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Effect of grain size and tungsten addition on microstructure and magnetic properties of Nd-Fe-B type magnets

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Properties

ABSTRACT

Purpose: The paper presents the results of the microstructural and magnetic examinations of Nd-Fe-B type magnets produced by the mechanical powder milling method and doped with tungsten.
Design/methodology/approach: The effect of the grain size and addition of tungsten on the microstructure and magnetic properties of nanocrystalline alloys of the basic composition of $Nd_{10}Fe_{84}B_6$, as produced by the method of mechanical alloying in the process of prolonged milling, was investigated in the study. Powders were subjected to milling for a duration ranging from 10 to 120 hours in an Ar protective atmosphere. Moreover tungsten was added to the base alloy that exhibited the best magnetic parameters. The tungsten content of alloys varied in a broad range from 0 to 33 at%.
Findings: The examinations have shown that the grinding duration, for which the best magnetic properties are obtained, is 90 hours. Prolonged grinding has a significant effect on the grain size and microstructure refinement. The alloy addition in the form of tungsten, similarly as in the case of prolonged grinding, leads to a structure refinement. In the case of W addition, an increase in the coercive field, with a simultaneous decrease in the value of remanence and magnetic energy density (BH)max, is observed.
Practical implications: Development of relatively cheap $Nd_{10}Fe_{56}W_{28}B_6$ magnets of good service properties.
Originality/value: Determination of the effect of grain size and tungsten content on the magnetic properties and microstructure of the Nd-Fe-B magnets.
Keywords: Magnetic properties; Nd-Fe-B magnets; Microstructure

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1. Introduction

Magnetically hard materials play a vital role in many areas of life (e.g. the electronic industry - heads, converters, sensors; the automotive industry - indicators, starters, driving motors; the aircraft and aerospace industries - couplings, magnetrons, frictionless bearings; medicine - malignant cell separators, artificial heart elements; and articles of common use - video recorders, clocks, loudspeakers, etc.). A modern magnet can be a tiny ring in the mechanism of a CD player, an important element of many industrial and military machines, spacecrafts or motorcars, or a big block producing the levitation force for a train of the future, in which a magnetic cushion is used in the design of rail vehicles, thanks to which record speeds are achieved.

A true breakthrough in the development of magnetically hard materials turned out to be the 1984 invention of the compound $Nd_2Fe_{14}B$ that is characterized by strong magnetocrystalline anisotropy [1,2]. The good magnetic properties of compounds of the $RE_2Fe_{14}B$ type (where RE denotes rare-earth elements) are due to the ferromagnetic coupling of sublattice magnetic moments of rare-earth metals and iron for light lanthanides, and antiferromagnetic coupling for heavy lanthanides. Responsible for the mechanism of coercivity in those magnets is the nucleation and growth of opposite magnetization magnetic domains [3]. A big advantage of such magnets is undoubtedly their low price with excellent magnetic properties. Compared to Sm-Co type magnets, they have a low Curie temperature of 588 K [4] and low corrosion resistance [5]. Complex relationships exists between the technology of production of magnetic materials and their microstructure and magnetic properties, which constitute one of the subjects of interest of materials engineering. So, the attaining of optimal magnetic properties is closely dependent on the technological process in which the proper phase composition and microstructure of the material are produced. Magnets of this type are produced in several basic processes [6], such as the classic powder metallurgy using the HDDR process [7], rapid cooling from the liquid state [2], mechanical alloying, prolonged milling or arc-plasma spraying [8]. The composition of those alloys was modified many times over the years [9]. Some studies on the effect on tungsten (as an alloy addition) on the microstructure and magnetic properties of Nd-Fe-B alloys also came out in recent years [10,11]. This paper presents the results of the microstructural and magnetic examinations of Nd-Fe-B type magnets produced by the mechanical powder milling method and doped with tungsten.

2. Material and investigation methods

The studies were carried out on magnets of the basic composition of $Nd_{10}Fe_{84}B_6$, as fabricated by the mechanical alloying method using the process of prolonged milling of Nd, Fe powders and an Fe-B alloy of known composition. Powders were subjected to grinding for a duration ranging from 10 to 120 hours in an Ar protective atmosphere. After grinding, the samples were heat treated at a temperature of 923 K and for a duration of 30 minutes. Alloys were also examined within the study, in which part of the iron atoms were substituted with tungsten atoms. The tungsten content of alloys varied in a broad range from 0 to 33 at%. Tungsten was added to the base alloy that exhibited the best magnetic parameters. Samples with the addition of tungsten were milled for 90 hours. A structural X-ray analysis was conducted using a DRON - 2 diffractometer with a CoKα cobalt tube. Magnetic tests on the material were carried out on a LakeShore VSM vibration magnetometer in a magnetic field of up to 2.1T at room temperature. Microstructural examinations were made using a NEOPHOT-32 metallographic microscope and a JSM-5400 type JOEL scanning electron microscope coupled with a LINK-ISIS system 300 EDX X-ray microanalyzer manufactured by Oxford Instruments.

3. Investigation results and discussion

On the basis of the X-ray diffraction examination, the phase composition of the $Nd_{10}Fe_{84}B_6$ magnet was determined, as dependent on the milling duration and tungsten content. In all of the alloys examined, the existence of the following phases was identified: the desirable magnetically hard phase $Nd_2Fe_{14}B$, and magnetically soft phases: α-Fe and a slight amount of the Nd_2Fe_{17} phase (Fig. 1).

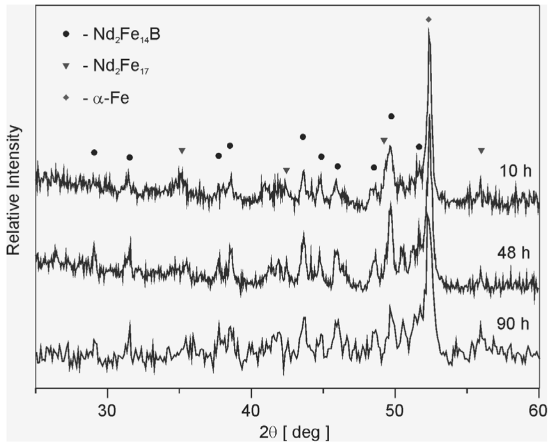

Fig. 1. X-ray diffraction patterns of $Nd_{10}Fe_{84}B_6$ alloy subjected to milling by 10, 48 and 90 hours, respectively

Substituting part of the iron atoms in the alloy ground for 90 hrs with tungsten atoms results in new, clear peaks appearing on the diffraction pattern, with the arrangement and intensities corresponding to free tungsten. As the tungsten content increases, the intensity of the spectral lines originating from both the magnetically hard phase $Nd_2Fe_{14}B$ and the magnetically soft phase α-Fe significantly decreases, which indicates a reduction in the volumetric fraction of these phases. Thus, e.g. for the alloy with 28 at% tungsten, the peaks coming from the magnetically soft phase α-Fe are not recorded [12].

The observations of the microstructure of $Nd_{10}Fe_{84}B_6$ alloy samples with different grinding durations found that with increasing grinding duration a microstructure refinement follows. Figure 2 shows the image of the $Nd_{10}Fe_{84}B_6$ alloy microstructure for milling durations of 24, 72 and 120 hours, respectively.

For short grinding durations, light and dark areas were observed in the microstructure pictures, being the effect of formation of a unique layered structure. Observations of the microstructure of these materials carried out additionally using a scanning electron microscope confirmed these findings (Fig. 3).

The formation of such a layered structure is associated with the high-energy grinding process, during which the powders are strongly defected, which results in the formation of a structure being characteristic of the mechanical alloying process, composed of particles of the magnetically hard phase $Nd_2Fe_{14}B$ with particles of the magnetically soft phase α-Fe located in their interior, as was confirmed by the analysis of chemical composition of the areas subjected to EDX detection. After prolonged grinding, these powders crack and are broken up, after which they are joined again to form a highly refined structure.

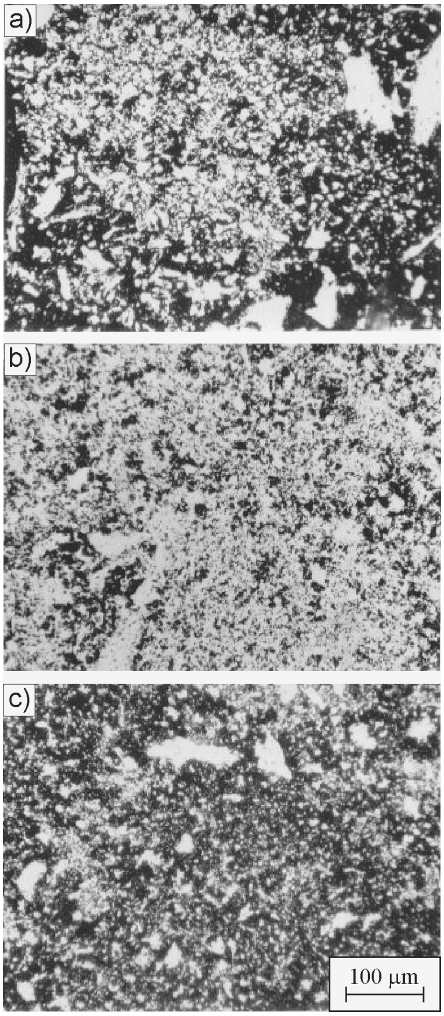

Fig. 2. Microstructure of $Nd_{10}Fe_{84}B_6$ alloy subjected to milling by (a) 24, (b) 72 and (c) 120 hours, respectively

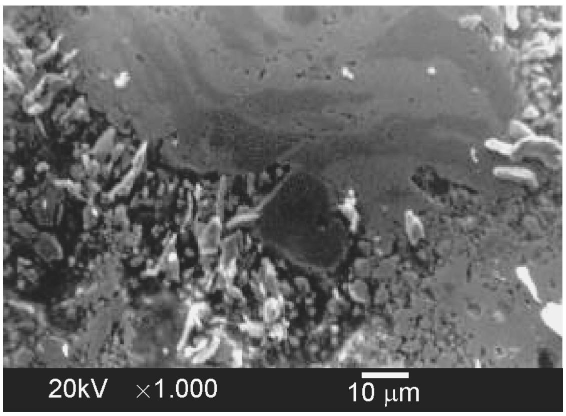

Fig. 3. Microstructure of $Nd_{10}Fe_{84}B_6$ alloy subjected to milling for a duration of 48 hours obtained using a scanning electron microscope JOEL type JSM-5400

With the increase in grinding duration, a reduction in the grain size of both the magnetically hard phase $Nd_2Fe_{14}B$ and the magnetically soft phase α-Fe was found (Fig. 4). In the case of the magnets, whose powders were ground for a duration of 90 hours, the microstructure is homogeneous, and the grain size of the magnetically hard phase $Nd_2Fe_{14}B$ is 34.9 nm, while that of the magnetically soft phase α-Fe is 16.2 nm. The structure obtained by high-energy ball milling, being a mixture of nanocrystalline particles of the $Nd_2Fe_{14}B$ magnetically hard phase and fine particles of the α-Fe magnetically soft phase, is, according to reference [6], a specific structure in which exchangeable couplings occur between neighbouring grains.

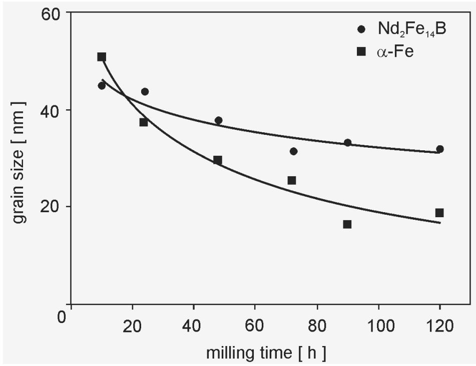

Fig. 4. Grain size of $Nd_2Fe_{14}B$ phase and α-Fe phase constituting the $Nd_{10}Fe_{84}B_6$ magnet annealed at 923 K for 30 min. depending on the time of powders milling, calculated on the basis of X-ray diffraction spectra

Introducing tungsten to the base composition results in an improvement in the structure of the material. In these magnets, no areas of inhomogeneous chemical composition were found, as was the case in the alloys not containing tungsten. The performed EDX analysis did not reveal any inhomogeneities in the areas of the examined alloys of a tungsten content above 16 at%. It was also found that, in the case of samples with the addition of tungsten, the alloy microstructure was refined with the increase in tungsten content. Figure 5 illustrates the microstructures of the $Nd_{10}Fe_{84-x}W_xB_6$ alloy with a tungsten content of 2.5, 12 and 28 at%, respectively. It was observed that the alloy not containing tungsten exhibited a highly porous structure, with visible irregular areas of very refined particles. As tungsten was added to the base composition, the powder particles become increasingly smaller and distributed uniformly within the entire volume of the sample. With large tungsten contents of the order of 28 at% and more, the particles of the highly refined powder accumulate into agglomerates.

During the studies of $Nd_{10}Fe_{84}B_6$ alloy samples for magnetic properties it was found that with the increase in grinding duration from 10 to 120 hours, the remanence J_r increased from the value of 0.276 T, attained a maximum for 90 hours (J_r = 0.914 T), and then decreased to 0.878 T after 120 hours of grinding. A similar behaviour was shown by the variations of coercivity $_JH_c$, saturation magnetization J_s, and the maximum magnetic energy density $(BH)_{max}$. The maximum magnetic properties were achieved in the $Nd_{10}Fe_{84}B_6$ magnet produced from powders after

90 hours of grinding, being as follows: J_r = 0.914 T; $_JH_c$ = 251.1 kA/m; J_s = 2.12 T and $(BH)_{max}$ = 67.7 kJ/m3. In the case of the $Nd_{10}Fe_{84-x}W_xB_6$ alloys the studies found that the addition of tungsten to the base composition of the magnets resulted in a further increase in coercivity $_JH_c$ from 251.1 kA/m for the alloy containing no tungsten to 1350 kA/m for the alloy containing 28 at% tungsten. Figure 6 shows example hysteresis loops for the $Nd_{10}Fe_{84}B_6$ base composition alloys ground for 90 hours and for the $Nd_{10}Fe_{84-x}W_xB_6$ alloy containing 28 at% tungsten.

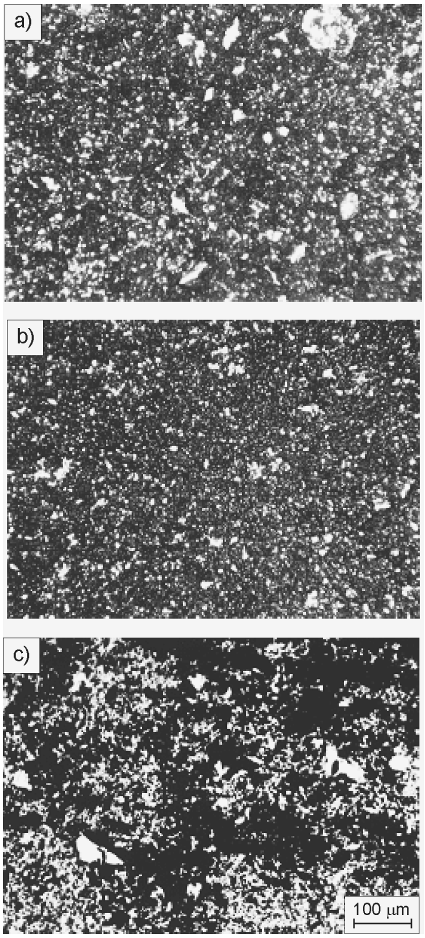

Fig. 5. The microstructures of the $Nd_{10}Fe_{84-x}W_xB_6$ alloy with a tungsten content of (a) 2.5, (b) 12 and (c) 28 at%, respectively

tungsten, similarly as in the case of prolonged grinding, leads to a structure refinement. In the case of W addition, an increase in the coercive field, with a simultaneous decrease in the value of remanence and magnetic energy density $(BH)_{max}$, is observed. The studies on this group of alloys, though being started almost three decades ago, have been still continued. The reason behind this is undoubtedly the unabated interest in relatively cheap magnets of good service properties.

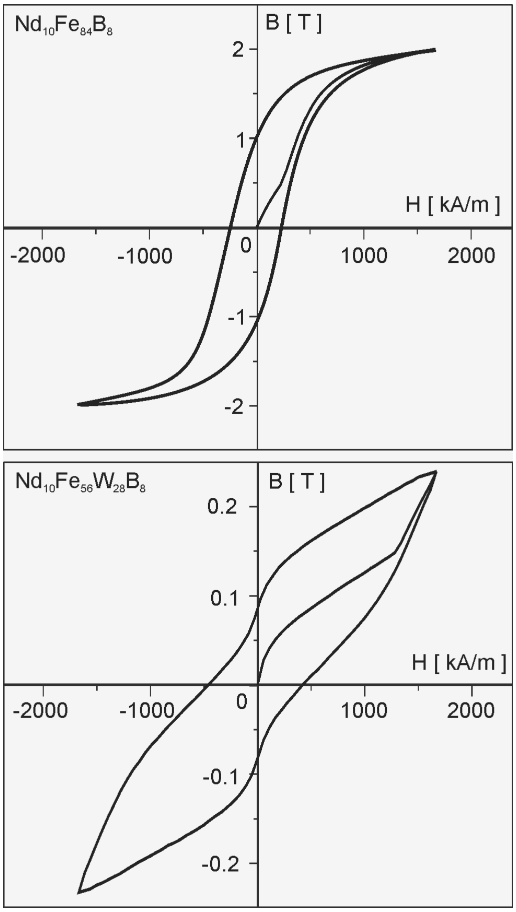

Fig. 6. The initial magnetization curves and magnetic hysteresis loops for the $Nd_{10}Fe_{84}B_6$ alloy milled for 90 h and the $Nd_{10}Fe_{56}W_{28}B_6$ alloy, respectively, performed at room temperature in a magnetic field up to 1.67 MA/m

4. Conclusions

The paper has presented the results of the microstructural and magnetic examinations of $Nd_{10}Fe_{84}B_6$ alloys subjected to prolonged milling. The composition of the $Nd_{10}Fe_{84}B_6$ alloy was modified by adding tungsten in place of iron atoms. The examinations have shown that the grinding duration, for which the best magnetic properties are obtained, is 90 hours. Prolonged grinding has a significant effect on the grain size and microstructure refinement. The alloy addition in the form of

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