

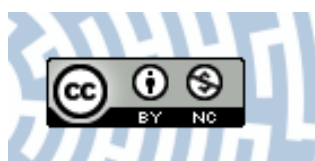


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Author: Grzegorz Dercz, R. Babilas, R. Nowosielski, Lucjan Pająk

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G. DERCZ*, R. BABILAS**, R. NOWOSIELSKI**, L. PAJĄK*

THE INFLUENCE OF MANUFACTURING CONDITIONS ON MICROSTRUCTURE AND MAGNETIC PROPERTIES OF BaFe₁₂O₁₉ POWDERS

WPLYW WARUNKÓW WYTWARZANIA NA MIKROSTRUKTURĘ I WŁASNOŚCI MEGNETYCZNE PROSZKÓW BaFe₁₂O₁₉

The aim of the paper was a trial of using mechanical alloying process of mixture iron oxide and barium carbonate to produce BaFe₁₂O₁₉ powders. The milling process was carried out in a vibratory mill for 10, 20 and 30 hours. The size distributions of powder particles showed that the size of tested particles increases with the increase of milling time indicating the agglomeration process of particles. The milling process of Fe₂O₃ and BaCO₃ mixture for studied milling times causes decrease of the crystallite size of involved phases and leads to increase of Fe₂O₃ phase content and decrease of BaCO₃ one. The milling process did not lead to formation of BaFe₁₂O₁₉ phase, thus it probably causes setting of Fe₂O₃ on surface layer of BaCO₃ powder particles. The XRD investigations of Fe₂O₃ and BaCO₃ mixture milled for 10, 20 and 30 hours and annealed at 1000°C for 1 hour enabled the identification of hard magnetic BaFe₁₂O₁₉ phase. For applied magnetic field of 800 kA/m, the coercive force is equal to 343 kA/m, 358 kA/m and 366 kA/m whereas the remanence is equal to 0.118 T, 0.109 T and 0.127 T for the samples after milling for 10, 20 and 30 hours, respectively.

Keywords: Barium ferrite; permanent magnets; high-energy ball milling; Rietveld, RVSM

Celem pracy była próba wykorzystania procesu mechanicznej syntezy mieszaniny tlenku żelaza (Fe₂O₃) i węglanu baru (BaCO₃) do wytworzenia proszków BaFe₁₂O₁₉. Proces mielenia przeprowadzono w młynie wibracyjnym w czasie 10, 20 oraz 30 godzin. Rozkłady wielkości cząstek proszków wykazały, że wielkość cząstek wzrasta ze wzrostem czasu mielenia wskazując, że w trakcie procesu mielenia następuje proces aglomeracji cząstek. Proces mielenia mieszaniny Fe₂O₃ i BaCO₃ dla zastosowanych czasów prowadzi do zmniejszenia wielkości krystalitów tych faz oraz do wzrostu udziału fazy Fe₂O₃ i spadku udziału fazy BaCO₃. Mielenie mieszaniny Fe₂O₃ i BaCO₃ w czasie 10, 20 i 30 godzin z następnym wyżarzaniem w 1000°C w czasie 1 godziny, prowadzi do powstania fazy magnetycznie twardej BaFe₁₂O₁₉. Dla przyłożonego pola magnetycznego 800 kA/m najwyższą wartość koerecji i remanencji uzyskano dla próbki mielonej w czasie 30 godzin i wyżarzanej w 1000°C, odpowiednio 366 kA/m i 0,127 T.

1. Introduction

Magnetism of all known elements and compounds has been tested and many materials were found to have some soft and hard magnetic properties [1,2]. Shams et al. [3] have shown that barium ferrites are well known hard magnetic materials, which are based on iron oxide. These materials are also called as barium hexaferrite as noticed Carp et al. [4] and could not be easily replaced by any other magnets.

BaFe₁₂O₁₉ barium ferrites are widely used in magnetic recording media, microwave devices and electromagnetic shielding fields as confirmed by Ding et al. [5]. Mali et al [6] have also mentioned that barium ferrite possesses relatively high Curie temperature, coercive

force, magnetic anisotropy field and good chemical stability and corrosion resistivity.

Barium ferrites are still widely used although they have less magnetic strength than rare earth magnets. The way of comparison of ferrite magnets and rare earth ones proposed by Martienssen and Warlimont [7] can be performed by determining the ratio of remanence (B_r), which is about 1:3, the ratio of coercive force (H_c), which is also 1:3 and the ratio of the maximum energy product (B_H)_{max}, which is about 1:10.

Many methods of synthesis have been developed to obtain a low production cost of barium ferrite [8-11]. Preparation of barium ferrite usually includes a stage of preparation of barium carbonate and iron oxide mixture

* INSTITUTE OF MATERIALS SCIENCE, UNIVERSITY OF SILESIA, 40-007 KATOWICE, 12 BANKOWA STR., POLAND

** INSTITUTE OF ENGINEERING MATERIALS AND BIOMATERIALS, SILESIAN UNIVERSITY OF TECHNOLOGY, 44-200 GLIWICE, 18 KONARSKIEGO STR., POLAND

and its annealing. Barium ferrites are also used to form sintered and elastic magnets with polymer matrix as introduced Makled et al. [12].

2. Experimental

The aim of the paper was a trial of using mechanical alloying process of mixture iron oxide (Fe_2O_3) and barium carbonate (BaCO_3) to produce $\text{BaFe}_{12}\text{O}_{19}$ powders. For synthesis of $\text{BaFe}_{12}\text{O}_{19}$, a mixture of Fe_2O_3 (99% purity) and BaCO_3 (99% purity) powders was used with composition of $1.1\text{BaCO}_3 + 6\text{Fe}_2\text{O}_3$. The ball milling process was carried out in a vibratory mill SPEX 8000 CertiPrep Mixer/Mill type for 10, 20 and 30 hours under argon atmosphere. The weight ratio of balls to milled material was 5:1. The heat treatment process of milled powders was realized in the electric chamber furnace THERMOLYNE 602°C at 1000°C in the air under atmosphere pressure for 1 hour.

X-ray data collection was carried out using the X-Pert Philips diffractometer equipped with curved graphite monochromator on diffracted beam and a tube provided with copper anode. The profiles of diffraction lines were recorded by "step-scanning" mode in 2θ range from 20° to 140° and 0.05° step. The Rietveld analysis was performed applying DBWS-9807 program that is an update version for Rietveld refinement with PC and

mainframe computers. The pseudo-Voigt function was used in the describing of diffraction line profiles at Rietveld refinement. The phase abundance was determined using the relation proposed by Hill and Howard [13]. The crystallite sizes of Fe_2O_3 and BaCO_3 phases were estimated using Williamson-Hall method [14].

The magnetic hysteresis loops of obtained powder material were measured by the Resonance Vibrating Sample Magnetometer (R-VSM). The idea of R-VSM presented by Wrona et al. [15] is based on the Faraday induction law and the original Foner solution. Samples oscillate parallelly to the direction of external magnetic field and the configuration of pick-up coils in the form of small Smith coils was applied.

The diameters of examined powder particles were determined using Fritsch Particle Sizer "Analysette 22" in measuring range from $0.1\ \mu\text{m}$ to $1180\ \mu\text{m}$.

3. Results and discussion

Comparison of diffraction patterns of as-prepared Fe_2O_3 and BaCO_3 mixture (0 h) and after milling for different times (10, 20, 30 h) shows the broadening of diffraction lines of both involved phases (Fig. 1). This effect indicates that ball milling causes the decrease of the crystallite size of tested phases and leads to homogenization of the milled mixture.

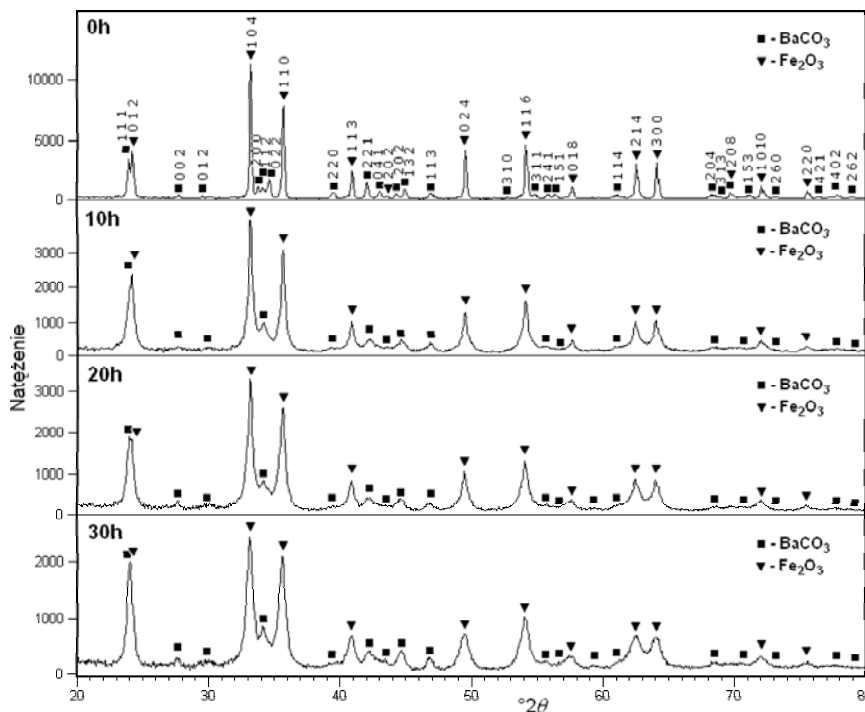


Fig. 1. X-ray diffraction patterns of Fe_2O_3 and BaCO_3 mixture after 0, 10, 20 and 30 hours of milling process

The crystallite size (D) of both Fe_2O_3 and BaCO_3 phases in as-prepared sample is above 100 nm. After milling process for 30 hours this size, diminishes to about 33 nm and 17 nm for Fe_2O_3 and BaCO_3 phases, respectively (Fig. 2).

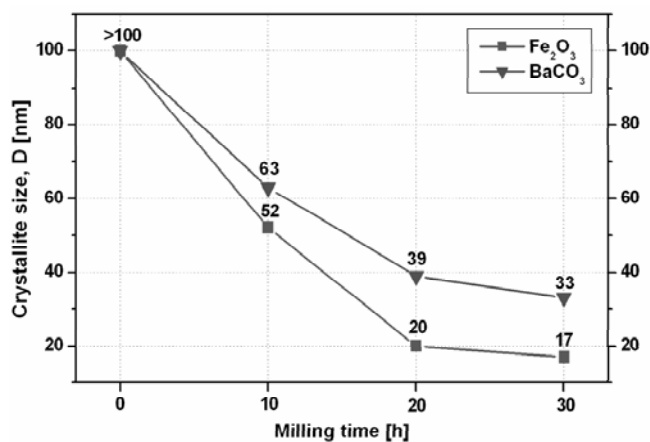


Fig. 2. Changes of average crystallite size (D) with the increase of milling time for Fe_2O_3 and BaCO_3 phases

The iron oxide (Fe_2O_3) phase is the main component of the tested mixture in asprepared sample (85.5(9) wt.%). On the other hand the content of BaCO_3 phase is much lower (14.5(2) wt.%). The milling process of Fe_2O_3 and BaCO_3 mixture leads to increase of the content of Fe_2O_3 phase and to decrease of the content of

BaCO_3 one (Fig. 3). After 30 hours of high-energy ball milling the contents of Fe_2O_3 and BaCO_3 phases are 91.0(9) and 9.0(1) wt.%, respectively. The milling process did not lead to formation of $\text{BaFe}_{12}\text{O}_{19}$ phase, thus it probably causes setting of Fe_2O_3 on surface layer of BaCO_3 powder particles.

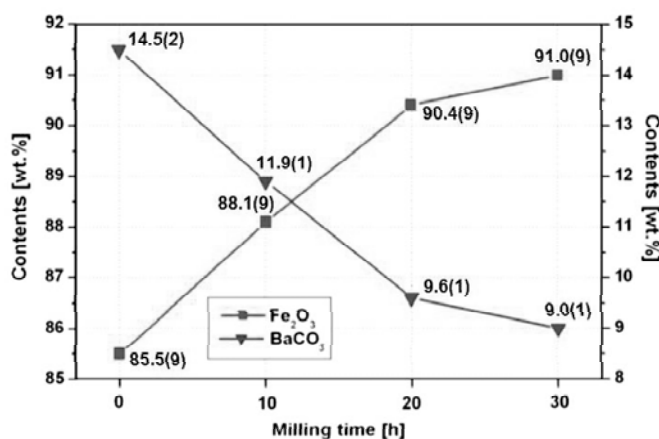


Fig. 3. Contents of Fe_2O_3 and BaCO_3 phases after different times of milling process

Figure 4 shows the SEM images of the sample milled for 10 and 30 hours, respectively. The images reveal that the specimens consist of fine-grained spherical particles. Moreover, the strong agglomeration of powders milled 30 hours was noticed.

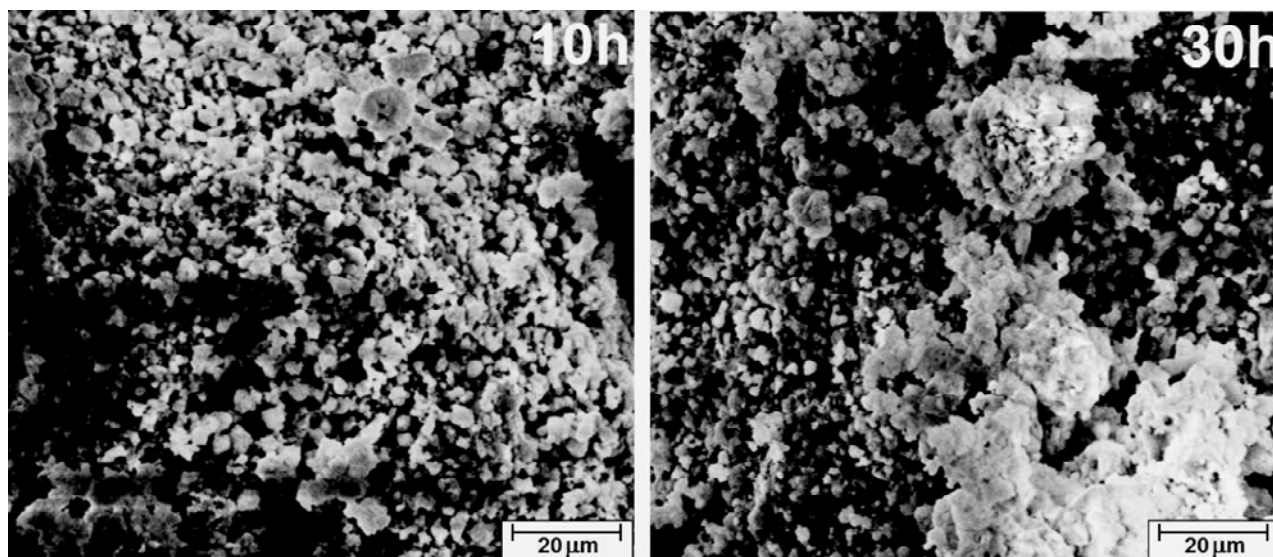


Fig. 4. The SEM images of milled samples for 10 (a) and 30 (b) hours

The size parameters of powder particles of Fe_2O_3 and BaCO_3 mixture after milling for 10, 20, 30 hours and their statistical means are presented in Table 1. The

increase of the size of powder particles as a result of milling process is clearly seen indicating the agglomeration of powder particles during milling.

The powder particle size of Fe_2O_3 and BaCO_3 mixture after different times of milling process

No.	Powder particle size [μm]	Milling time		
		10 h	20h	30h
1.	Arithmetic mean diameter	4.43(1)	6.63(8)	7.20(5)
2.	Geometric mean diameter	2.36(7)	3.07(4)	4.03(8)
3.	Quadratic square mean diameter	6.03(3)	9.56(9)	9.78(8)
4.	Harmonic mean diameter	1.03(3)	1.13(3)	1.74(1)
5.	Standard deviation	2.10(5)	2.57(6)	2.68(4)
6.	Median	3.16(5)	4.06(5)	4.82(9)

The X-ray diffraction investigations of Fe_2O_3 and BaCO_3 mixture milled for 10, 20 and 30 hours and annealed at 1000°C enabled the identification of hard magnetic $\text{BaFe}_{12}\text{O}_{19}$ phase (Fig. 5). Moreover, the X-ray

analysis also revealed presence of small amount of Fe_2O_3 phase in examined samples. The iron oxide is a rest of the reaction between BaCO_3 and Fe_2O_3 , which forms the $\text{BaFe}_{12}\text{O}_{19}$ compound.

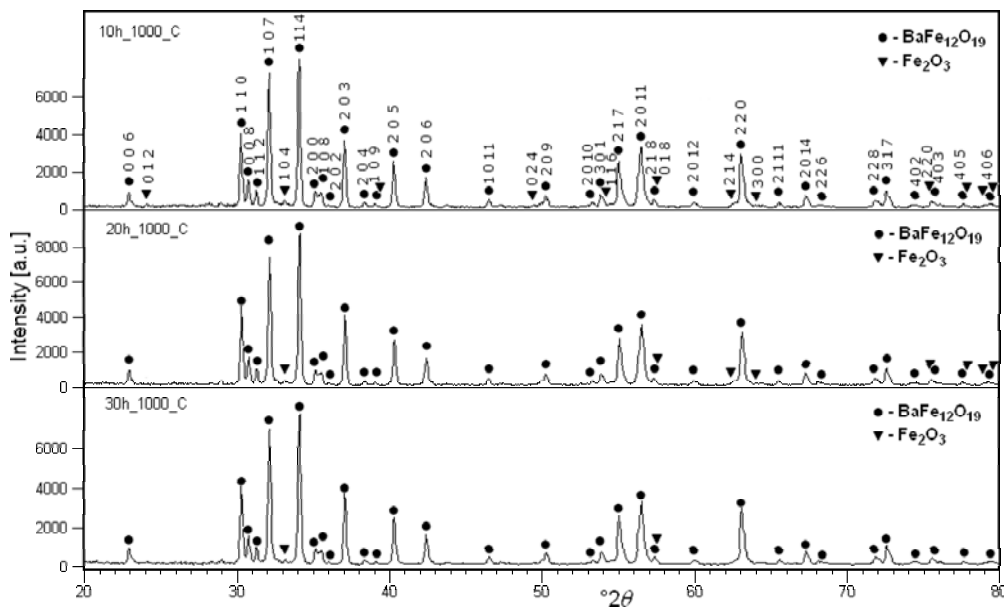


Fig. 5. X-ray diffraction pattern of Fe_2O_3 and BaCO_3 mixture after 10, 20, 30 hours of milling and annealing at 1000°C

The calculated weight percent of the each phases for the samples after annealed process using the mixture milled for 10, 20 and 30 hours reveals changes in the contents of both $\text{BaFe}_{12}\text{O}_{19}$ and Fe_2O_3 phases. At the milling time 10 h the fraction of the $\text{BaFe}_{12}\text{O}_{19}$ and Fe_2O_3 phases equal to 98.5(9) wt.% and 1.5(2) wt.%, respectively. Consecutive the longer milling time (20 and 30 h) the higher contents of the barium ferrites phase were observed up to a 98.9(9) and 99.1(9) wt., while iron oxide mass fraction decreases to 1.1(1) and 0.9(1) wt. for samples milled 20 and 30 hours, respectively. The values of fitting parameters R_{wp} , R_{exp} , and S (goodness-of-fit) obtained for all annealed samples are in the range of: $R_{wp}=8.38.8.84\%$, $R_{exp}=5.42.5.67\%$, and $S=1.54.1.56$.

The hysteresis loops of Fe_2O_3 and BaCO_3 mixture after different times of milling, measured at room tem-

perature in the applied magnetic field of 800 kA/m, are shown in Figure 6. The hard magnetic properties of tested mixture are very low because of lack of hard magnetic phase. The effect of milling and annealing at 1000°C on hard magnetic properties is presented in Figure 7. The coercive force is equal to 343 kA/m, 358 kA/m and 366 kA/m whereas the remanence is equal to 0.118 T, 0.109 T and 0.127 T for the samples milled for 10, 20 and 30 hours, respectively and annealed at 1000°C . The coercive force is equal to 343 kA/m, 358 kA/m and 366 kA/m whereas the remanence is equal to 0.118 T, 0.109 T and 0.127 T for the samples milled for 10, 20 and 30 hours, respectively and annealed at 1000°C . The high values of coercivity are certainly associated with the microstructure and phase composition of investigated powders after milling and annealing processes.

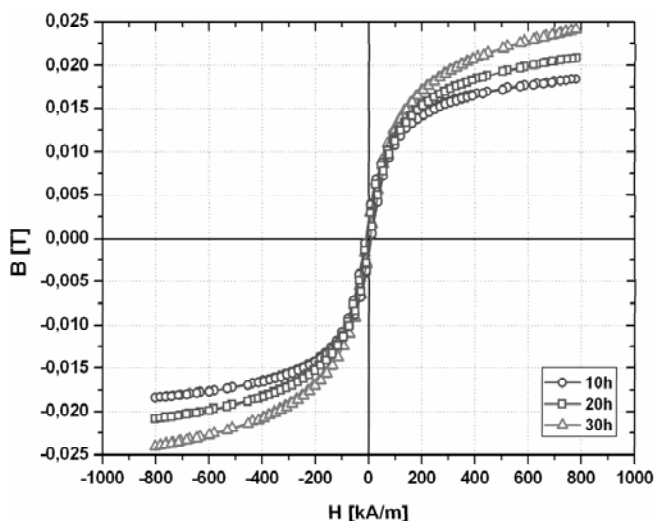


Fig. 6. Hysteresis loops of Fe_2O_3 and BaCO_3 mixture after different milling times

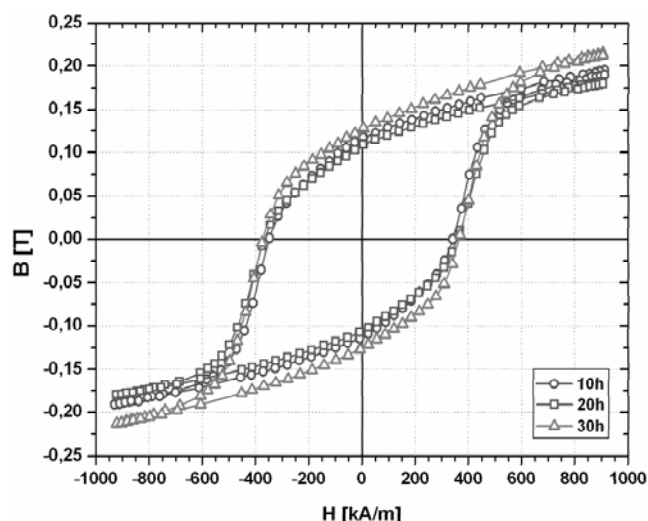


Fig. 7. Hysteresis loops of Fe_2O_3 and BaCO_3 mixture after different milling times and annealing at 1000°C

4. Conclusions

The investigations performed on the milled and annealed Fe_2O_3 and BaCO_3 mixture allowed to formulate the following statements:

1. Milling process causes the increase of the size of powder particles, the decrease of crystallite size of both Fe_2O_3 and BaCO_3 phases and enriching of BaCO_3 powder surface layer by Fe_2O_3 .
2. As a result of milling and annealing at 1000°C processes hard magnetic $\text{BaFe}_{12}\text{O}_{19}$ phase is formed.

Small amount of Fe_2O_3 phase is also present in the annealed samples.

3. Coercive force and remanence values of studied powders are dependent on the milling time.
4. The best coercive force was obtained for powders milled for 30 hours and annealed at 1000°C .

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