

EFFECT OF MILLING MEDIUM ON THE STRUCTURE AND MAGNETIC PROPERTIES OF MECHANICALLY ALLOYED BARIUM FERRITE

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Abstract. Mechanical alloying of the mixture of Fe_2O_3 and BaCO_3 powders in water leads to partial decomposition of barium carbonate and probably formation of barium hydrate $\text{Ba}(\text{OH})_2$. Application of steel vials for the milling in water results in their faster abrasive wear which is accompanied by enrichment of the powders in iron, in the form of Fe_3O_4 phase. Phase constitution of the materials studied after ferritization at 1000 °C/1h obtained by milling in water, consists of $\text{BaFe}_{12}\text{O}_{19}$ matrix with BaFe_2O_4 and Fe_3O_4 precipitates, whereas the sample obtained by milling in air contains only $\text{BaFe}_{12}\text{O}_{19}$ matrix with numerous Fe_3O_4 precipitates. The change in the microstructure does not explain however the differences observed in the magnetic properties, especially in the shape of the hysteresis loops. After milling in water the demagnetisation is dominated by nucleation of reverse domain whereas for the specimen milled in air conditions of pinning to the coercivity mechanism is evidenced.

1. INTRODUCTION

Hard magnetic barium ferrites maintain their strong position on the magnet market, due to their low cost and chemical resistance [1]. Recently nanocrystalline ferrites attract substantial attention due to their prospective applications for magnetic recording [2].

Magnetic properties strongly depend on the grain size [3]. High coercivity materials have nanoscale crystallites [4]. Nanocrystalline barium ferrite can be obtained by mechanical alloying [5].

The process uses Fe_2O_3 and BaCO_3 as starting components and comprises two stages: (i) high energy ball milling of the powders and (ii) annealing (ferritization) of the milling product [6]. After the

first stage the only crystalline phase present was Fe_2O_3 [5]. Increase of the further ferritization temperature resulted in increasing volume fraction of the $\text{BaFe}_{12}\text{O}_{19}$ phase and coarsening of the microstructure. Intensity of these both processes, influences the magnetic properties in the opposite manner and determines on the optimal ferritization temperature.

Homogenous distribution of the powder particles after milling is an important factor affecting the ferritization process and the magnetic properties of magnets. From this point of view, milling in water should be beneficial for the material properties, because distribution of particles size is narrower than in the case of milling in air [3], however, most of the reported experiments were carried out in air.

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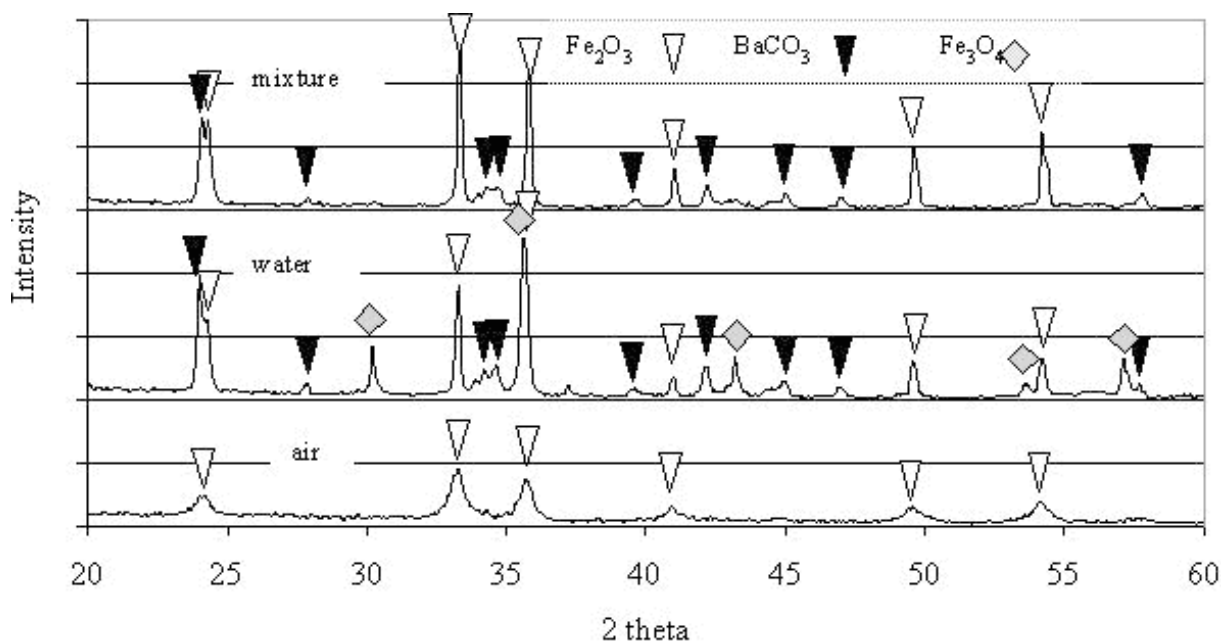


Fig. 1. Diffraction patterns of mixture of Fe_2O_3 and BaCO_3 powders after milling in water and air, respectively.

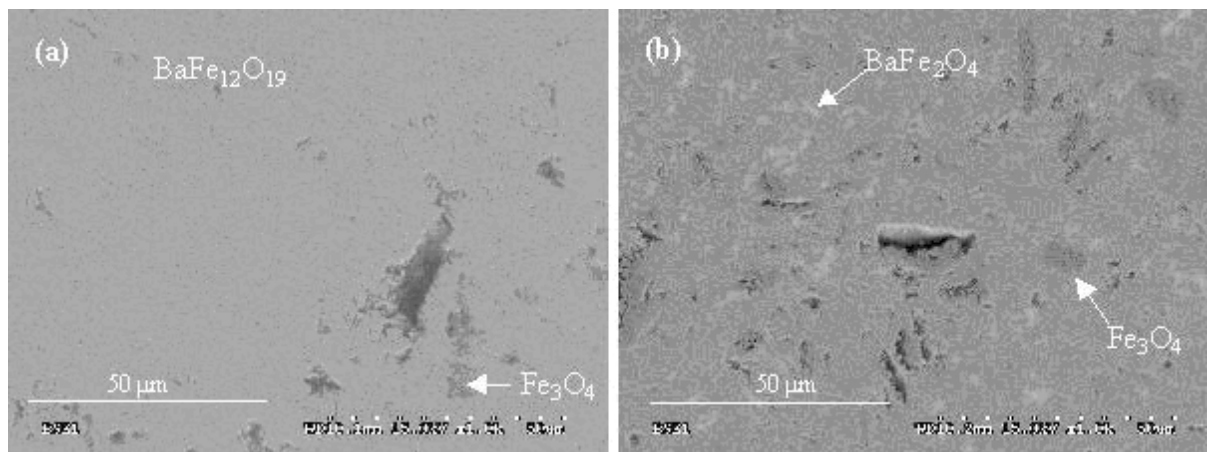


Fig. 2. BSE image of shock compacted magnets produced by milling for 8 h in air (a) and water (b), respectively and ferritization at $1000\text{ }^\circ\text{C}$, for 1 h in air.

In this study the powders were mechanically alloyed in water and air, respectively. The phenomena occurring in both processes, in the course of intensive milling of Fe_2O_3 and BaCO_3 powders, phase constitution after milling and further ferritization, as well as the magnetic properties were analysed.

2. EXPERIMENTAL

A mixture of powders: $5\text{Fe}_2\text{O}_3$ and 1BaCO_3 (atomic ratio iron to barium $\text{Fe}/\text{Ba} = 10$) (Aldrich, purity 99%,

grain size $< 5\text{ }\mu\text{m}$) was subjected to milling in Spex 8000 mill, in air or water. Mass ratio balls to powder was 10:1. Phase constitution of powders was studied using XRD. The ferritization was carried out at a $1000\text{ }^\circ\text{C}$ for 1 h in air. The magnetic properties were measured using VSM magnetometer. The gases evolved in the course of milling in water were analysed by mass chromatography GC-MS. The SEM observations were performed on the samples obtained by shock compacting. The details are described in [7].

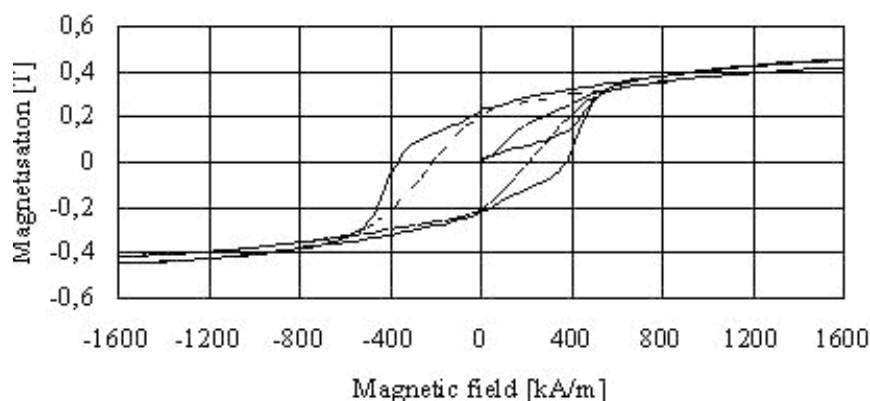


Fig. 3. Hysteresis loops for the magnets produced by milling for 8 h in water (dashed line) and air (solid line), respectively and ferritization at 1000 °C, for 1 h in air.

3. RESULTS AND DISCUSSION

Milling of the mixture of Fe_2O_3 and BaCO_3 powders in air, for 8h, resulted in amorphisation of barium carbonate [8] (Fig. 1), only peaks representing Fe_2O_3 phase are visible. The peaks from BaCO_3 phase are hidden in background. Gaseous products of the milling process were not detected.

Milling in water is accompanied by intense gas evolution. After 8h milling the only gaseous product detected was CO and N_2 . After 50hs milling the vial atmosphere contained 26% of air, 70% of hydrogen, and about 4% of organic compounds (ethane, methane, ethylene). Increased concentration of hydrogen ions in solution ($\text{pH}=8$), observed after milling, points to the presence of the OH -groups. One can assume that the milling starts with partial decomposition of the BaCO_3 and formation of BaO_2 peroxide, and CO according to the reaction: $\text{BaCO}_3 \rightarrow \text{BaO}_2 + \text{CO} \uparrow$. The BaO_2 peroxide reacts further: $\text{BaO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ba}(\text{OH})_2 + \text{O}_2$.

Oxygen produced in the reaction promotes oxidation of vials following the reaction: $2\text{Fe} + \text{O}_2 \rightarrow 2\text{FeO}$. Extended milling time promotes inhibition of the BaCO_3 decomposition.

Hydrogen, found in the vial after 50 hs milling, is formed in the course of the reaction of oxidation of iron from the vial in water. Formation of organic compounds and lack of CO in the gaseous products suggests that the conditions of the high-energy ball milling are sufficient for the synthesis of CO in the presence of H_2 following the reaction: $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$. X-ray phase analysis did not

show the presence of FeO , however, some proportion of Fe_3O_4 was detected (Fig. 1). This fact suggests the following reaction: $\text{FeO} + \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$. Ferritization at 1000 °C, for 1h in air, leads to formation of barium ferrite irrespective, of the milling medium. SEM investigations of these samples show different phase constitution (Fig. 2). The sample obtained by milling in water contains $\text{BaFe}_{12}\text{O}_{19}$ matrix with BaFe_2O_4 and Fe_3O_4 precipitates. In the sample obtained by milling in air only the $\text{BaFe}_{12}\text{O}_{19}$ matrix with few Fe_3O_4 precipitates was observed. The milling medium strongly affect also the coercivity. After milling in water the coercivity is markedly lower. The shapes of the hysteresis loops, and specifically the shape of the initial magnetization curves, evidence the differences in the magnetization mechanism for the specimen milled in different media (Fig. 3). After milling in water the demagnetization occurs by the characteristic for ferrites mechanism dominated by nucleation of reverse domain. However, the curve shape for the ferrites prepared by milling in air suggest substantial contribution from the pinning of domain walls to the magnetisation mechanism. Taking into account comparable crystallite size, for the both specimens, the grain boundaries cannot be regarded as pinning centres. Comparison of the microstructure of the both types of samples does not explain the differences in the coercivity mechanisms. Thus, we conclude that the coercivity mechanisms are determined by invisible here nanostructured elements of the microstructure.

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