THE INFLUENCE OF MANUFACTURING CONDITIONS ON MICROSTRUCTURE AND MAGNETIC PROPERTIES OF BaFe$_{12}$O$_{19}$ POWDERS

Wpływ warunków wytwarzania na mikrostrukturę i własności magnetyczne 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$_2$O$_3$ and BaCO$_3$ mixture for studied milling times causes decrease of the crystallite size of involved phases and leads to increase of Fe$_2$O$_3$ 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$_2$O$_3$ on surface layer of BaCO$_3$ powder particles. The XRD investigations of Fe$_2$O$_3$ 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 próba wykorzystania procesu mechanicznej syntezy mieszaniny tlenku żelaza (Fe$_2$O$_3$) i węglanu baru (BaCO$_3$) do wytworzenia proszków 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$_2$O$_3$ i BaCO$_3$ dla zastosowanych czasów prowadzi do zmniejszenia wielkości krystalitów tych faz oraz do wzrostu udziału faz Fe$_2$O$_3$ i spadku udziału faz BaCO$_3$. Mielenie mieszaniny Fe$_2$O$_3$ i BaCO$_3$ w czasie 10, 20 i 30 godzin z następnym wyzarzaniem w 1000°C w czasie 1 godziny, prowadzi do powstania fazy magnetycznie twardzej BaFe$_{12}$O$_{19}$. Dla przyłożonego pola magnetycznego 800 kA/m najwyższą wartość koercji i remanencji uzyskano dla próbki mielonej w czasie 30 godzin i wyzarzanej 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 Martenssen 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
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 (Fe₂O₃) and barium carbonate (BaCO₃) to produce BaFe₁₂O₁₉ powders. For synthesis of BaFe₁₂O₁₉, a mixture of Fe₂O₃ (99% purity) and BaCO₃ (99% purity) powders was used with composition of 1.1BaCO₃ + 6Fe₂O₃. 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 Fe₂O₃ and BaCO₃ 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 μm to 1180 μm.

3. Results and discussion

Comparison of diffraction patterns of as-prepared Fe₂O₃ and BaCO₃ 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 Fe₂O₃ and BaCO₃ mixture after 0, 10, 20 and 30 hours of milling process](image-url)
The crystallite size ($D$) of both Fe$_2$O$_3$ 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$_2$O$_3$ and BaCO$_3$ phases, respectively (Fig. 2).

![Graph 1](image1.png)

**Fig. 2.** Changes of average crystallite size ($D$) with the increase of milling time for Fe$_2$O$_3$ and BaCO$_3$ phases

The iron oxide (Fe$_2$O$_3$) phase is the main component of the tested mixture in as-prepared 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$_2$O$_3$ and BaCO$_3$ mixture leads to increase of the content of Fe$_2$O$_3$ 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$_2$O$_3$ and BaCO$_3$ phases are 91.0(9) and 9.0(1) wt.%, respectively. The milling process did not lead to formation of BaFe$_{12}$O$_{19}$ phase, thus it probably causes setting of Fe$_2$O$_3$ on surface layer of BaCO$_3$ powder particles.

![Graph 2](image2.png)

**Fig. 3.** Contents of Fe$_2$O$_3$ 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.

![SEM Images](image3.png)

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

The size parameters of powder particles of Fe$_2$O$_3$ 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$_3$O$_4$ and BaCO$_3$ mixture after different times of milling process

<table>
<thead>
<tr>
<th>No.</th>
<th>Powder particle size [µm]</th>
<th>Milling time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10 h</td>
</tr>
<tr>
<td>1.</td>
<td>Arithmetic mean diameter</td>
<td>4.63(1)</td>
</tr>
<tr>
<td>2.</td>
<td>Geometric mean diameter</td>
<td>2.36(7)</td>
</tr>
<tr>
<td>3.</td>
<td>Quadratic square mean diameter</td>
<td>6.03(3)</td>
</tr>
<tr>
<td>4.</td>
<td>Harmonic mean diameter</td>
<td>1.03(3)</td>
</tr>
<tr>
<td>5.</td>
<td>Standard deviation</td>
<td>2.10(5)</td>
</tr>
<tr>
<td>6.</td>
<td>Median</td>
<td>3.16(5)</td>
</tr>
</tbody>
</table>

The X-ray diffraction investigations of Fe$_3$O$_4$ 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$_3$O$_4$ phase in examined samples. The iron oxide is a rest of the reaction between BaCO$_3$ and Fe$_3$O$_4$, which forms the BaFe$_{12}$O$_{19}$ compound.

![X-ray diffraction pattern](image)

Fig. 5. X-ray diffraction pattern of Fe$_3$O$_4$ 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$_3$O$_4$ phases. At the milling time 10 h the fraction of the BaFe$_{12}$O$_{19}$ and Fe$_3$O$_4$ 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 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%, $R_{exp}$ =5.42.567%, and $S$= 1.54.1.56.

The hysteresis loops of Fe$_3$O$_4$ 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.
4. Conclusions

The investigations performed on the milled and annealed Fe$_2$O$_3$ 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$_2$O$_3$ and BaCO$_3$ phases and enriching of BaCO$_3$ powder surface layer by Fe$_2$O$_3$.
2. As a result of milling and annealing at 1000°C processes hard magnetic BaFe$_{12}$O$_{19}$ phase is formed.
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.

REFERENCES


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