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Mechanosynthesis of Nd–Fe–B alloys

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A mechanical alloying technique has been applied for Nd–Fe–B alloy synthesis from the mixture of neodymium, iron and Fe–B powders. The direct formation of $Nd_2Fe_{14}B$ phase (ϕ phase) was not observed, but an Nd–Fe multilayer structure was formed during the milling process. Annealing of milled powders at 1023 K for 1 h resulted in magnet formation. The dependence of the magnetic properties on milling time was observed. For the applied milling device and parameters, the optimum milling time proved to be 4 h and the coercive force reached a value of about 1000 kA m^{-1}.

1. Introduction

A mechanical alloying (MA) technique allows synthesis of fine-grained alloys and intermetallic compounds from elemental powders [1, 2]. There have also been some attempts to apply this method to obtain Nd–Fe–B magnets [3–5]. These magnets can be produced by various technologies [6]. In all of them, the presence of fine-grained $Nd_2Fe_{14}B$ phase (ϕ phase) in the alloy is necessary to obtain good magnetic properties.

The previous results reported in literature confirm that the application of the MA technique does not lead to the synthesis of either ϕ phase or amorphous phase directly from the starting Nd–Fe–B powder mixture. The Nd–Fe multilayer structure is formed because the difference in free enthalpy between the amorphous phase and the layered structure is always positive [7]. Thus, prolonged milling can only be the first stage of the Nd–Fe–B magnet production process, making the nanoscale mixing of the components possible. The second stage of the process must be annealing, which leads to the diffusion reactions in powder mixtures, described elsewhere [8]. The annealing processes should allow the formation of ϕ phase and allow optimum magnetic properties to be obtained.

The formation of ϕ phase takes place through two groups of reactions [8].

(A) Neodymium dissolves iron and subsequently Fe_2B, in order to form a neodymium-rich liquid L(Nd, Fe, B) at a temperature higher than the ternary eutectic temperature (928 K). This liquid reacts with iron, forming Nd_2Fe_{17} phase. Simultaneously, the diffusion of boron occurs and the following reaction takes place

$$Nd_2Fe_{17} + L(Nd, Fe, B) \rightarrow Nd_2Fe_{14}B + L'(Nd, Fe, B) \quad (1)$$

(B) Fe_2B reacts with a liquid

$$Fe_2B + L(Nd, Fe, B) \rightarrow Nd_2Fe_{14}B + NdFe_4B_4 \quad (2)$$

This reaction is slower than type A. In order to avoid incomplete dissolution of Fe_2B or excessive ϕ phase grain growth (due to iron dissolution), the Fe_2B grains should be very small.

The magnetic properties of the obtained alloy depend on the annealing time and temperature [9, 10]. The temperature of the process is very important and the optimum value is around 970 K [7].

The purpose of this work was to find the relationship between the milling parameters, phase and structural transformations upon annealing and magnetic properties of the Fe–Nd–B magnets. Particular attention was paid to the degree of mutual mixing of iron and neodymium powders in the milling process, because the contribution of each reaction to the formation of phase structure is determined by the thickness of the Nd–Fe layers on milled powder particles.

2. Experimental procedure

Pure iron and neodymium powders (200 μm, Treibacher Chemische Werke products, 99.3% purity) and prealloyed Fe–B powders were mixed in the composition $Nd_{18.5}Fe_{75}B_{6.5}$ and subjected to the milling processes. Mechanical alloying (MA) was carried out at room temperature in a high-energy vibrational ball mill, using stainless steel balls of 10 mm diameter. The weight of the mixed powders was 10 g and the ball-to-powder weight ratio was 5:1. To minimize oxygen contamination, the milling treatments were performed under a constant flow of argon. Wet MA processes were also performed and toluene was used as a lubricant. After MA the powders were compacted and vacuum annealed for 1 h at 1023 K.

The X-ray investigations were performed on a Philips diffractometer in continuous scanning mode, using CuK_α radiation ($\lambda = 0.154$ nm). Small quantities of the powder were withdrawn at different time intervals to evaluate the extent of alloying.

The mixing processes and the formation of the layered microstructure of powder particles at different

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stages of milling were followed by scanning electron microscopy. SEM also allowed particle size and morphology observations.

Magnetic properties were determined by hysteresis measurements and thermomagnetic analysis performed on a magnetic balance. For magnetic measurements, samples after compacting and annealing at 1023 K for 1 h, were used.

3. Results and discussion

X-ray diffraction analysis reveals the existence of iron, neodymium and Fe_2B lines after different milling times for the powders milled in argon as well as in toluene. As an example, Fig. 1 shows the X-ray results obtained for the powders milled in toluene. The intensity of the iron peaks decreases with increasing milling time and simultaneously different neodymium lines appear. The diffraction lines of ϕ phase are absent. Thus, the result obtained is in agreement with previous ones. The synthesis of ϕ phase directly from starting components during the MA process is not possible.

Fig. 2 shows scanning electron micrographs of ball-milled powders after selected milling times. In the first stage of the process the powder particles exhibit a flaky morphology. After a longer milling time the particles become more regular and almost round in shape.

Simultaneously, a considerable change in the particle size is observed. While the biggest particle dimension at the beginning of milling can be estimated as more than 100 μm, after 10 h processing this value is about 10 μm for the spherical particles.

SEM examinations of the cross-sections of polished particles reveal that in the early stage of milling the powders consist of many layers of neodymium (dark) and iron (white colour in Fig. 3). This multilayer microstructure becomes finer with increasing milling time. After 10 h processing, further refinement of the microstructure occurs, but still at least a two-phase structure is distinguishable from the micrograph.

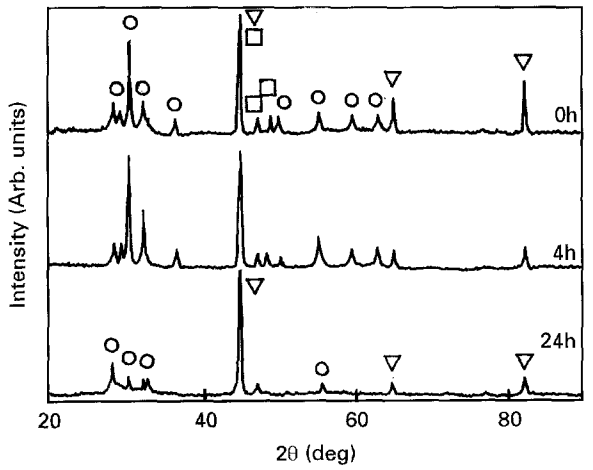

Figure 1 X-ray patterns of the Nd–Fe–B powders milled in toluene for different times. (○) Nd, (▽) Fe, (□) Fe_2B.

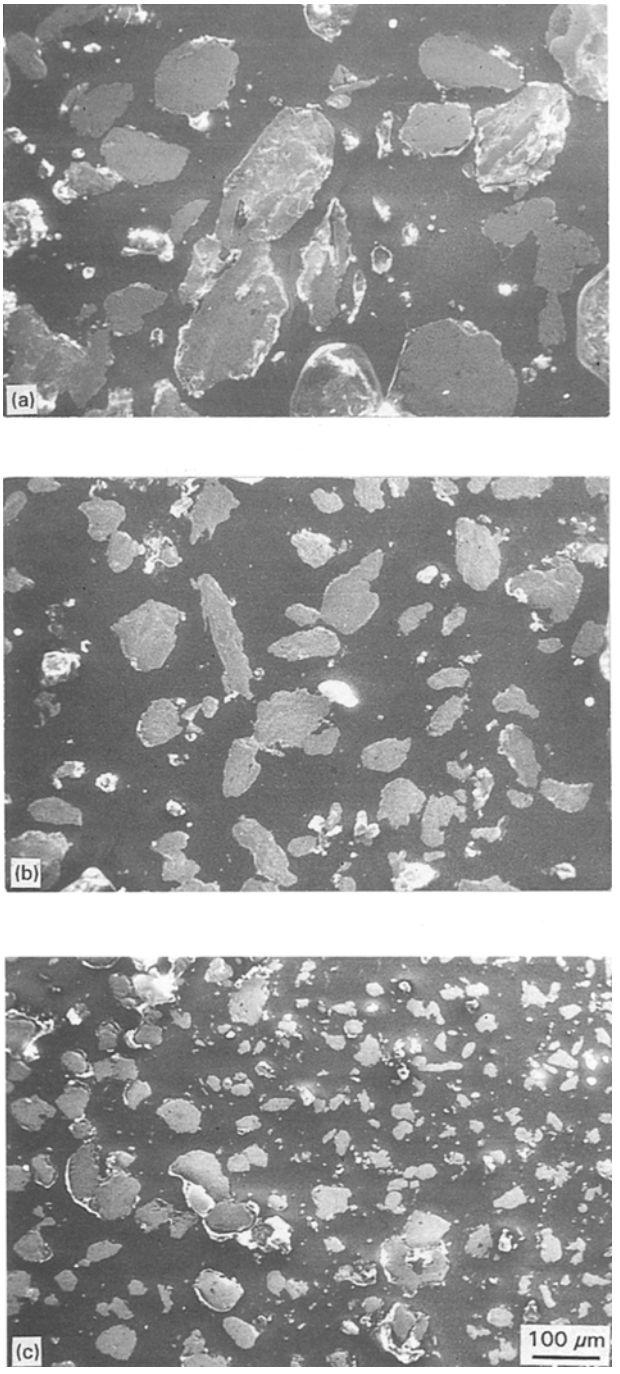

Figure 2 Nd–Fe–B particles size and morphology as a function of milling time: (a) 1 h, (b) 4 h and (c) 10 h.

A strong dependence of magnetic properties and the hysteresis loop shape on milling time is observed. Fig. 4a and b present hysteresis loops for the powders milled and annealed at 1023 K for 1 h. For a short milling time (2 h) the shape of the hysteresis loop is typical for the alloys with a low boron content. After such a short processing time, the powder particles are probably too large for boron migration from the Fe–B phase to a new developing one. This effect is not observed for a longer milling time.

The dependence of coercive force on milling time is shown in Fig. 5 for the samples milled in toluene and in argon and subsequently annealed at 1023 K for 1 h. The maximum value of measured coercive force is observed after 4 h milling in toluene. After a longer

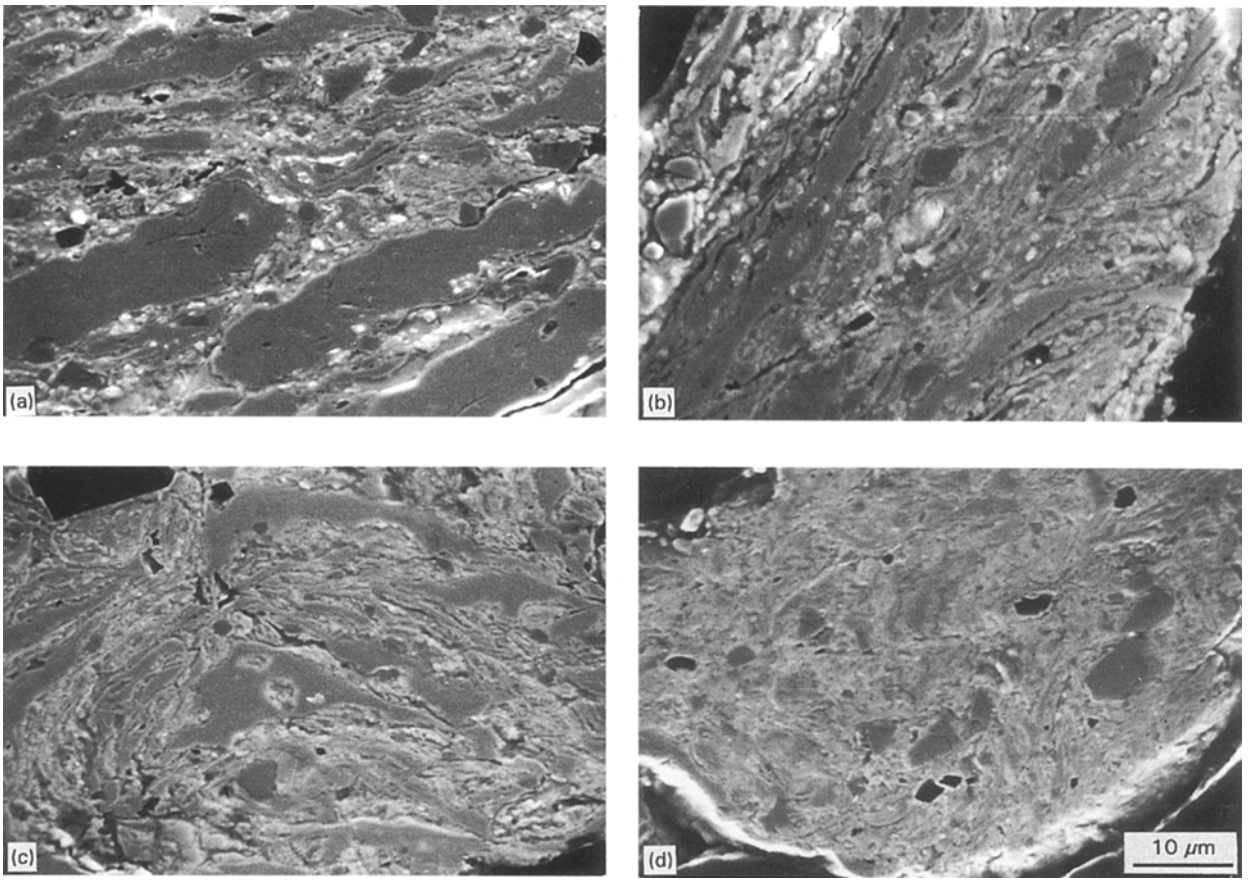

Figure 3 Microstructure of Nd–Fe–B powders mechanically alloyed for different times: (a) 1 h, (b) 4 h, (c) 6 h and (d) 10 h.

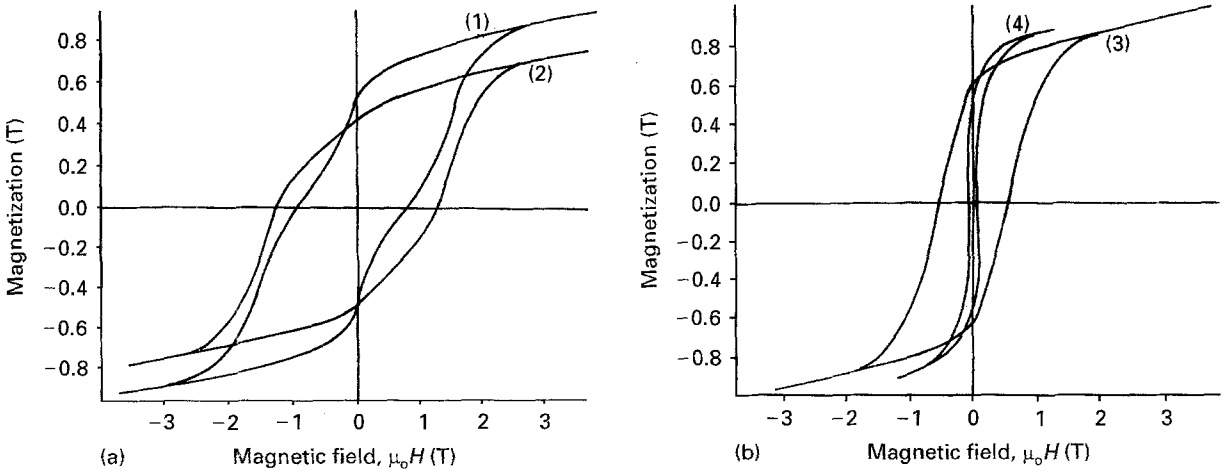

Figure 4 (a, b) Hysteresis loops for the powders milled for (1) 2 h, (2) 3 h, (3) 6 h and (4) 12 h and subsequently annealed at 1023 K for 1 h.

time the coercive force decreases through powder oxidation during milling [5]. The decrease of coercive force after reaching a maximum is faster for the samples milled in argon because of faster oxidation processes than in toluene.

On the other hand, the observed remanence does not depend so strong on milling time (Fig. 5). However, the maximum value is registered again after about 4 h milling.

The obtained results confirm a strong influence of milling parameters on the magnetic properties of the samples after annealing. The measured values of coercive force (about 1000 kA m^{-1}) are similar to those reported by other authors [7].

The samples after ball milling and annealing at 1023 K for 1 h were subjected to thermomagnetic analysis. This technique enables magnetic transformations to be followed at the Curie temperature or structural transformations of ferromagnetic phases to be observed as a function of temperature.

Fig. 6 shows the magnetic force as a function of temperature for the samples before milling (i.e. only

annealed) and after milling for 1, 4 and 12 h and subsequently annealed. The result obtained for the first sample indicates the occurrence of two different ferromagnetic phases characterized by Curie temperatures 344 and 590 K, respectively. The first phase appears in a large quantity, while the quantity of the second one is small. The phases can be identified as Nd_2Fe_{17} and $Nd_2Fe_{14}B$ (ϕ phase), respectively. Just 1 h milling leads to the increase of ϕ phase and a considerable decrease of Nd_2Fe_{17} phase. After 4 h processing, the latter is almost negligible and ϕ phase is the basic one.

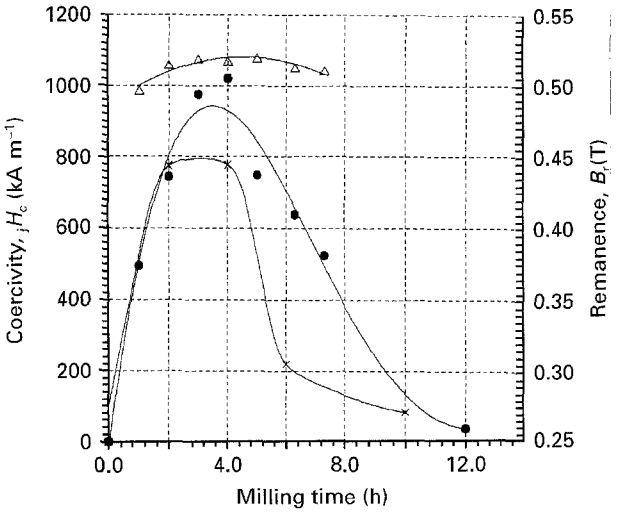

Figure 5 Dependence of coercive force (MA in (●) toluene and (×) argon) and (△) remanence on milling time for the powders annealed after milling at 1023 K for 1 h.

The result obtained for a sample milled for longer time (12 h) is quite different. ϕ phase still exists, but the registered change of magnetic force, corresponding to its transformation, is much smaller and at temperatures above the Curie temperature the magnetic force increases. This behaviour can be attributed to the decomposition of ϕ phase through oxidation.

On the basis of thermomagnetic measurements, one can conclude that after annealing at 1023 K for 1 h the Nd_2Fe_{17} phase is the first to appear. The refinement of the components during the MA process leads to the formation of ϕ phase. The same result can be obtained by increasing the annealing temperature. Thus, according to previous studies, the dissolution of boron is a crucial point for the $Nd + Fe + Fe_2B \rightarrow Nd_2Fe_{14}B$ reaction. The prolongation of milling time results in refinement of Fe–B powder particles and the formation of the desired phase structure. On the other hand, the powder refinement causes fast oxidation of the material. It seems to be reasonable, from the point of view of the optimization of magnetic properties to limit the milling time and, at the same time, to change the method of boron alloying. Boron should be alloyed as a very fine powder or as a phase which is easy to dissolve during annealing.

Selected samples (before milling and after 4 and 12 h processing) were compacted at 1023 K for 1 h and subjected to SEM observations. The micrograph of

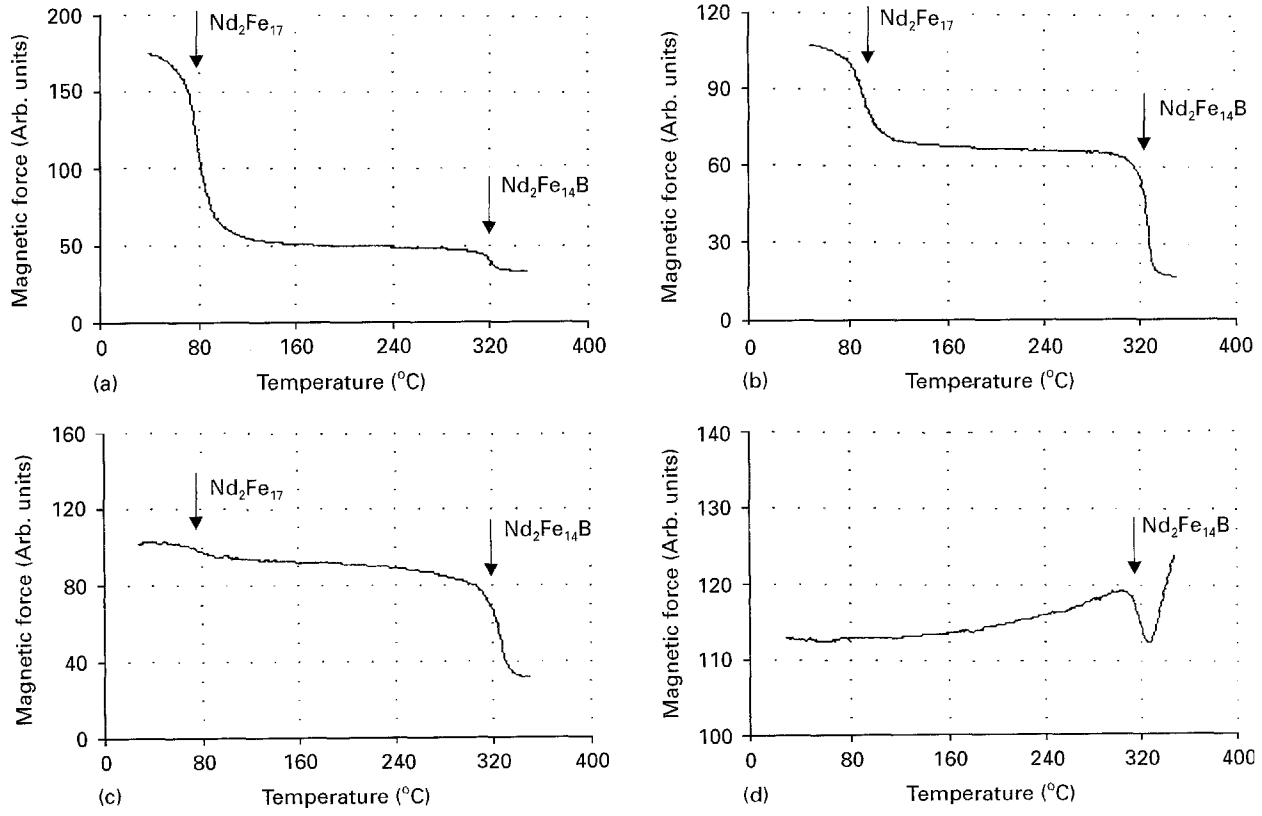

Figure 6 Magnetic force as a function of temperature for the samples before milling (i.e. only annealed) and after milling for 1, 4 and 12 h and annealing at 1023 K for 1 h.

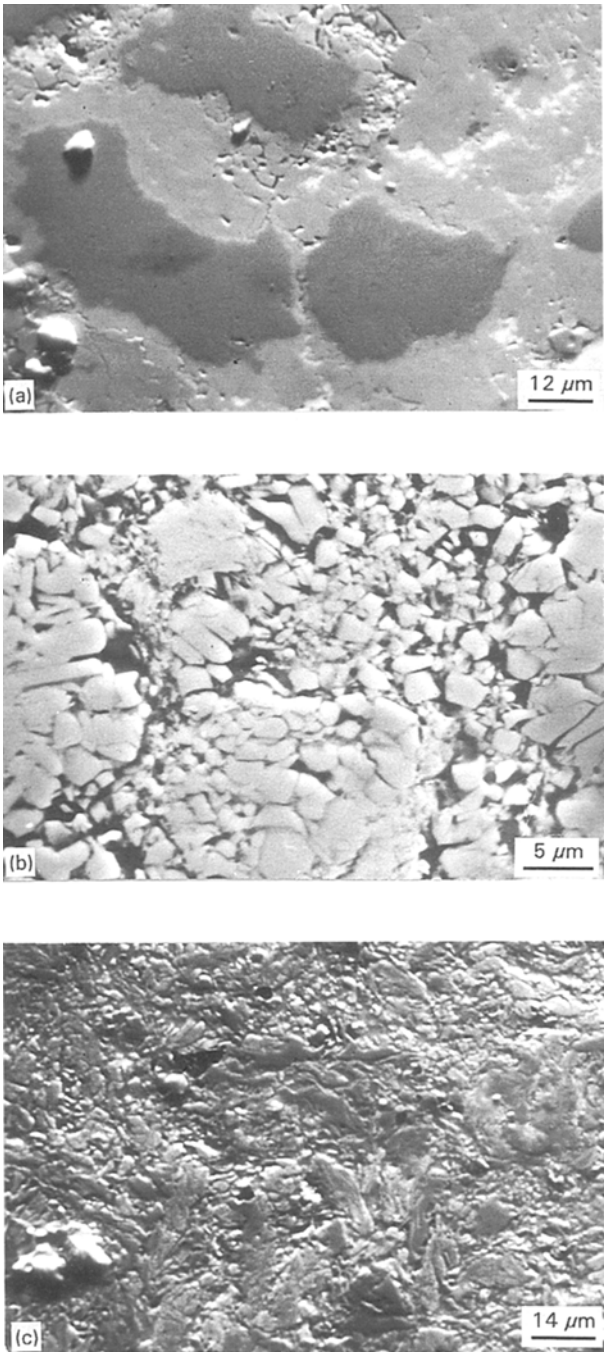

Figure 7 Microstructure of the Nd–Fe–B samples (a) before MA, and after mechanical alloying for (b) 4 h and (c) 12 h and subsequent annealing at 1023 K for 1 h.

the unmilled sample reveals dark and grey areas, which correspond to iron and neodymium, respectively (Fig. 7a). Upon milling, considerable refinement of the microstructure is observed (Fig. 7b, c). The employed annealing parameters do not lead to grain growth.

4. Conclusions

It has been confirmed that mechanical alloying of a mixture of neodymium, iron and Fe–B powders does not result in the direct synthesis of $Nd_2Fe_{14}B$ phase (ϕ phase). The obtained powders exhibit an Nd–Fe multilayer structure. The longer the milling time, the smaller is the thickness of the layers observed.

Annealing of milled powders at 1023 K for 1 h leads to magnet formation. The magnetic properties of the magnets strongly depend on milling time. The microstructure of the alloy also exhibits such a dependence. For the applied device and milling parameters, the optimum milling time in toluene proves to be 4 h. A shorter milling time is insufficient for Fe–B phase refinement and, as a result, boron-poor phases are observed. A longer milling time causes powder oxidation. Toluene protects the powders against oxidation better than an argon atmosphere, as coercive force and remanence measurements have shown. The coercive force of the obtained magnets reaches a value of about 1000 kA m^{-1}.

Acknowledgement

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