, también se obtuvo un polvo de alta coercitividad. Los ensayos realizados en el marco de este trabajo probaron que la acción simultánea de la molienda y temperatura ofrece mejores efectos que la aplicación por separado de la molienda y posterior recocido.

Descriptores: Molienda a alta temperatura; Polvos Nd-Fe-B; Molienda mecánica.

PACS: 75.50.Ww; 75.50.Cd; 75.20.En

1. Introduction

At the present, most magnetic Nd-Fe-B materials are produced by sintering. There is however also demand for hard magnetic powders intended for the manufacture of bonded magnets. Such powders can be produced by spraying the alloy in the melted state, or by the refinement of the alloy in the solid state followed by an appropriate modification of its structure. The method most important from the technical point of view consists of milling rapidly cooled and then thermally processed ribbons. The highly coercive powders may also be produced using the HDDR method, mechanical alloying and mechanical milling.

In the last two methods, the basic operation is long-term high-energy milling which yields a mixture of nano-crystalline and amorphous phases. In the mechanical alloying it is the powders composed of the constituent elements of the alloy which are subjected to milling, whereas the mechanical synthesis utilizes the alloy in the powdered form. In both methods the powder mixtures obtained after milling are subjected to annealing in order to produce the $Nd_2Fe_{14}B$ phase with nano-metric grains.

In most of the methods described above the structure of the highly coercive Nd-Fe-B material is achieved in two stages: first, the $Nd_2Fe_{14}B$ phase is decomposed to obtain a structure entirely amorphous or with nanocrystalline precipitates, then the $Nd_2Fe_{14}B$ phase is recrystallized to form grains with nanocrystalline sizes.

The present study is devoted to a new method of producing high-coercivity Nd-Fe-B powders in which the alloy is milled at a high temperature. The method permits combining the two stages of the process mentioned above (destruction and then reconstruction of the $Nd_2Fe_{14}B$ phase with the desired micro-structure) in a single operation.

In the literature there are no reports concerning hot-milling of magnetically hard alloys. Among the papers describing, in general terms, milling and mechanical synthesis of powders, we can find publications concerned with milling at low temperatures and a few studies devoted to milling at elevated temperatures. A research group at the University of Wollongong describes a method in which the milling operation is assisted with electric discharges ignited between a ball and the surface of the container [1]. 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.

In our experiment, a cast Nd-Fe-B material was milled at a high temperature with the aim to modify its microstructure so that it acquired hard magnetic properties.

2. Experimental

The material subjected to high-temperature milling was an alloy with the chemical composition $Nd_{14}Fe_{80}B_6$, cast in the form of plates about 20mm thick and then ground to obtain a powder with a grain size below 1mm. The milling process was conducted in a vibration ball mill using an argon protective atmosphere. The powder container was heated to an appropriate temperature. After the high-temperature milling was completed, the container with the powder inside was cooled to room temperature during about 5min.The container being cooled, the powder was removed from it by short-time milling (for about 20min) in the environment of toluene. 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 CuKα radiation. The thermal analysis was performed in a differential scanning calorimeter (DSC) at a heating rate of 40°C/min. The size of the $Nd_2Fe_{14}B$ crystallites was determined using the Scherrer method for the (202) peak.

3. Results

During milling in the ball mill at room temperature for 17h the $Nd_2Fe_{14}B$ phase was decomposed and the material became amorphous with nanocrystalline α-Fe precipitates distributed within it. This can be seen in Fig. 1a which shows the results of an X-ray phase analysis.

The diffractogram contains peaks from the $Nd_2Fe_{14}B$ phase and a very broad peak at a position characteristic of the (110)α-Fe line. The powder had very poor magnetic properties – Table I.

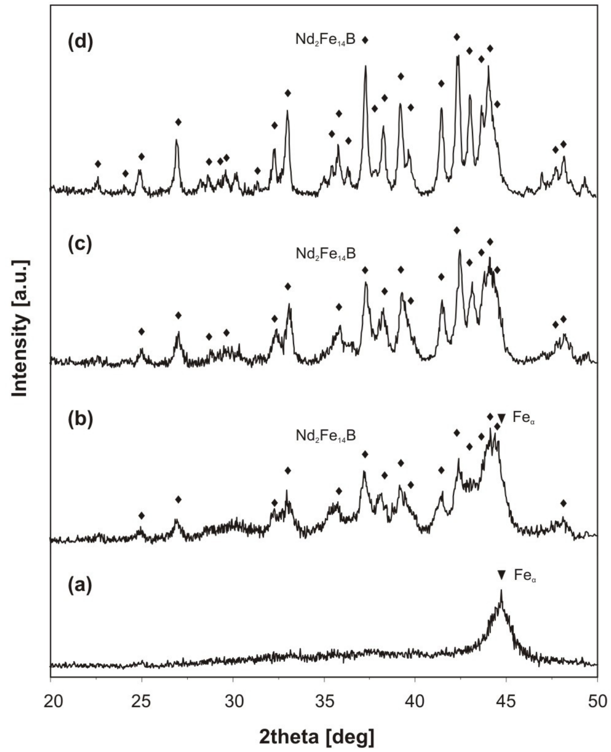

FIGURE 1. Diffraction phase analysis of the powders: after the initial stage of the process - milling at room temperature for 17h (a), and after the final stage of the process, milling at 455°C (b), 529°C, (c) and 650°C (d), for 30min.

TABLE I. Magnetic properties of the samples processed under various onditions

Processing	Coercivity [kA/m]	Remanence [T]	$(BH)_{max}$ [kJ/m^3]
Powder milled for 17h at r. t.	42	0.27	2.0
Powder milled for18h at r. t. and 30min at 520°C	840	0.65	63.0
Powder milled for 18h at r.t. and annealed in furnace at 520°C/30min	630	0.60	39.0
Powder milled for 8,5h at 520°C	716	0.51	38.0

The next experiments included milling at room temperature for 17h, then milling with the powder container heated to a desired temperature (which took 30min) and, in the final stage of the process, continuing the milling at this temperature for further 30min. The powders thus prepared contained the $Nd_2Fe_{14}B$ phase with such a grain size that ensured good magnetic properties (Figs. 1b, 1c and 1d). When the milling temperature was increased, the intensity of the

$Nd_2Fe_{14}B$ peaks increased and the α-Fe peak vanished. The magnetic properties of the powders, in particular the coercivity, appeared to depend on the temperature maintained during the final stage of the milling operation (Fig. 2).

The maximum was achieved at a temperature of about 530°C, but even at a relatively low temperature of 455°C the coercivity was high. There are many literature reports concerning the time-dependence of the coercivity in the amorphous Nd-Fe-B alloys obtained by various methods. The authors of ref.[2] examined the effect of the annealing temperature on the coercivity of the powders, produced by mechanical milling, in which the Nd content was 8%. They achieved the highest values of coercivity at temperatures between 600 and 650°C, whereas after annealing at the 550°C (the lowest in their experiments), the coercivity was considerably lower. In ref.[3], the authors annealed a mechanically synthesized $Nd_{15}Fe_{77}B_8$ alloy at 500°C and at 700°C (the optimum temperature) and found that the coercivity of the alloy annealed at the lower temperature even for a long time was more than twice as low as that of the alloy annealed at the higher temperature. According to the literature reports which present the DSC results obtained for amorphous Nd-Fe-B materials prepared by mechanical synthesis [2] and melt spinning [3], the $Nd_2Fe_{14}B$ phase crystallizes in one step but only at temperatures above 500°C, whereas in the alloy prepared by milling, the crystallization already begins at about 430°C, and the share of the $Nd_2Fe_{14}B$ phase after the annealing is about 10%. The identical thermal effect was observed in our experiments with the powder milled for 17h (examined directly after the milling by the micro-calorimetric method), but this effect was preceded by several transformations, superimposing on one another, which took place over a wide temperature range (the first clearly marked thermal effect occurred as early as at 235°C) – see Fig. 3. We can therefore suppose that, during amorphization of Nd-Fe-B alloys by milling, the $Nd_2Fe_{14}B$ phase most probably forms already at lower temperatures. When comparing the results available in the literature with our results, we can conclude that, in the high-temperature milling proposed by us, the optimum milling temperature is appreciably lower than the optimum annealing temperatures reported for the Nd-Fe-B materials amorphisized by the methods employed thus far. The remanence of the $Nd_{14}Fe_{80}B_6$ alloy also depends on the milling temperature but this effect is much weaker.

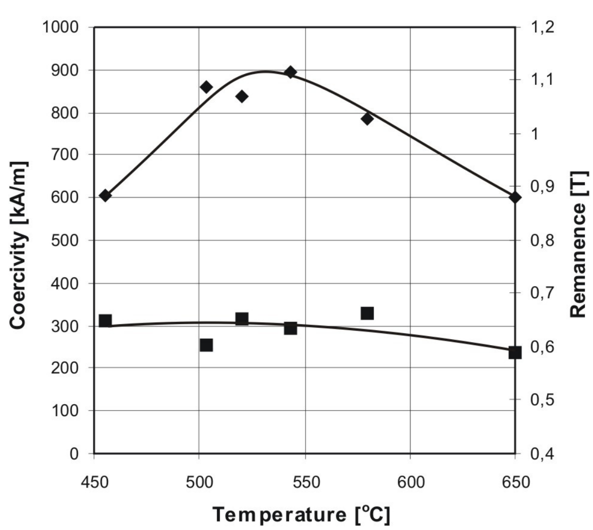

FIGURE 2. Effect of the temperature maintained during the final stage of the milling operation on the coercivity (◇) and remanence (■) of the $Nd_{14}Fe_{80}B_6$ powder.

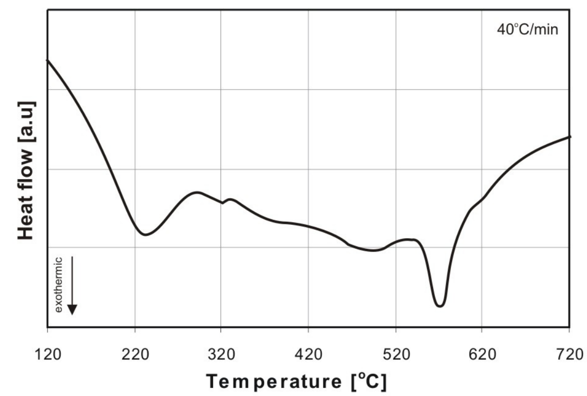

FIGURE 3. DSC curve obtained for the $Nd_{14}Fe_{80}B_6$ powder milled at a high-temperature for 17h.

In another experiment, the $Nd_{14}Fe_{80}B_6$ was subjected to milling for 17h, then, the powder thus obtained was transported to a furnace where it was heated to the annealing temperature of 520°C for 30min and maintained at this temperature for further 30min. Thus, the duration of the entire process (milling followed by annealing) was the same as that of the process conducted at the same temperature (520°C) but with milling combined with annealing in a single operation. The results, given in Table 1, appeared however to be not as good as those achieved with milling and annealing conducted simultaneously We can therefore suppose that the simultaneous joint action of milling and annealing brings about a certain advantageous effect which adds to that taking place in milling and annealing conducted separately.

We also experimented with the milling process conducted for 8.5h, all the time at a temperature of 520°C. This process also transformed advantageously the microstructure of the alloy and greatly improved its coercivity and other magnetic properties – Table 1. However the magnetic properties were worse then those of the powders obtained by long-time milling (17h) at room temperature and then at 520°C during the final 30min of the process. It can be expected that these properties depend on the milling time, and, thus, the optimization of this process parameter will permit their further improvement.

In the Nd-Fe-B alloys, it is the amorphous phase which is stable under the conditions of high-energy milling. An increase of the milling temperature stabilizes the crystalline $Nd_2Fe_{14}B$ phase, but, if the temperature is not sufficiently high, part of this phase may be expected to decompose. The process temperature also affects the grain size of the $Nd_2Fe_{14}B$ phase. Hence, the dependence of the magnetic properties of the alloy on this temperature has a well marked maximum. Although when the process is conducted at a low temperature the grains are refined, but the structure contains α-Fe precipitates and probably also non-equilibrium phases such as *e.g.* an amorphous phase.

After milling at a temperature of 455°C, the crystallite size was 17nm, whereas milling at 520°C gave crystallites 20nm in size. We can thus suppose that at a similar crystallite size, the magnetic properties of the material depend on the small differences in its phase composition, such as *e.g.* the share of the magnetically soft α-Fe phase (Fig. 1). At still higher temperatures, the crystallites were markedly grater. For example, when the process was conducted at a temperature of 650°C, their size was 34nm. The diffractogram of Fig. 1d shows no α-Fe in this material. Although milling at this high temperature gives the desired phase structure, the grains of the material grow larger and its coercivity decreases.

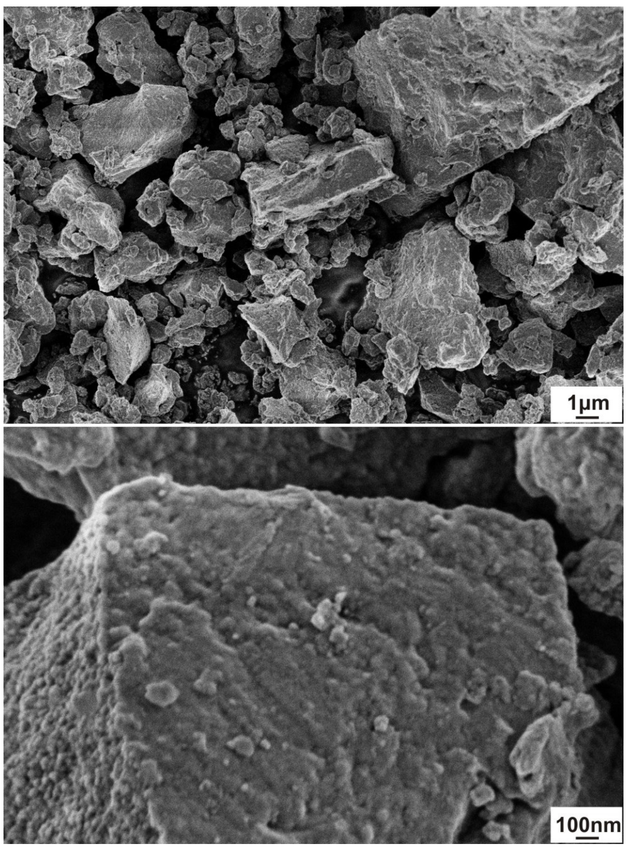

FIGURE 4. SEM images of the powders milled for 17h, with the final 30min stage conducted at 520°C.

The short-time milling in toluene (for 20min), used for removing the powder from the container, must have a significant influence upon the grain size of the powder but rather does not affect its microstructure and magnetic properties. SEM examinations showed however that the particle size of the powder was below 10μm, *i.e.* it was very fine compared to that of the commercial powders produced by milling ribbons. Fig. 4 shows SEM images of the powder milled for 17h, with the final 30min stage conducted at a temperature of 520°C. Within the powder particles we can see crystallites with nano-metric sizes separated by well-marked boundaries.

4. Conclusions

The proposed method of producing highly coercive Nd-Fe-B powders by milling the alloy at a high temperature gives very good results. The magnetic properties of the material thus produced, in particular its coercivity, strongly depend on the milling temperature. It was demonstrated that, by using the proposed method, the temperature at which we obtain powders with the desired phase composition is lower than that needed in annealing powders amorphisized by other methods. Moreover, the magnetic properties of these powders are better than those of the powders produced by milling and annealing conducted separately. The proposed method can have many applications, such as for example the production of the Nd-Fe-B powders with small particles, since at the high temperature the crystalline phase is stabilized and amorphization of the material is prevented.

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