MICROSTRUCTURE AND PROPERTIES INVESTIGATIONS OF ALLOYS PREPARED BY AGING OF Fe-BASED ALLOY POWDERS MIXTURED WITH NITRID POWDERS (BN, Si_3N_4, AlN)

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Abstract

In the present work, the route of preparation for specimens by high temperature aging of preliminary pressed mixture (briquettes) of the Fe powder with differ nitride powders (BN, Si_3N_4, AlN) is suggested and the microstructure and magnetic properties of the synthesized alloys are studied. The pressed briquettes from iron and nitride powders mixture in desired proportions were heated in the nitrogen atmosphere till temperatures of 1300-1550 °C and held for 3 hours, and subsequently cooled along with the furnace. As a result of the solid or liquid-phase reaction within the sintering process, the ceramic is formed upon the heat-treatment of briquettes and the spherical metal fragments exudation on the surface of ceramic part of the briquette was observed. After aging the sample (Fe+33 wt.% BN) the composition of the spherical metallic fragment was comprised of 50 % Fe-30 % N-20 % B. Themicrostructure includes the eutectic structure between primary iron grains. The eutectic consists of Fe precipitates, as dendrites and the dark boride phase. In eutectics, the boride phase composition changes B from 9 to 24 at. % close to the stoichiometry of the metastable Fe_3B compound. The microstructure of the metallic fragment of the sample (Fe + 35 wt.% Si_3N_4) consists of grains of the Fe-Si phase with composition 17 at. % Si - 83 at. % Fe. The microstructure of the metallic fragment of the sample (Fe + 22.5 wt.% AlN) consists of grains of the Fe-Al-based phase with composition 70 at. % Fe - 14.5 at. % Al - 15.5 at.% N. The obtained metal fragments are characterized by relatively high coercivity (8-10.3 kA/m) comparable to those fine films and nanosized iron powders produced by gas nitrogenation.

Keywords: Powder metallurgy, boron nitride, silicon nitride, aluminium nitride, microstructure

1. INTRODUCTION

The nitrides of Fe and rare-earth intermetallic compounds have attracted an increasing interest due to their unique magnetic properties and potential applications as permanent magnets [1-4]. The recent investigations are associated with search of new hard magnetic compounds with lean rare-earth compositions. One focus was governed to the ordered compound α"-$Fe_{16}N_2$ for which as increased saturation as well a considerable anisotropy constant have been reported. The second, the $RFe_{12}N$ compounds that saturation could be higher than those of $Nd_2Fe_{14}B$ while maintaining a comparable anisotropy field. The preparation of nitrides involves a number of difficulties. In the last years, Fe-N alloys were prepared in forms of thin layer or nanosized powders by gas-solid reaction of Fe and N_2, NH_3 or NH_3/H_2 via vapor deposition or magnetic sputtering and subsequent annealing [5]. Synthesis of Fe-N alloy under high pressure by gas-solid reaction is difficult to be performed. In particular, it is not possible to obtain pure α"-$Fe_{16}N_2$ by gas nitrogenation because the solubility of nitrogen in austenite is less than the required 11.1 at. % per the established stoichiometry. Therefore, it is important to use the solid N source for the preparation of Fe-N alloys.

In the present work, the route of preparation for Fe-N alloys by high temperature aging of preliminary pressed mixture (briquettes) of the Fe powder with differ nitride powders (BN, Si_3N_4, AlN) is suggested and the microstructure and magnetic properties of the synthesized alloys are studied.

2. EXPERIMENTAL PROCEDURE

The following materials have been used in the present work: commercially manufactured iron powder of grade PZhR 3.200.28 (mass fraction): C ≤ 0.05; Si ≤ 0.05; Mn ≤ 0.20; S ≤ 0.02; P ≤ 0.02; particles size from 0.05 to 0.16 µm; powder of boron nitride with the content of the main component at least 97%; fraction's content with the particles size less than 100 µm. The crystalline boron with boron content of at least 97% was also used in the present work. Powder mixing was performed in a turbulence mixer C2.0 with frequency of 40 rpm within 1 hour. The compacting (briquettes) from powder mixtures were prepared by the hydraulic laboratory press under the pressure of 40 MPa. Heat treatment of briquettes was conducted in the electric vacuum furnace VOzh-16-22 (crucibles - Al_2O_3). During heat treatment in gas, nitrogen with nitrogen content of 99.996% and argon with the argon content of 99.993% were used there. X-ray diffraction spectra were measured by XRD DRON-4 with CoK_α radiation; quality and quantity phase analyses were measured by Rietveld full-profile analysis method using software program as well the described method in the present work [6]. The microstructure of samples was examined by scanning electron microscopy (SEM) method on Hitachi S-3400N with accessory for energy-dispersive X-ray micro-analysis (EDX). Magnetic characteristics were measured by hysteresisgraph AMT-4 and vibrating sample magnetometer VSM-250.

3. RESULTS AND DISCUSSION

3.1. Fe-4 %B alloy prepared by melting

The as-cast Fe-4 wt.% B alloy was prepared from iron powder and crystalline boron by melting in an argon-arc furnace. The SEM/BSE images of this alloy are shown in **Figure 1**. The image in **Figure 1a** demonstrates the eutectic microstructure that corresponds to the diagram Fe-B. The dark regions are the iron boride phase, and the light gray imaged regions correspond to iron-based solid solution. The high magnification image in **Figure 1b** shows the heterogeneous composition of the gray regions.

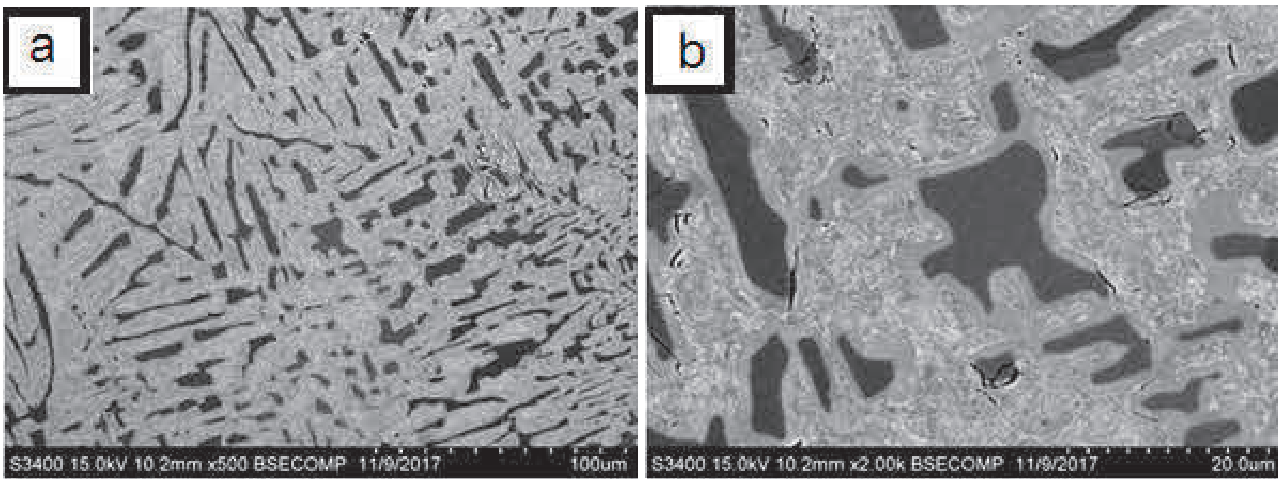

Figure 1 SEM microstructural images of the as-cast Fe-4 wt.% B alloy prepared by melting in an argon-arc furnace

The as-cast sample has $\acute{o}_s$ = 205-215 emu/g and coercive field of H_{ci} = 8-8.5 kA/m, which is attributed to hard-magnetic materials.

3.2. Fe-based alloy prepared by mixturing Fe and BN powders

Figure 2 shows images of the sample (Fe+33 wt.% BN)prepared by heating in the nitrogen atmosphere to a temperature of 1550 °C, 3 h. The pressed briquette from a mixture of iron and boron nitride powders was heating in the nitrogen atmosphere to a temperature of 1550 °C, holding for 3 hours, and then cooling with furnace. As a result of the solid or liquid-phase reaction within the sintering process, the heat-treated sample (see insert in **Figure 2a**) consists of two parts: a sintered composite (hereinafter referred to as "ceramic") and spherical metal fragments which were crystallized as drops on the surface of the ceramic. The composition measured at the surface of the metal fragment corresponds to 20 at.% B - 30 at.% N - 50 at.% Fe (**Figure 2b**).

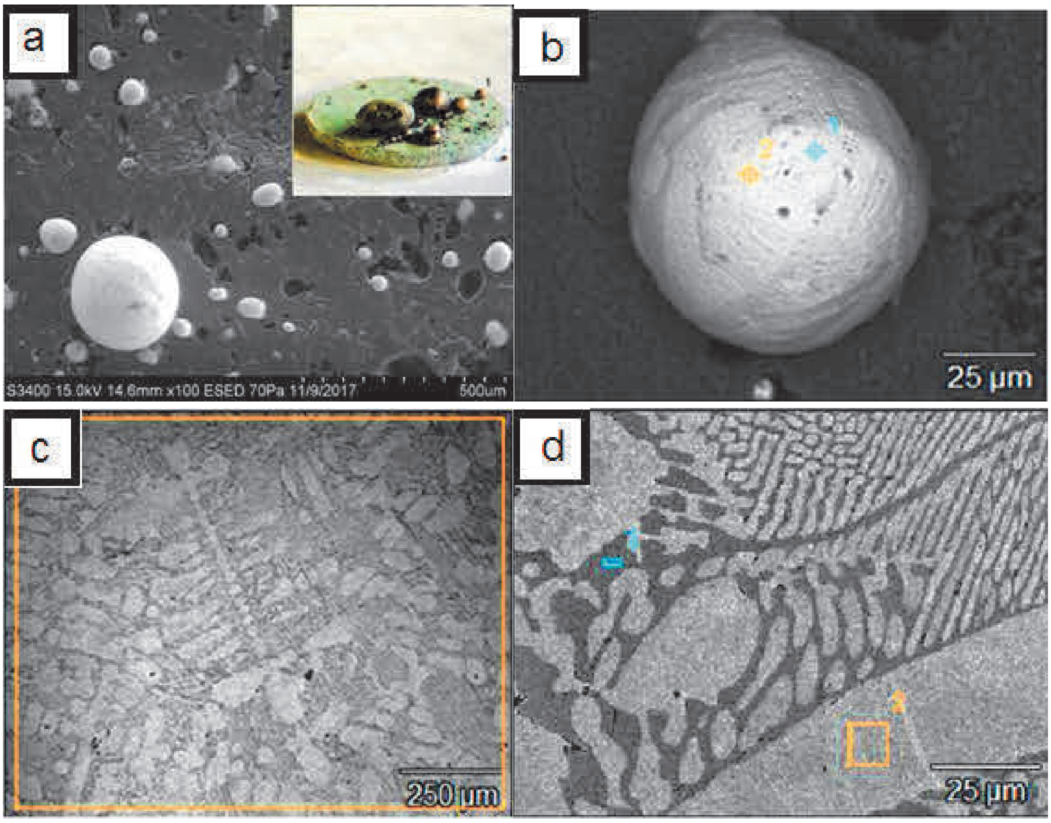

Figure 2 SEM microstructural images of the sample (Fe+33 wt.% BN) prepared by heating to a temperature of 1550 °C. The surface of the ceramic part (a); the spherical metal fragment (b); BSE SEM images of the metal fragments after polishing (c, d)

The composition of the metal fragment after polishing is 8.3 at.% B - 5.8 at.% N - 85.9 at.% Fe (**Figure 2c**). The eutectic structure between light primary iron grains consists of Fe precipitates, as dendrites and dark boride phase. In eutectics, the boride phase composition changes from 9 to 24 at.% B close to the stoichiometry metastable Fe_3B compound. The composition of the light regions corresponds to 100 at.% Fe (**Figure 2 d**). X-ray diffraction analysis showed that iron, Fe_2B phase and a small amount of Fe_3B metastable phase, as well as iron nitrides in the total amount up to 16% by volume, are present in the structure of the metal part of the sintered sample. The observed eutectic structure differs a bit from ordinary eutectic structure Fe-Fe_3C and Fe-Fe_2B, in which the intermediate phases (carbides, borides) grow as the leading phase, and the second phase, a solid solution based on iron, forms three-dimensional dendrites with rounded section of branches. Low boron content in the leading phase (9-24 at.% B), compared with stoichiometric Fe_2B, suggests that the missing amount of boron is associated with the replacement of a part of the boron atoms in this phase by nitrogen atoms, and with the presence in the leading phase, along with borides, iron nitrides. The as-cast sample has $ó_s$ = 110 emu/g and coercive field of H_{ci} = ~10.3 kA/m, which obviously is attributed to hard-magnetic materials. In the work [7] the single phase of Fe_xN was produced by mechanical milling a mixture of Fe and boron nitride. However, Fe-B alloy was no obtained during these experiments. This fact was concluded that that Fe-B compound is prepared with more difficulty than the Fe-N compound [7]. But the present experimental results mentioned above indicate that mainly Fe-B alloy was formed by the solid-state reaction of Fe and BN during aging but Fe-N compound was also produced.

3.3. Fe-based alloy prepared by mixing Fe and Si_3N_4 powders

Figure 3 shows images of the sample (Fe + 35 wt.% Si_3N_4)prepared by heating to a temperature of 1500 °C, 3 h. BSE SEM image of the ceramic part shows the mixture of the Fe-based and Si-N particles(a).BSE SEM image of the metal fragment shows the single-phase microstructure(b). The composition of the metal fragment is 18 at. % Si-82 at.% Fe. The sample has coercive field of H_{ci} ~4.7 kA/m, $\acute{o}_s$ = 106 emu/g.

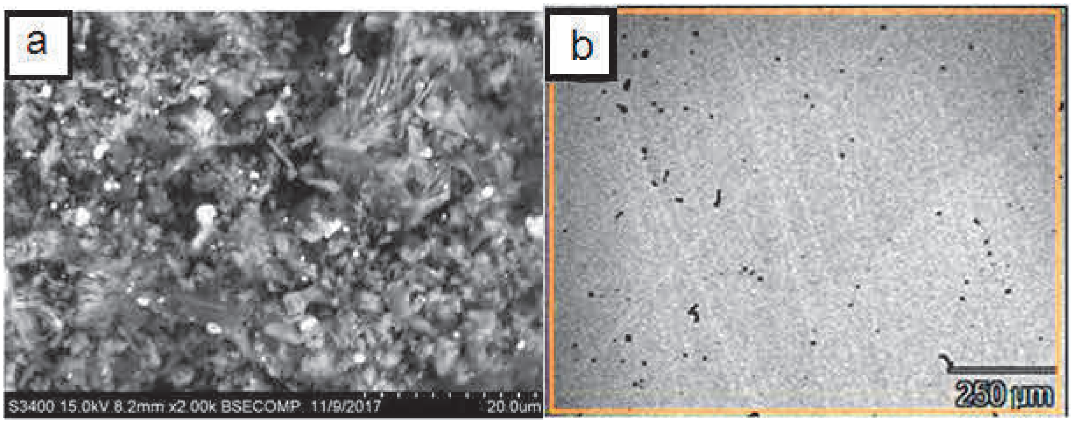

Figure 3 SEM microstructural images of the sample (Fe + 35 wt.% Si_3N_4)prepared by heating to a temperature of 1500 °C. BSE SEM images of the ceramic part (a) and of the metal fragment (b)

3.4. Fe-based alloy prepared by mixing Fe and AlN powders

Figure 4 shows images of the sample (Fe + 22.5 wt.% AlN) prepared by heating in the nitrogen atmosphere to a temperature of 1500 °C, 3 h. BSE SEM image of the ceramic part shows the mixture of the Fe-based and AlN particles(a). BSE image of the metal fragment shows the single-phase microstructure (b). The composition of the metal fragment is 15 at. % Al -16 at. % N-69 at. % Fe. The sample has coercive field of H_{ci} ~5.8 kA/m, $\acute{o}_s$ = 111 emu/g.

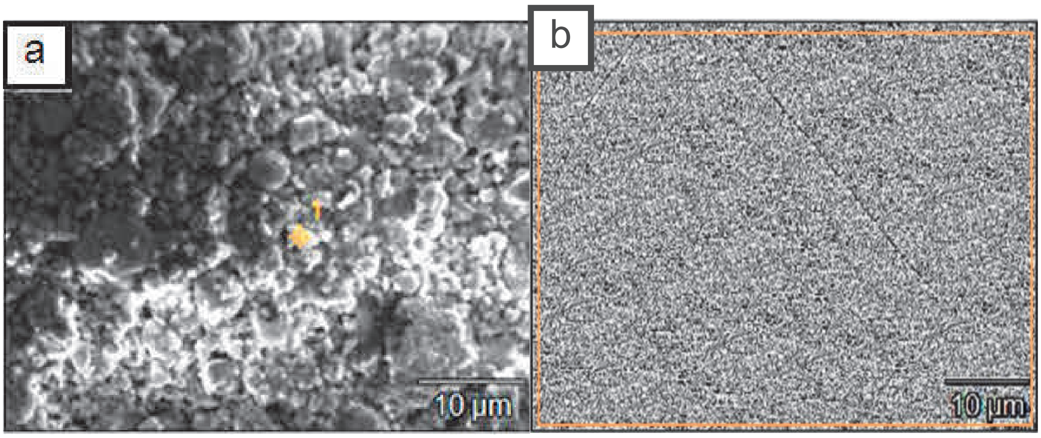

Figure 4 SEM microstructural images of the sample (Fe + 22.5 wt.% AlN) prepared by heating to a temperature of 1500 °C. BSE SEM images of the ceramic part (a) and of the metal fragments (b)

4. CONCLUSION

The route of preparation for alloys by high temperature aging of preliminary pressed mixture (briquettes) of the Fe powder with differ nitride powders (BN, Si_3N_4, AlN) was investigated. The resulting products of solid-state reaction between Fe and nitride were the metal fragments of spherical shape formed on the ceramic part surface of the sintered briquette. For the Fe-BN mixture these fragments comprise of iron borides similar to the composition of intermetallic compound Fe_3B and nitride phase as components of the eutectic, while the ceramic part consists of boron nitride, iron, and iron nitride. For the Fe-Si_3N_4 and Fe-AlN mixtures the metallic fragments consisted of iron-based solid solution which comprises silicon or aluminium and nitrogen. It is demonstrated that metal fragments of sintered briquettes exhibit hard-magnetic properties, H_{ci}= 10 - 30 kA/m, hence, the method of their fabrication is promising in developing of free rare-earth hard magnetic materials.

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