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Structure and properties of barium ferrite powders prepared by milling and annealing

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ABSTRACT

Purpose: Microstructure and magnetic properties analysis of barium ferrite powder obtained by milling and heat treatment

Design/methodology/approach: The milling process was carried out in a vibratory mill, which generated vibrations of the balls and milled material inside the container. After milling process the powders were annealed in electric chamber furnace. The X-ray diffraction methods were used for qualitative phase analysis of studied powder samples. The morphology of Fe_2O_3 and $BaCO_3$ powders after milling was analyzed using the scanning electron microscopy (SEM) method. The distribution of powder particles was determined by a laser particle analyzer. The magnetic hysteresis loops of examined powder material were measured by resonance vibrating sample magnetometer (R-VSM).

Findings: The milling process of iron oxide and barium carbonate mixture causes decrease of the crystallite size of involved phases and leads to increase the content of Fe_2O_3 phase and decrease of $BaCO_3$ content. Milling process causes enriching of surface layer of powder particles by Fe_2O_3. The X-ray investigations of tested mixture milled for 30 hours and annealed at 950°C enabled the identification of hard magnetic $BaFe_{12}O_{19}$ phase and also the presence of Fe_2O_3 phase in examined material. The Fe_2O_3 phase is a rest of $BaCO_3$ dissociation in the presence of Fe_2O_3, which forms a compound of $BaFe_{12}O_{19}$. The best coercive force for the mixture of powders annealed at 950°C for 10, 20 and 30 hours is 349 kA/m, 366 kA/m and 364 kA/m, respectively. From morphology images and distribution of powder particle size it can be concluded, that the size of tested powder particles increases with increasing time of milling process. The increase of milling time up to 20 hours leads to joining of smaller particles in bigger ones; agglomerates are formed.

Practical implications: The barium ferrite powder obtained by milling and annealing can be suitable component to produce sintered and elastic magnets with polymer matrix.

Originality/value: The results of tested barium ferrite investigations by different methods confirm their utility in the microstructure and magnetic properties analysis of powder materials.

Keywords: X-ray phase analysis; R-VSM; High-energy ball milling; Barium ferrite

METHODOLOGY OF RESEARCH, ANALYSIS AND MODELLING

1. Introduction

Barium ferrites are well known hard magnetic materials, which are based on iron oxide. They are also called as ferrite magnets and could not be easily replaced by any other magnets [1-4].

Hexagonal barium ferrite having the chemical formula of $BaFe_{12}O_{19}$ are widely used in magnetic recording media, microwave devices and electromagnetic shielding fields [5,6]. Barium ferrite possesses relatively high Curie temperature, coercive force and magnetic anisotropy field, as well as its excellent chemical stability and corrosion resistivity [7,8].

Ferrite magnets are still widely used although they have less magnetic strength than rare earth magnets. Comparing ferrite magnets and rare earth magnets could be concluded 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 $(BH)_{max}$, which is about 1:10.

Many methods of synthesis have been developed to obtain a low production cost of powder particles of barium ferrite. The rare earth magnets are used where weight and size are very important from the cost and performance point of view [9,10].

The chemical compositions of the typical hard magnetic ferrite compounds are presented in Table 1. Magnetic properties of commercial ferrite magnets are shown in Figure 1. Figure 2 shows a phase diagram of Fe_2O_3 – BaO system. The barium ferrite phase with chemical composition of $BaO{\cdot}6Fe_2O_3$ is visable in the region of system, where a content of BaO is about 15 mol.% [10].

The aim of the this paper is the microstructure analysis and magnetic properties characterization of $BaFe_{12}O_{19}$ powder obtained by milling and heat treatment.

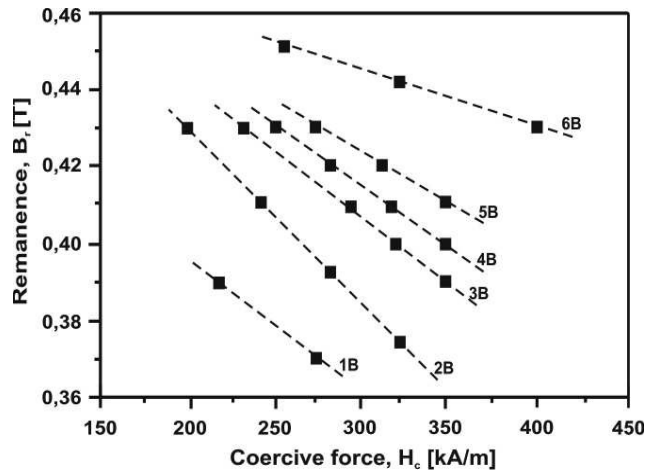

Fig. 1. Magnetic properties of Hitachi Metals ferrite magnets series YBM (1B–6B) [10]

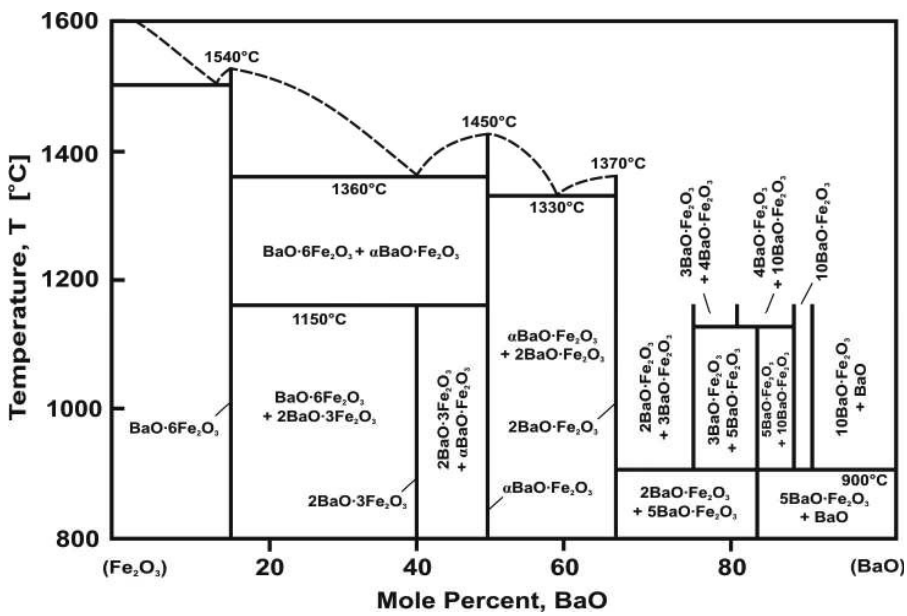

Fig. 2. Phase diagram of Fe_2O_3 - BaO system [10]

Table 1.
Chemical composition of BaO-MeO-Fe_2O_3 hexagonal magnetic compounds (MeO – metal oxide) [10]

No.	Molecular formula	Chemical composition (mol.%)		
		MeO	BaO	Fe_2O_3
1.	$BaO \cdot 6Fe_2O_3$	-	14.29	85.71
2.	$2MeO \cdot BaO \cdot 8Fe_2O_3$	18.18	9.09	72.71
3.	$2MeO \cdot 2BaO \cdot 6Fe_2O_3$	20	20	60
4.	$2MeO \cdot 3BaO \cdot 12Fe_2O_3$	11.76	17.65	70.59

2. Material and research methodology

For synthesis of $BaFe_{12}O_{19}$, mixture of iron oxide Fe_2O_3 (99% purity) and barium carbonate $BaCO_3$ (99% purity) powders was used with composition $1.1BaCO_3 + 6Fe_2O_3$ (Fig.3.).

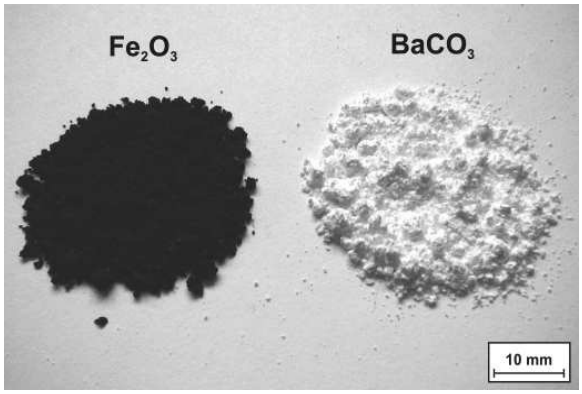

Fig. 3. External morphology of Fe_2O_3 and $BaCO_3$ powders used for milling process

Ball milling process was carried out in a vibratory mill type SPEX 8000 CertiPrep Mixer/Mill for 10, 20 and 30 hours under argon atmosphere. The weight ratio of balls to milled material was 5:1. The mill generated vibrations of the balls and the material inside the container [11,12].

After milling process the powders were annealed in the electric chamber furnace THERMOLYNE 6020C in 900, 950 and 1000°C in the air at atmosphere pressure for 1 hour.

Phase analysis was carried out using the X-Pert Philips diffractometer equipped with curved graphite monochromator on diffracted beam and a tube provided with copper anode. It was supplied by current intensity of 30 mA and voltage of 40 kV.

The length of radiation ($\lambda Cu_{K\alpha}$) was 1.54178 Å. The data of diffraction lines were recorded by "step-scanning" method in 2θ range from 10° to 90° 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 [13]. 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 [14-16].

The magnetic hysteresis loops of obtained powder material were measured by the Resonance Vibrating Sample Magnetometer (R-VSM). The idea of R-VSM is based on the Faraday induction law and the original Foner solution [17]. As distinct from Foner's VSM in the R-VSM sample oscillations are forced by piezoelectric transducer. Sample oscillates parallely to the direction of external magnetic field and configuration of pick-up coils in the form of small Smith coils were applied.

The morphology of Fe_2O_3 and $BaCO_3$ powders after milling was analyzed using the OPTON DS940 scanning electron microscope with the ISIS software for the computer recording of images.

The diameter sizes 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 Fe_2O_3 and $BaCO_3$ mixture before milling (Fig.4) and after 30 hours of milling (Fig.5) shows the broadening of diffraction lines and decrease of their intensity. These effects indicate that ball milling causes decrease of the crystallite size of tested phases and leads to homogenizing the milled mixture. Statement the diffraction patterns of as-prepared and milled powders at different times are shown in Figure 6.

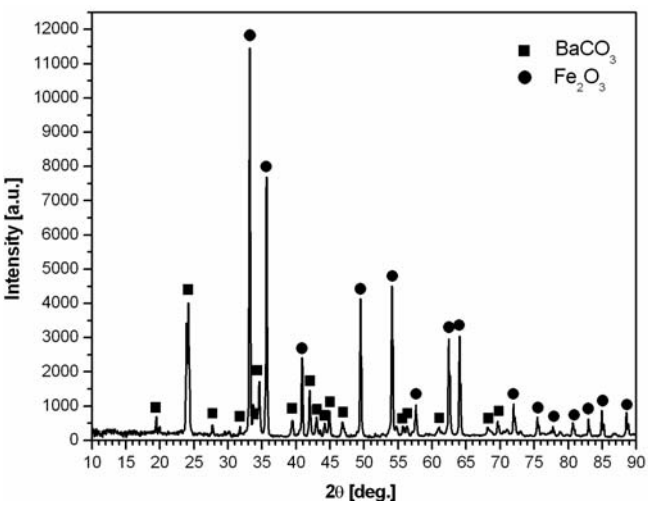

Fig. 4. X-ray diffraction pattern of Fe_2O_3 and $BaCO_3$ mixture as a starting material for milling

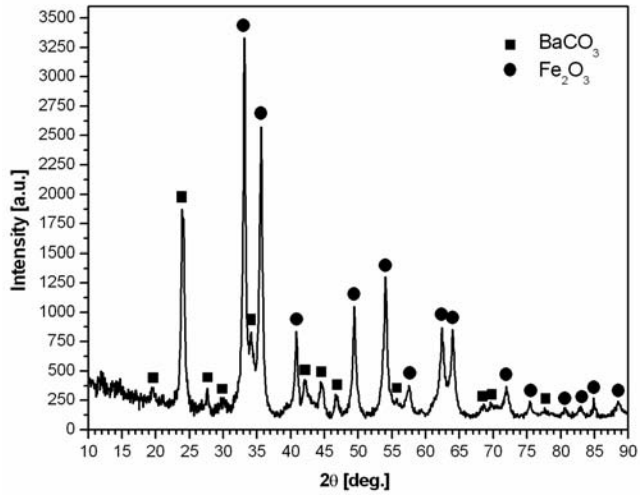

Fig. 5. X-ray diffraction pattern of Fe_2O_3 and $BaCO_3$ mixture after 30 hours of milling

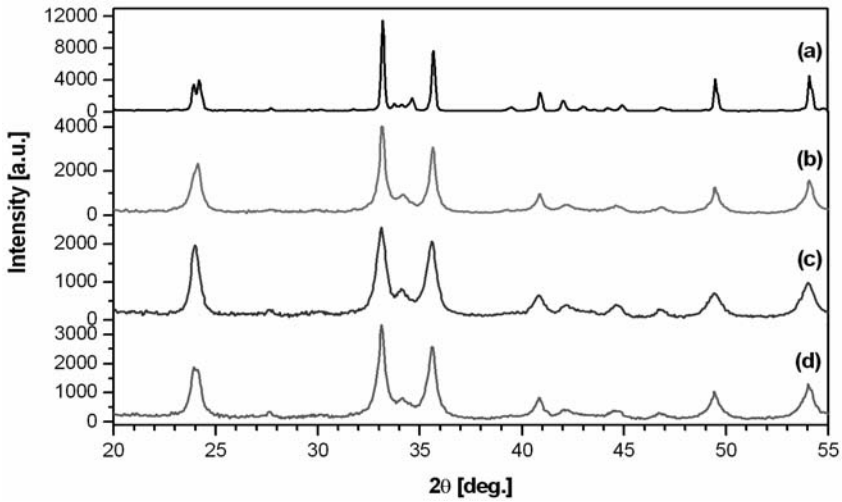

Fig. 6. X-ray diffraction patterns of Fe_2O_3 and $BaCO_3$ mixture after different times of milling: a) as-prepared, b) 10 h, c) 20 h, d) 30 h

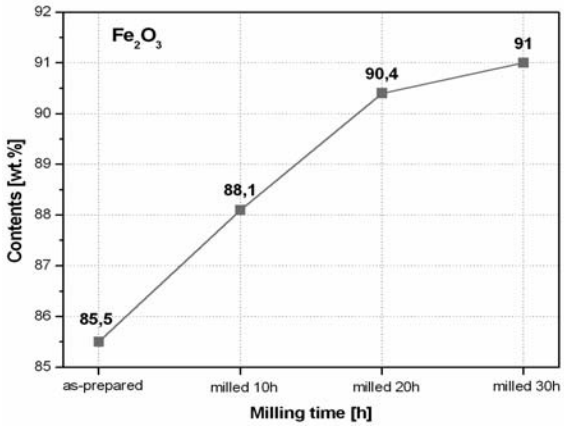

Fig. 7. Contents of Fe_2O_3 phase in as-prepared state and after different times of milling

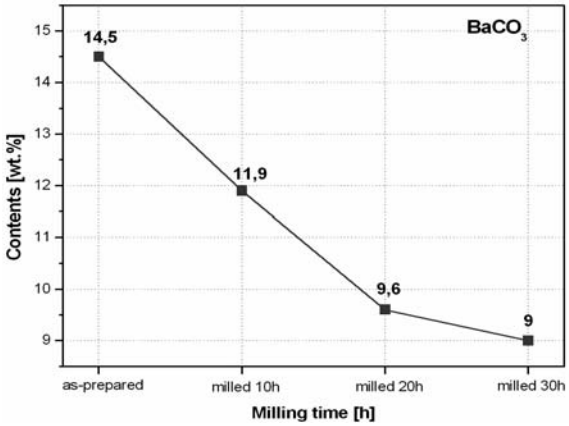

Fig. 8. Contents of $BaCO_3$ phase in as-prepared state and after different times of milling

The iron oxide (Fe_2O_3) phase appeared to be the main component of the tested mixture in as-prepared state (85.5 wt.%). On the other hand the content of $BaCO_3$ phase is much lower (14.5 wt.%).

The milling process of examined Fe_2O_3 and $BaCO_3$ mixture leads to increase the content of Fe_2O_3 phase and decrease the content of $BaCO_3$ (Fig.7,8). After 30 hours of high-energy ball milling the content of Fe_2O_3 is 91 wt.% and 9 wt.% for $BaCO_3$ phase. Milling process causes enriching of surface layer of powder particles by Fe_2O_3.

The distribution of powder particles size of mixture Fe_2O_3 and $BaCO_3$ powders milled for 10, 20, 30 hours is presented in Figure 9. The sizes of tested powders and their statistical means are presented in Table 2.

The arithmetic mean diameter of examined population of Fe_2O_3 and $BaCO_3$ powders after 10 hours of milling is 4,43(1) μm. The representative diameter of examined powders (median) has a value of 3,16(5) μm. After 20 hours of milling the arithmetic mean diameter has a value of 6.63(8) μm and median reaches a value of 4.06(5) μm.

Moreover, the arithmetic mean diameter of tested powders after 30 hours of milling is 7.20(5) μm and median has a value of 4.82(9) μm.

Figure 10 shows the morphology of tested mixture Fe_2O_3 and $BaCO_3$ powders and observed by the scanning electron microscope. From morphology images and distribution of powder particle size can be concluded, that the size of tested powder particles increases with increasing time of milling process.

After 10 hours of milling the shape of tested powder particles is irregular. Figure 10a shows a large quantity of small particles. The increase of milling time up to 20 hours leads to joining of smaller particles in bigger ones, which form agglomerates (Fig.10b). After 30 hours of milling process the quantity of agglomerates increase. The agglomerates are getting to have regular and spherical shape (Fig.10c).

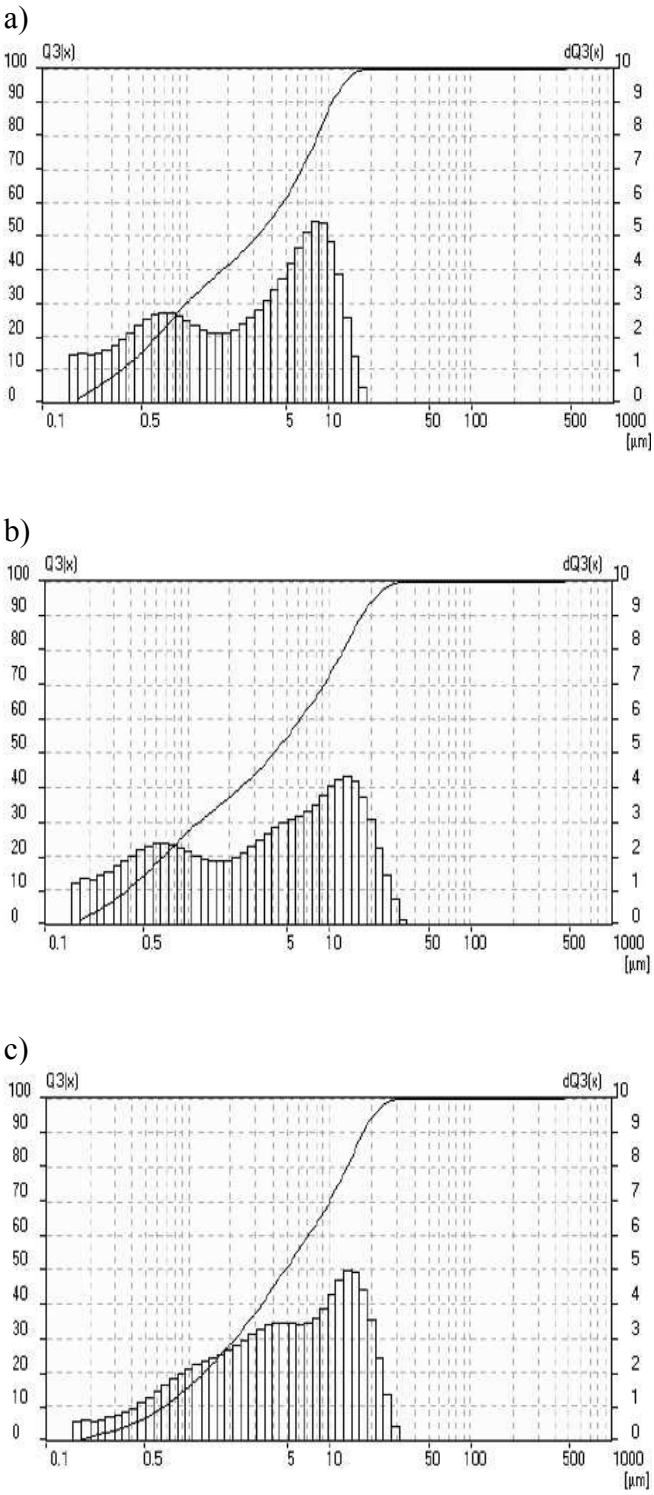

Fig. 9. Distribution and summary curve of powder particle size of Fe_2O_3 and $BaCO_3$ mixture after different milling times: a) 10 h, b) 20 h, c) 30 h

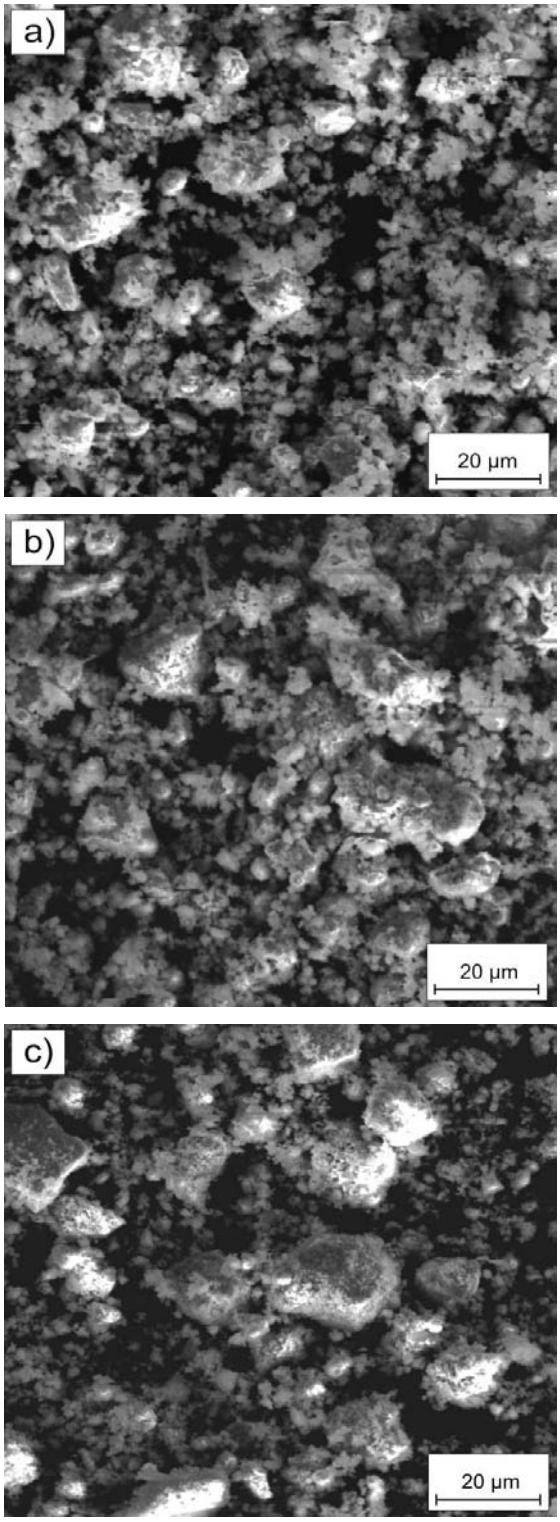

Fig. 10. SEM images of Fe_2O_3 and $BaCO_3$ mixture after different milling times: a) 10 h, b) 20 h, c) 30 h

Table 2.
Statistical means and powder particle size of Fe_2O_3 and $BaCO_3$ mixture after different time 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 30 hours and annealed at 950°C enabled the identification of hard magnetic $BaFe_{12}O_{19}$ phase (Fig.11). Moreover, the X-ray analysis also revealed presence of Fe_2O_3 phase in examined material. The iron oxide (Fe_2O_3) is a rest of $BaCO_3$ dissociation in the presence of Fe_2O_3, which forms a compound of $BaFe_{12}O_{19}$. The X-ray diffraction patterns of Fe_2O_3 and $BaCO_3$ mixture after different times of milling and annealing at 950°C are presented in Figure 14.

Moreover, the annealing and milling process causes increase content of hard magnetic phase ($BaFe_{12}O_{19}$) obtain after heat treatment and decrease of Fe_2O_3 phase. The effect of annealing temperature (900, 950, 1000°C) on content of $BaFe_{12}O_{19}$ and Fe_2O_3 phases for different times of milling is presented in Figure 12 and 13.

After 30 hours of milling process and annealing at 1000°C content of $BaFe_{12}O_{19}$ phase reaches a value of 99.5 wt.%. the increase of milling time and temperature of annealing leads to increase content of tested hard magnetic phase.

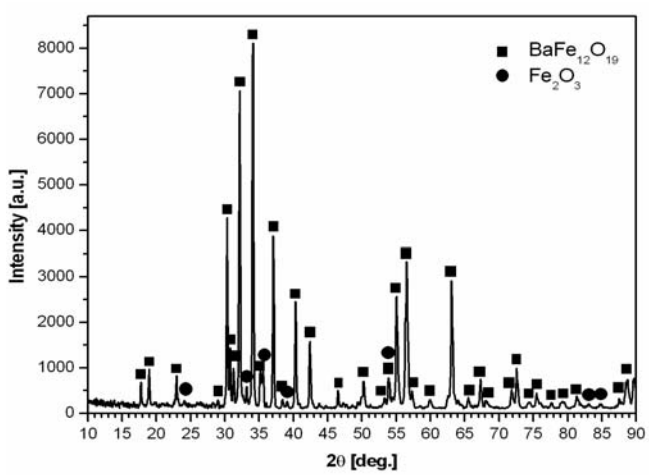

Fig. 11. X-ray diffraction pattern of Fe_2O_3 and $BaCO_3$ mixture after 30 hours of milling and annealing at 950°C

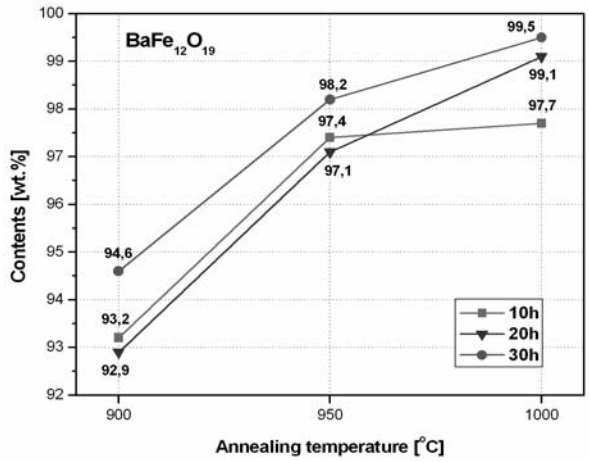

Fig. 12. Contents of $BaFe_{12}O_{19}$ phase after: 10, 20, 30 hours of milling and annealing at 900, 950 and 1000°C

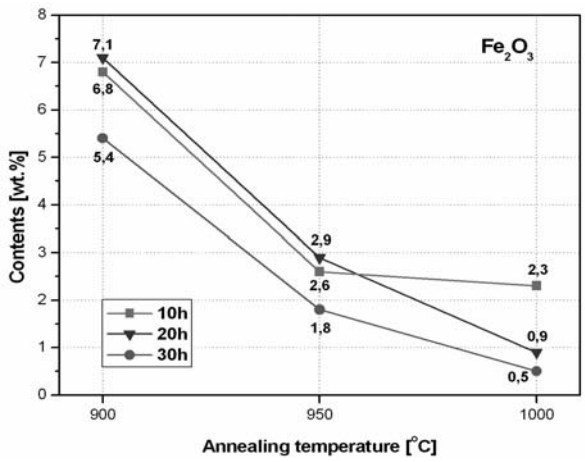

Fig. 13. Contents of Fe_2O_3 phase after: 10, 20, 30 hours of milling and annealing at 900, 950 and 1000°C

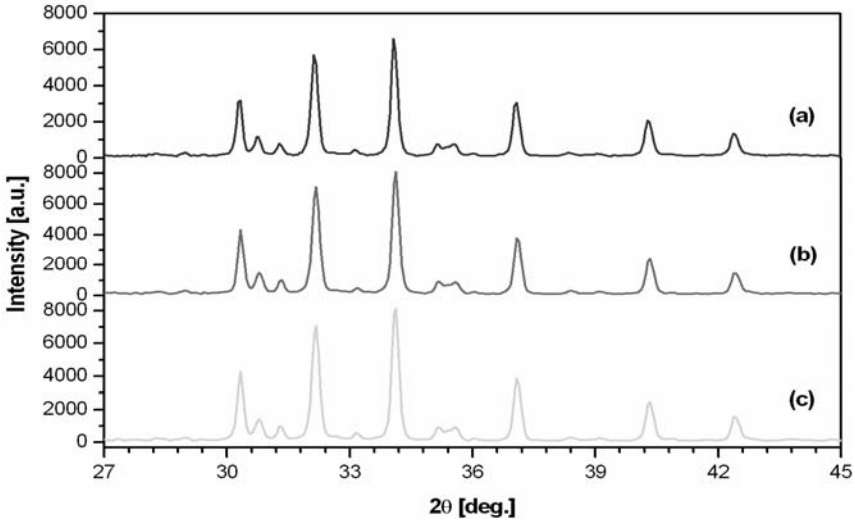

Fig. 14. X-ray diffraction patterns of Fe_2O_3 and $BaCO_3$ mixture after: a) 10 h, b) 20 h, c) 30 h of milling and annealing at 950°C

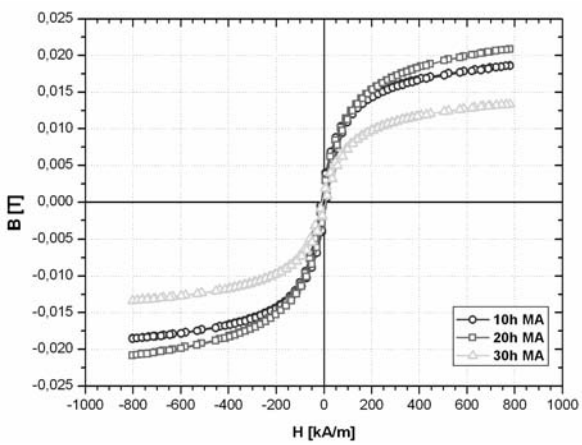

Fig. 15. Hysteresis loops of Fe_2O_3 and $BaCO_3$ mixture after different milling times

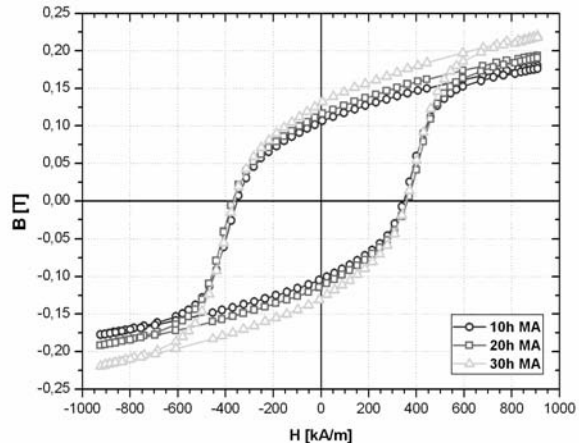

Fig. 16. Hysteresis loops of Fe_2O_3 and $BaCO_3$ mixture after different milling times and annealing at 950°C

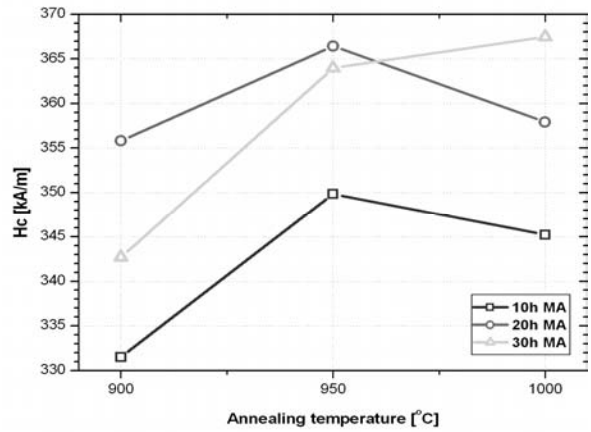

Fig. 17. Coercive force as a function of annealing temperature of Fe_2O_3 and $BaCO_3$ mixture for different milling times

The hysteresis loops of Fe_2O_3 and $BaCO_3$ mixture after different times of ball milling is shown in Figure 15. The hard magnetic properties of tested mixture are very low, because of lack of hard magnetic phase. The effect of annealing temperature (950°C) on magnetic properties of Fe_2O_3 and $BaCO_3$ mixture for different times of milling is presented in Figure 16.

Sample annealed at 950°C have high value of coercivity. The best coercive force for mixture of powders annealed at 950°C is 349 kA/m, 366 kA/m and 364 kA/m after 10, 20 and 30 hours of milling, respectively. The high values of coercivity are certainly associated with the microstructure of investigated powder samples.

The coercivity decreases with increasing temperature of annealing above 950°C, as shown in Figure 17. This effect is related with increasing of the crystallite size at higher temperatures.

4. Conclusions

The investigations performed on the Fe_2O_3 and $BaCO_3$ mixture after milling and heat treatment allowed to formulate the following statements:

- the milling process of Fe_2O_3 and $BaCO_3$ mixture leads to crystallite refinement and increase the content of Fe_2O_3 phase and decrease the of $BaCO_3$ content. Milling process causes enriching of surface layer of powder particles by Fe_2O_3,
- the X-ray diffraction investigations of tested mixture milled for 30 hours and annealed at 950°C enabled the identification of $BaFe_{12}O_{19}$ and Fe_2O_3 phases,
- the annealing and milling process causes increase content of hard magnetic phase ($BaFe_{12}O_{19}$) obtain after heat treatment,
- the coercive force of studied powders is dependent on time of ball milling and temperature of their annealing,
- the best coercive force was obtained for powders annealed at temperature of 950°C,
- the SEM images and distribution of powder particle size showed that the size of tested powder particles increases with increasing time of milling process,
- the increase of milling time up to 20 hours leads to joining of smaller particles in bigger ones, which form agglomerates.

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