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

THE INFLUENCE OF MANUFACTURING CONDITIONS ON MICROSTRUCTURE AND MAGNETIC PROPERTIES OF $BaFe_{12}O_{19}$ POWDERS

WPŁYW WARUNKÓW WYTWARZANIA NA MIKROSTRUKTURĘ I WŁASNOŚCI MEGNETYCZNE PROSZKÓW $BaFe_{12}O_{19}$

The aim of the paper was a trial of using mechanical alloying process of mixture iron oxide and barium carbonate to produce $BaFe_{12}O_{19}$ 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 Fe_2O_3 and $BaCO_3$ mixture for studied milling times causes decrease of the crystallite size of involved phases and leads to increase of Fe_2O_3 phase content and decrease of $BaCO_3$ one. The milling process did not lead to formation of $BaFe_{12}O_{19}$ phase, thus it probably causes setting of Fe_2O_3 on surface layer of $BaCO_3$ powder particles. The XRD investigations of Fe_2O_3 and $BaCO_3$ mixture milled for 10, 20 and 30 hours and annealed at 1000°C for 1 hour enabled the identification of hard magnetic $BaFe_{12}O_{19}$ 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 proba wykorzystania procesu mechanicznej syntezy mieszaniny tlenku żelaza (Fe_2O_3) i węglanu baru ($BaCO_3$) do wytworzenia proszkow $BaFe_{12}O_{19}$. 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 Fe_2O_3 i $BaCO_3$ dla zastosowanych czasów prowadzi do zmniejszenia wielkości krystalitów tych faz oraz do wzrostu udziału fazy Fe_2O_3 i spadku udziału fazy $BaCO_3$. Mielenie mieszaniny Fe_2O_3 i $BaCO_3$ w czasie 10, 20 i 30 godzin z następnym wyżarzaniem w 1000°C w czasie 1 godziny, prowadzi do powstania fazy magnetycznie twardej $BaFe_{12}O_{19}$. Dla przyłożonego pola magnetycznego 800 kA/m najwyższą wartosc koercji 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.

$BaFe_{12}O_{19}$ 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 $BaFe_{12}O_{19}$ powders. For synthesis of $BaFe_{12}O_{19}$, a mixture of Fe_2O_3 (99% purity) and $BaCO_3$ (99% purity) powders was used with composition of $1.1BaCO_3 + 6Fe_2O_3$. 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 parallely 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 μm to 1180 μm.

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.

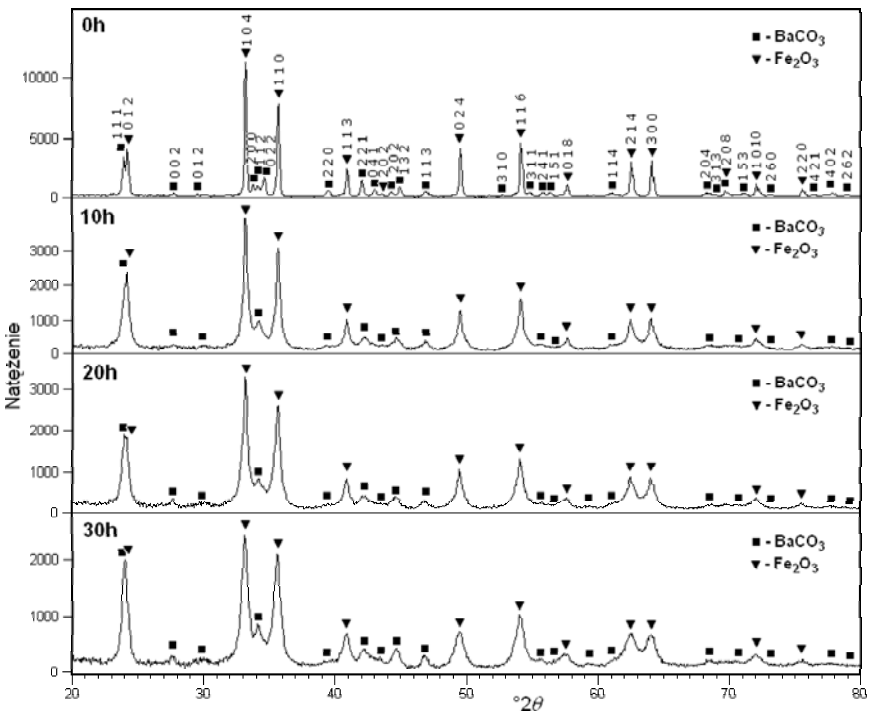

Fig. 1. X-ray diffraction patterns of Fe_2O_3 and $BaCO_3$ mixture after 0, 10, 20 and 30 hours of milling process

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).

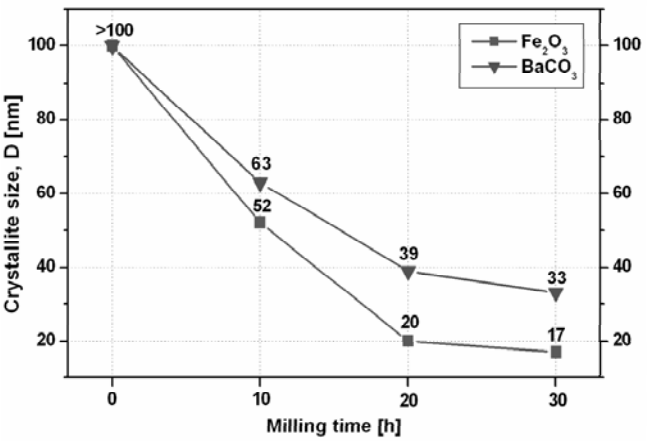

Fig. 2. Changes of average crystallite size (D) with the increase of milling time for Fe_2O_3 and $BaCO_3$ phases

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 $BaFe1_2O_{19}$ phase, thus it probably causes setting of Fe_2O_3 on surface layer of $BaCO_3$ powder particles.

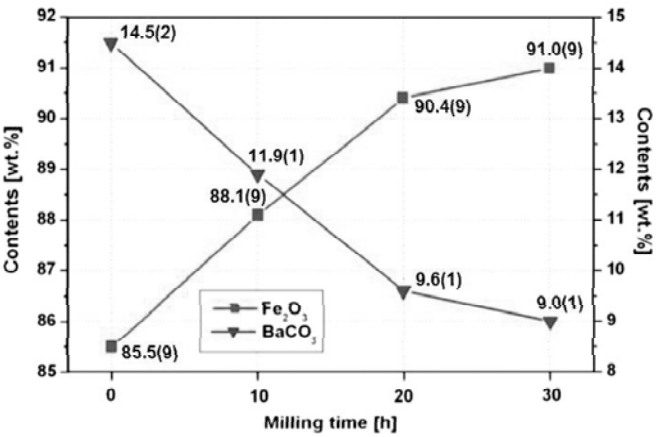

Fig. 3. Contents of Fe_2O_3 and $BaCO_3$ phases after different times of milling process

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.

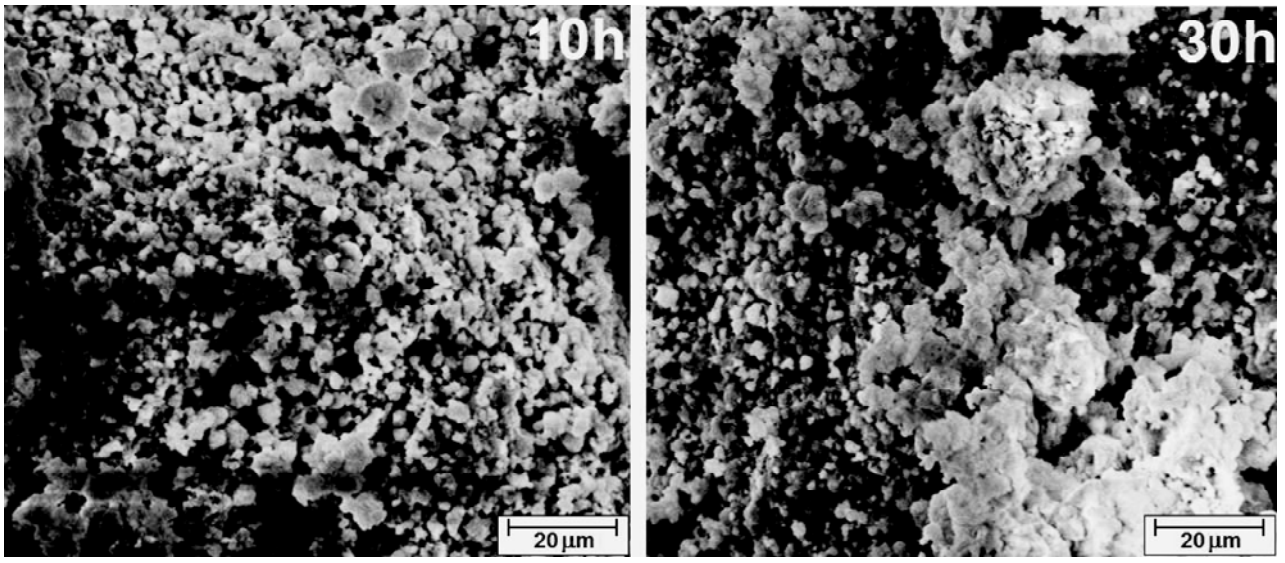

Fig. 4. The SEM images of milled samples for 10 (a) and 30 (b) hours

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.

TABLE 1

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 $BaFe_{12}O_{19}$ 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 $BaFe_{12}O_{19}$ compound.

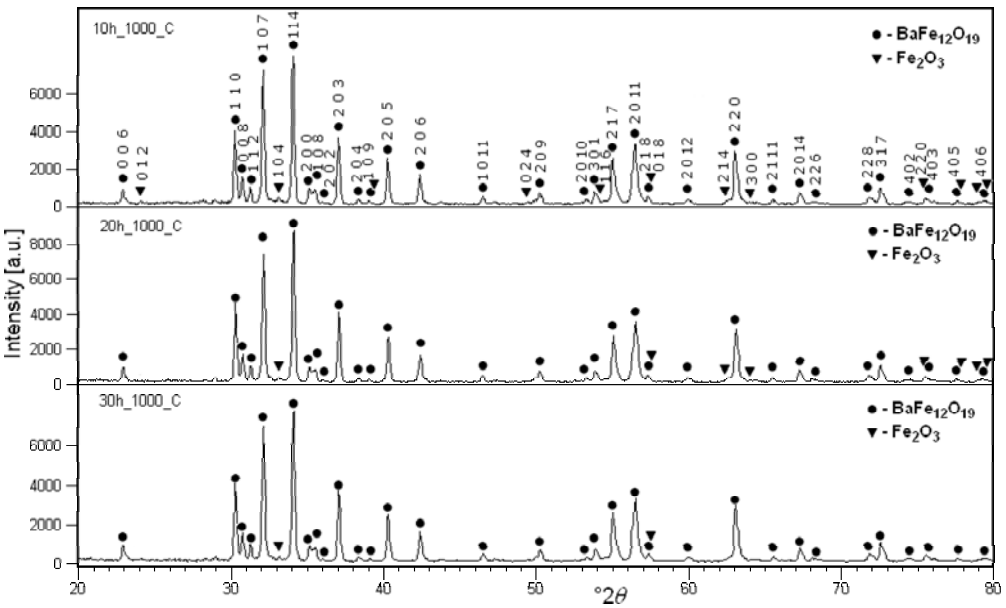

Fig. 5. X-ray diffraction pattern of Fe_2O_3 and $BaCO_3$ mixture after 10, 20, 30 hours of milling and annealing at 1000°C

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 $BaFe_{12}O_{19}$ and Fe_2O_3 phases. At the milling time 10 h the fraction of the $BaFe_{12}O_{19}$ 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 temperature 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.

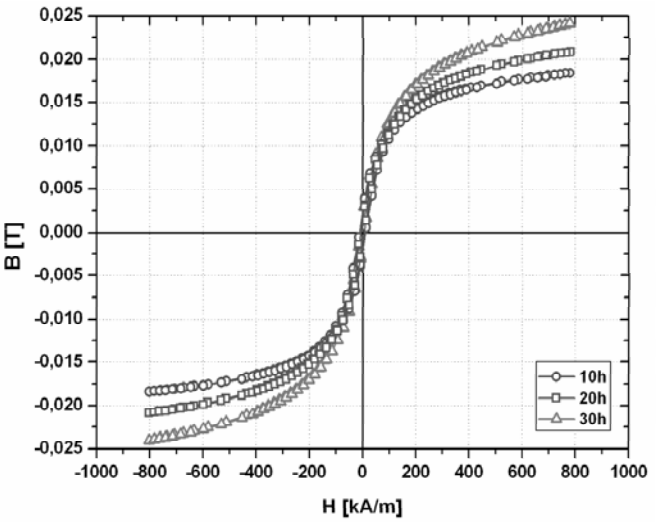

Fig. 6. Hysteresis loops of Fe_2O_3 and $BaCO_3$ mixture after different milling times

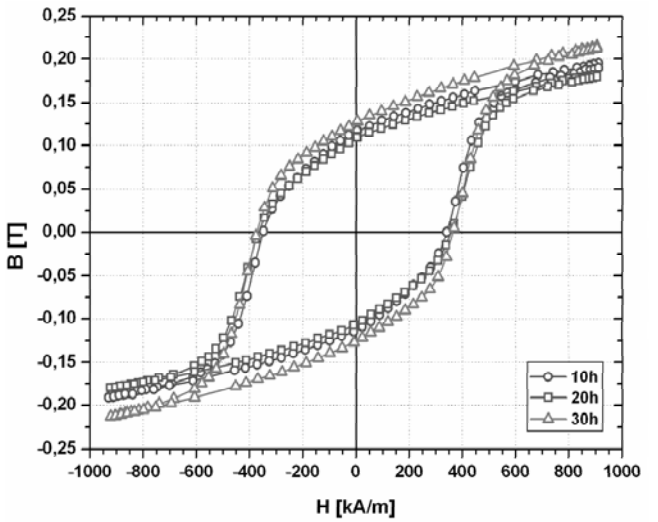

Fig. 7. Hysteresis loops of Fe_2O_3 and $BaCO_3$ mixture after different milling times and annealing at 1000°C

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 $BaFe_{12}O_{19}$ 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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