STRUCTURE AND MAGNETIC PROPERTIES IN THE MIXTURE OF FE AND BN POWDERS AFTER HIGH-ENERGY BALL MILLING AND ANNEALING

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Abstract

The effect of high-energy ball milling a mixture of Fe and h-BN with weight ratio of Fe:BN = 15, 4, 1, 0.36 on the phase composition and magnetic properties of the synthesized material has been investigated. High-energy ball milling demonstrated a significant change in the phase content, structure, and magnetic characteristics upon MA and followed annealing at 600 ^{0}C, in particular upon annealing, and the coercivity of the MA powder reached H_C = 43 kA/m (540 Oe).

Keywords: Mechanical alloying, mixture of Fe and BN, iron nitrides, saturation magnetization, coercivity

1. INTRODUCTION

Permanent magnets play a crucial role in new areas of science and technical. Currently, the most widely used permanent magnets are $Nd_2Fe_{14}B$ and $SmCo_5$, both containing rare-earth (RE) elements. The RE crisis has stimulated researchers to investigate new magnetic alloys with moderate properties between hard ferrites and RE permanent magnets. Among the RE-free hard magnetic materials, the metastable tetragonal α"-$Fe_{16}N_2$ phase of iron nitrides has attracted considerable attention due to the low cost of Fe and high magnetization of α"-$Fe_{16}N_2$. The usual approach to form nitrides is gas-phase interstitial modification [1]. In the past years, the efforts to synthesize bulk samples of the Fe-N phases have been made [2-5]. However, the synthesis of Fe-N alloys by gas-solid reaction is usually difficult to be performed. Therefore, it is of interest in using a kind of solid N source in producing of new Fe-N phases. It is suggested the BN powder to be as a candidate for new-phase production [6-8]. One of approaches to obtain iron nitrides is the solid-state reactions by mechanical activation milling (mechanical alloying, MA) a mixture of Fe and *h*-BN [9-13] or Fe and NH_4NO_3 [14-17].

The aim of this work thus was to investigate the phase composition, structure and magnetic properties of materials prepared via mechanical alloying of a mixture of Fe and h-BN powders with a weight ratio Fe:BN from 15 to 0.36 after their extraction from the mill chamber in the air and upon the subsequent annealing at 600 ^{0}C in the nitrogen atmosphere.

2. EXPERIMENTAL

The powder mixtures of Fe (PZhR-3.200.28) and *h*-BN (manufactured by "Plazmoterm") were prepared with weight ratio of Fe:BN = 15, 8, 4, 1 and 0.36. The high-energy ball milling was carried out in the Aktivator-2S in the nitrogen atmosphere with milling lifetime varied from 7 to 60 h. The MA powders were compacted using press moulding at 40 MPa. The pressed samples were annealed within 2-5 h in the nitrogen atmosphere at 200-600 °C. The X-ray phase analysis was performed by diffractometer DRON-4 using CoK_α radiation. Qualitative and quantitative phase analyses were done using the software described in [18]. The microstructure of samples was observed in the scanning electronic microscope (SEM) JEOL JSM-6610LV. The differential thermal analysis (DSC) was carried out in the synchronic thermal analyzer Netzsch STA 449 F3 Jupiter (the

heating rate was 10 K/min). Magnetic properties were examined by the vibrating sample magnetometer VSM 250 (Dexing Magnet Tech Co. Ltd) in magnetic field up to 2.5 T.

3. RESULTS AND DISCUSSION

The powder mixtures were studied with ratio of Fe:B = 15; 8; 4; 1 and 0.36). It is found that α-Fe lines and an X-ray amorphous phase (AP) are identified for the samples with ratio of Fe:BN ≤ 4 by the XRD analysis upon MA, 60 h, whereas for others, only the α-Fe lines are characterized. **Figure 1** shows diffraction of Fe, h-BN, Fe:BN = 1 powders upon MA, 60 h and Fe:BN = 1 followed by MA powder annealing at 600 °C, 2 h. The MA of pure Fe powder resulted in lines broadening and a slight change in lattice parameter a of α-Fe. The period is increased from 0.2866 to 0.2869 nm upon MA, 60 h (**Figure 1a**). Two halos are observed in regions near θ = 30° and 50° in the ground BN-powder spectra (**Figure 1b**), which indicate X-ray amorphous phase (XAP) formation upon MA, 60 h. In the pattern profile of the MA powder with ratio of Fe:BN = 1 there are only α-Fe peaks and the halo near θ ≈ 30° occurred (**Figure 1c**). The lattice period of α-Fe is incremented to 0.2872 nm upon MA, 60 h due to a feasible presence of B atoms in addition to the N in the interstitial positions of the Fe lattice. An observed asymmetric broadening of Fe (110) line in the area of smaller angles indicates the onset of iron nitride formation. Annealing the MA powders at 600 °C for 2 h narrowed the α-Fe peaks and decreased the volume of XAP, and produced weak new lines at small angles, probably from iron nitrides (**Figure 1d**).

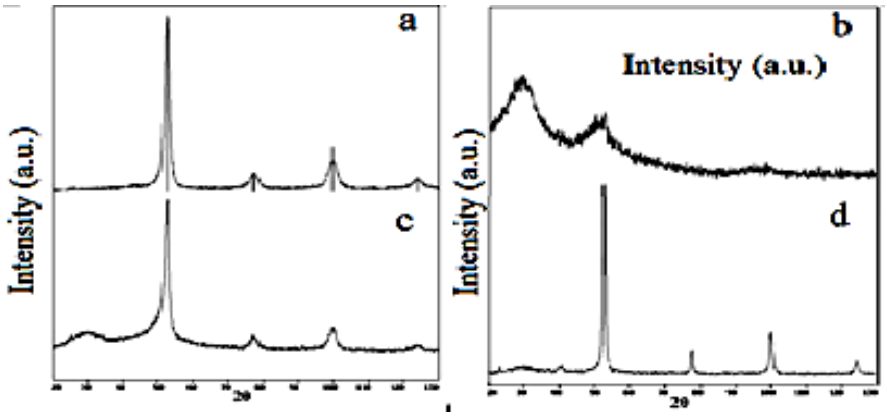

Figure 1 The XRD diffraction patterns of powders upon MA, 60 h: (a) pure Fe; (b) pure BN; (c) Fe:BN = 1 powder, and (d) the same powder upon annealing at 600 °C. Vertical dashed lines show the α-Fe peaks

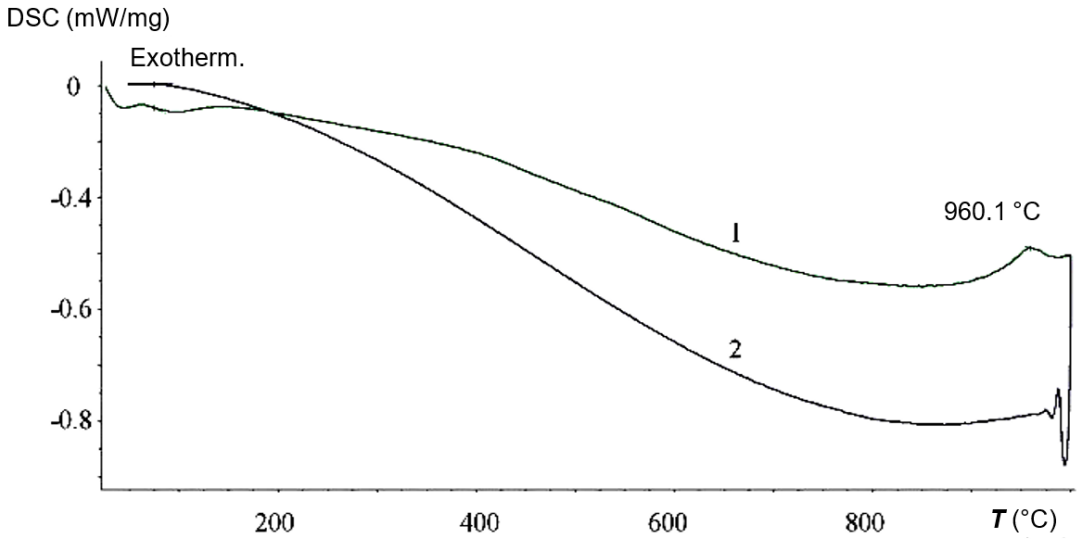

Figure 2 DSC data of the sample Fe:BN = 1 upon MA, 60 h: (*1*) heating, (*2*) cooling

Differential scanning calorimetry demonstrates (**Figure 2**) that exothermic maximum on DSC curves in the range of 20 to 700 °C specific to amorphous phase transformation into crystalline phase, as the first order phase transition, is not observed. Contrarily, the delivered DSC results indicate the endothermic behaviour, besides the sample weight reduce is observed at temperatures exceeding 500 °C.

It is known [19] that after the MA procedure the contact of BN particles with air at the stage of powder extraction from the mill chamber is reported to boron oxides and nitrogen oxides formation. Under the conditions considered in [19], this transformation occurs at temperatures above 1500 °C at 5.5 GPa. Therefore, we assume that the absence of an exothermic peak on DSC curves may be associated with crystallization of amorphous BN, which occurs at temperatures exceeding the data given in **Figure 2**.

Figure 3 shows the microstructure of the pure Fe powder and Fe:BN = 15, 4, 1 powders upon MA, 60 h. The images were obtained via SEM of compacted powders. The pure Fe upon MA (**Figure 3a**) is consisted of particles with average sizes of 500–3000 nm, some of which have anisotropic shapes. The MA powders of Fe:BN = 15 and 4 are contained of equiaxial particles with sizes of 200–500 nm (**Figures 3b,c**). The Fe:BN = 1 powder upon MA is contained of low contrast Fe particles (average size, ~100 nm) in the amorphous-like matrix phase (**Figure 3d**).

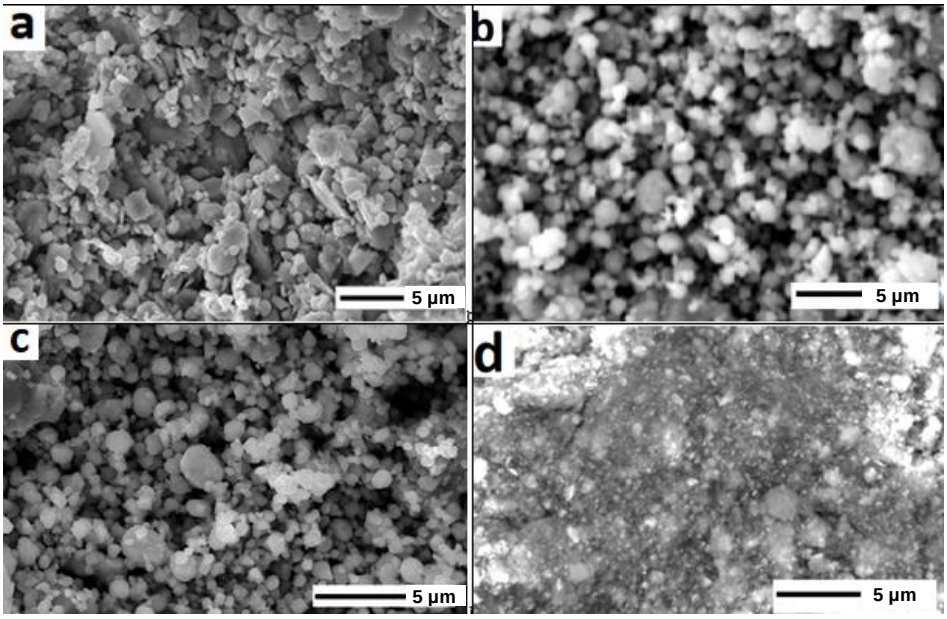

Figure 3 SEM images of the samples upon MA, 60 h: (a) pure Fe; (b) Fe:BN = 15; (c) Fe:BN = 4 and Fe:BN = 1 (d)

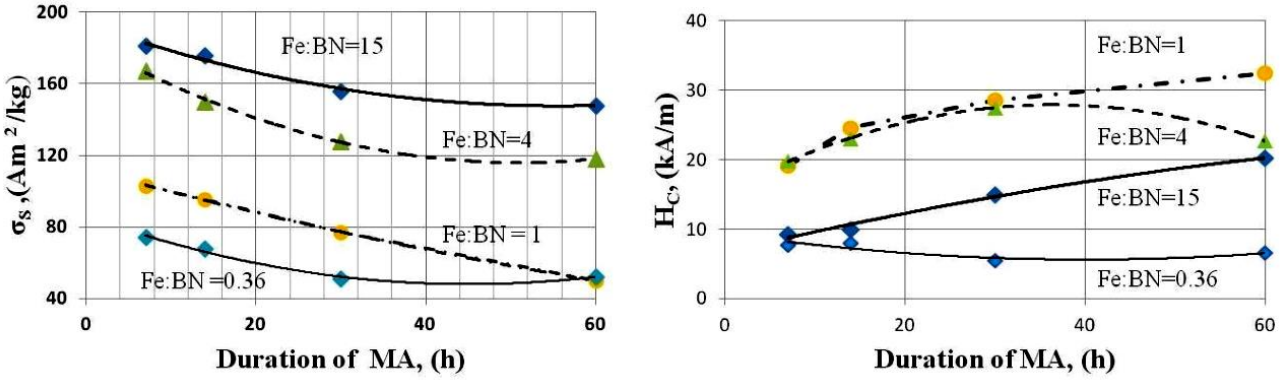

Figure 4 Dependences in σ_S and H_c of the Fe-BN samples upon MA, 60 h versus MA lifetime

Figure 4 shows the influence MA duration on magnetic properties of the samples Fe:BN = 15, 4, 1, 0.36 upon MA, 60 h. Apparently, a specific saturation magnetization is reduced monotonically, while the coercivity is increased with the MA lifetime arise to 60 h. The maximal value of H_c is observed on MA powders with a weight ratio Fe:BN = 1.

In our previous work [11], the elemental composition of the powder with ratio of Fe:BN = 1 upon MA for 60 h via X-ray photoelectron spectroscopy (XPS) has been investigated. The obtained data revealed two processes induced by the high-energy milling of Fe and *h*-BN mixtures as: i) the physical milling of particles and ii) interaction between mechanically activated particles of Fe and BN with atmospheric oxygen and water vapour after their extraction from the mill chamber.

The effect of iron content in the Fe-BN mixture after MA, 60 h to the size of coherence scattering regions (<D>) and microscopic deformation value **<ε>** is shown in **Figure 5a**. The changes of <D> and **<ε>** with increasing duration of MA for the sample Fe:BN = 15 are shown in **Figure 5b**. The second process results in interaction the MA powder with O_2 and H_2O during the MA , and produces chemical bonds Fe-N, Fe-B, and Fe–O on the surfaces of Fe particles due to the formation of iron nitrides, borides, and metahydroxide FeO(OH) [20]. In addition, the interaction between boron and oxygen results in the formation of amorphous B_2O_3. The annealing of the Fe-BN powders upon MA at temperatures ranging from 200 to 600 °C in the nitrogen atmosphere leads to the Fe_4N nitride formation and decomposition of FeO(OH), which transforms to oxide Fe_3O_4 in the surface layers of α-Fe particles.

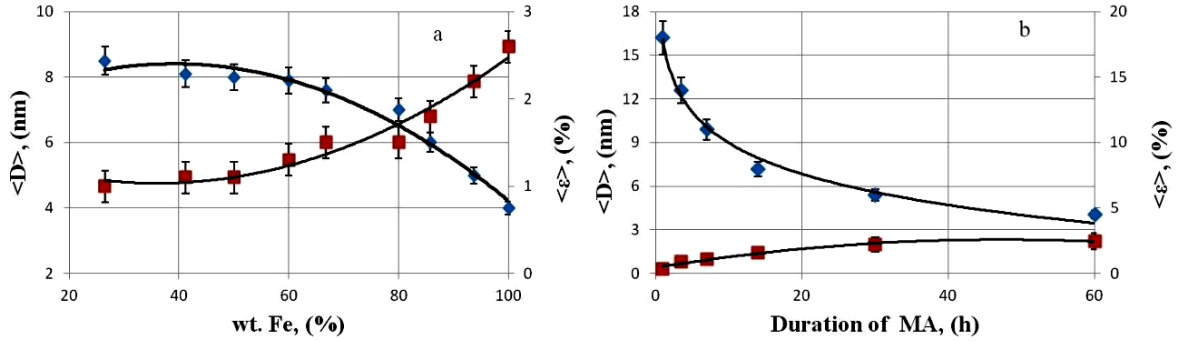

Figure 5 Dependences of <D>size and <ε> value versus iron contents in the powders Fe-BN upon MA, 60 h (a) and versus the duration of MA for the sample Fe:BN = 15 (b)

Figure 6 presents the hysteresis loops of the Fe:BN = 1 powder upon MA, 60 h and followed by 2 h of annealing in the nitrogen atmosphere at 600 °C. All hysteresis characteristics are increased after annealing: H_c from 32.5 kA/m to 42 kA/m, σ_s from 40.6 to 65.7 A·m²/kg, σ_r from 9 to 15 A·m²/kg.

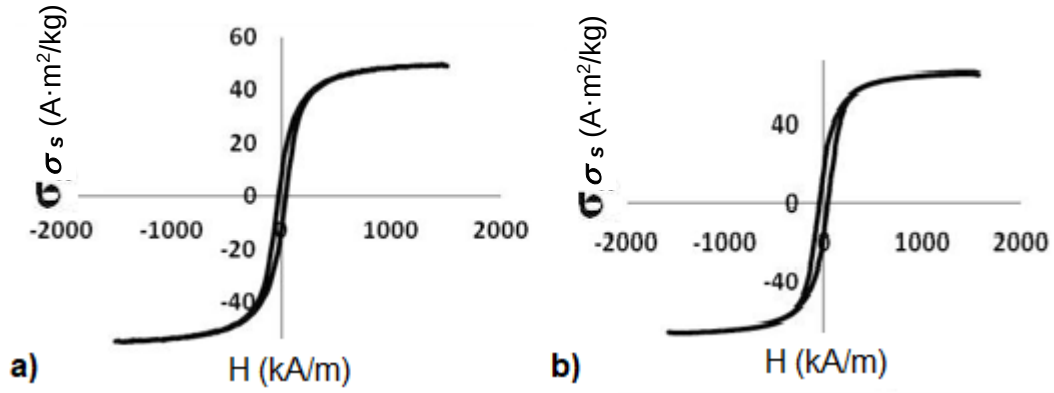

Figure 6 Hysteresis loops of the Fe:BN = 1 powders (a) upon MA, 60 h, and (b) after annealing the MA powders in nitrogen at 600 °C

The demagnetization curves analysis demonstrates that the coercivity is related to domain walls pinning on non-equilibrium structural defects (dislocations, vacancies, internal strains, and surface impurities) are originated during MA. The other reason of pinning may be concerned with nanoparticles of oxides and nitrides formed in the surface layer of iron particles during MA and subsequent annealing, when the influence of non-equilibrium structural defects are relaxed and their influence as pinning centres decreased.

4. CONCLUSION

Our studies showed that the high-energy milling of Fe and h-BN powders mixture in a planetary ball mill allows obtaining the magnetically hard material from initially soft magnetic iron. The coercivity of milled powders increases with the raise of the mechanical milling duration.

The annealing of the Fe-BN powders after MA at temperatures ranging from 200 to 600 °C in the nitrogen atmosphere leads to the nanoparticles Fe_4N and Fe_3O_4 formation in the surface layers of α-Fe particles which resulted in pinning of domain walls and high coercivity. The maximum obtained magnetic properties for the sample Fe:BN = 1 followed by annealing at 600 °C within 2 hours in the nitrogen atmosphere as follows: saturation magnetization σ_s = 66 Am^2/kg, H_c = 42 kA/m.

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