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Microstructure of polymer composite with barium ferrite powder

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Materials

ABSTRACT

Purpose: The aim of the paper is the microstructure characterization of commercial $BaFe_{12}O_{19}$ powder and its composite material in polymer matrix; XRD (X-Ray Diffraction) and SEM (Scanning Electron Microscopy) methods were applied.
Design/methodology/approach: The Rietveld method appeared to be very useful in the verification of the qualitative phase composition and in the determination of phase abundance. Hill and Howard procedure was applied for quantitative phase analysis. The parameters of the individual diffraction line profiles were determined by PRO-FIT Toraya procedure. The morphology of barium ferrite powders and a fracture surface of the examined composite material was analyzed using the scanning electron microscope.
Findings: The X-ray diffraction analysis enabled the identification of $BaFe_{12}O_{19}$ and Fe_2O_3 phases in examined material. Basing on Rietveld and Toraya methods the determination of lattice parameters, crystallite size and the lattice distortion was performed. Distribution of powders of barium ferrite in polymer matrix is irregular and powder particles are of irregular shapes and different sizes.
Research limitations/implications: Maked researches are limited only to characterization the microstructure of commercial material, because obtained results will be helpful to prepare barium ferrite powders by mechanical alloying and subsequent annealing in the future. As prepared $BaFe_{12}O_{19}$ powders will be used as the starting material for magnets bonded with polymer material.
Originality/value: The obtained results of investigations by different methods of structure analysis confirm their useful in the microstructure analysis of powder materials.
Keywords: Composites; X-ray phase analysis; Rietveld method; Toraya procedure; Barium ferrite

1. Introduction

Ferrite-based composite magnets are an important type of permanent magnetic materials that has attracted attention since their development by Phillips researches [9,12,15-17,28,30]. Hexagonal hard ferrites such as barium ferrite seem to be the most interesting materials, because of their potential application in permanent magnets, microwave devices and processing information [1]. They are also widely applied to the electromagnetic wave shielding and stealth technology. They have high Curie temperature, together with large saturation magnetization, excellent chemical stability, corrosion resistance and they are relatively cheap to produce [8,10,18,36].

The aim of the present work is the microstructure characterization of commercial $BaFe_{12}O_{19}$ powder and its composite with polymer matrix; XRD (X-Ray Diffraction) and SEM (Scanning Electron Microscopy) methods were applied.

The X-ray diffraction and electron microscopy methods are of great importance in the microstructure characterization of complex, multiphase materials. The application of X-ray diffraction methods enables not only qualitative and quantitative phase analysis but also microstructure characterization (crystallite size, lattice distortions, dislocation densities, stacking faults and twins probability [29].

The Rietveld method [33, 34] and Toraya procedure [31] were applied as the tools of XRD patterns analysis. Rietveld method can be useful in the microstructure characterization and also in the verification of the qualitative phase composition [2-7, 20, 22-24]. The estimation of phase abundance in multiphase material is possible when detailed information on the structure of concerned phases is available [29]. PRO-FIT Toraya procedure enables the determination of profile parameters of the individual diffraction line. The SEM method was applied for the analysis of powder morphology.

The methods of powders metallurgy and sintering processes are the most often used to produce barium ferrites from barium carbonates and iron oxides [26, 27]. Ferritization is a very important stage of process of producing that type of materials. It allows to receive the hard magnetic phase - $BaFe_{12}O_{19}$. The grains of barium ferrite are also milled and oriented during forming in magnetic field [11, 14, 16, 35].

Manufacturing process of ferrite magnets starts on a stage of mixing of barium carbonates and iron oxides and also annealing of the mixture at 1350°C. At 600°C begins the process of $BaCO_3$ dissociation what in the presence of Fe_2O_3 leads to the sintesis of monoferrite ($BaFe_2O_4$). Next the monoferrite reacts with Fe_2O_3 and creates a compound of $BaFe_{12}O_{19}$. Prepared in this way ferrite is grinded in ball mills to reach the grain size of about 1 μm and reduce the multi domain structures. The powder is press and sintered at temperature of 1200°C (Fig. 1) [16,18,19].

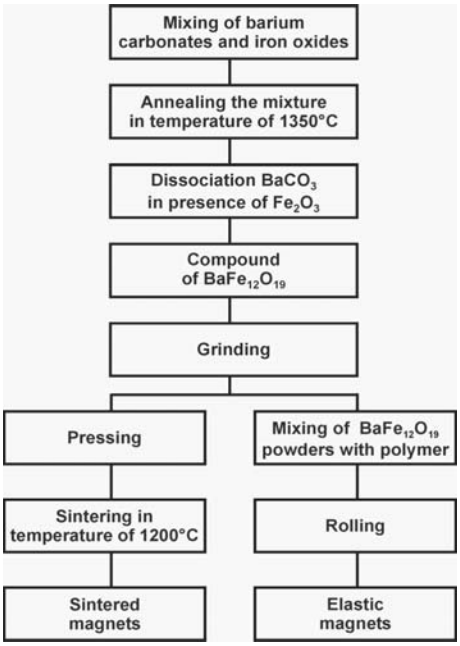

Fig. 1. The scheme of manufacturing process of sintered and elastic magnets with powders of barium ferrite [16]

Ferrites are often used to produce magnetic composite materials with polymer matrix. The powders of $BaFe_{12}O_{19}$ are mixed with polymer material and next rolling to obtain a polymer composite with form of a ribbon or a foil. However, the polymer matrix influence on magnetic properties of these composite materials. Nevertheless, polymer composites with barium ferrite powders are very attractive in view of their cost, good corrosion resistance and capability of high production rates [8,18,25].

2. Material and research methodology

The microstructure investigations were realized on the samples of commercial composite with polymer matrix (polyvinyl chloride), which contains powders of barium ferrite. The examined material was prepared in form of a ribbon with thickness 4 mm and width 7 mm (Fig. 2.). Technological process of forming of tested composite material usually includes methods of mixing $BaFe_{12}O_{19}$ powders with polymer material and rolling to get a form of a ribbon [16].

Fig. 2. External morphology of the tested composite material in form of ribbon

Phase compositions of the investigated material were determined using the the X-Pert Philips diffractometer employing the X-ray radiation ($\lambda Cu_{K\alpha}$ = 1.54178 Å) obtained from a tube provided with copper anode. The tube was powered by current intensity of 30 mA and voltage of 40 kV. The data of X-ray diffraction lines were performed by “step-scanning” method in 2θ range from 15° to 85° with 0.05° step.

The Toraya PRO-FIT procedure was used for determining profile parameters of individual diffraction lines. The Toraya method is based on Pearson VII function, which is useful for the description of line profiles.

The Rietveld analysis was performed applying DBWS-9807 program that is an update version of the DBWS programs 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 R_{wp} (weighted-pattern factor) and S (goodness-of-fit) parameters were used as numerical criteria of the quality of the fit of calculated to experimental diffraction data (1-3) [33]:

$$R_{wp} = \left[\frac{\sum_i w_i (y_i - y_{ci})^2}{\sum_i w_i (y_i)^2} \right]^{\frac{1}{2}} \cdot 100\ \% \tag{1}$$

$$R_{\exp} = \left[\frac{N - P}{\sum_i w_i y_i} \right]^{\frac{1}{2}} \cdot 100\ \% \tag{2}$$

$$S = \frac{\sum_i w_i (y_i - y_{ci})^2}{N - P} \tag{3}$$

where:
y_i – the experimental intensities,
y_{ci} – the calculated intensities,
$w_i = (1/y_i)$ – the weight experimental observations,
N – the number of experimental observations,
P – the number of fitting parameters.

The process of successive profile refinements modulates different structural and microstructural parameters of the simulated pattern to fit the experimental diffraction pattern. Profile refinement continues until convergence is reached in each case, with the value of the quality factor (S) approaching 1.

The phase abundance was determined using the relation proposed by Hill and Howard (4) [13]:

$$W_p = \frac{S_p (Z \cdot M \cdot V)}{\sum_{i=1}^{n} S_i (Z \cdot M \cdot V)_i} \cdot 100\%$$

where:
W_p – relative weight fraction of phase p in the mixture of n phases (wt. %),
S – Rietveld scale factor,
Z – number of formula units per unit cell,
M – mass of the formula unit (in atomic mass units),
V – unit cell volume (in Å^3).X-ray diffraction patterns of metallic phases may be broadened mainly due to:

- instrumental effect,
- small crystallite size,
- lattice distortion.

The instrumental broadening effect was determined by NIST SRM660a standard. Moreover, Williamson-Hall method was used to estimate the crystallite sizes and lattice distortions of tested barium ferrite ($BaFe_{12}O_{19}$) phase [32].

The content of the barium ferrite powders in tested composite material is 90.6 wt.% and 65.2 vol.%. The values of mass and volumetric contents are presented in Table 1.

Table 1.
Mass, volumetric contents of powders bounded with polyvinyl chloride in tested composite

No.	Characteristic	Phase	Unit	Value
1.	Mass contents	$BaFe_{12}O_{19}$ + Fe_2O_3	wt.%	90.6
		PVC	wt.%	9.4
2.	Volumetric contents	$BaFe_{12}O_{19}$ + Fe_2O_3	vol.%	65.2
		PVC	vol.%	34.8

The morphology of the barium ferrite powders and a fracture surface of the composite material was analyzed using the OPTON DS540 scanning electron microscope with the ISIS software for the computer recording of images.

Moreover, the diameter sizes of examined powders were determined by using Fritsch Particle Sizer "Analysette 22" in measuring range from 0.1 μm to 1181.86 μm.

3. Results and discussion

The X-ray diffraction investigations revealed the presence of $BaFe_{12}O_{19}$ and the Fe_2O_3 phases in examined material (Fig. 3).

The values of lattice parameters determined by Rietveld method (the accuracy in their determination found using alumina plate SRM 1976 standard is ±0.015%) and these found in ICDD files for all concerned phases are also given in Table 2.

The barium ferrite phase appeared to be the main component of the sample (97.8 wt.%). On the other hand the content of Fe_2O_3 phase is much lower (2.2 wt.%).

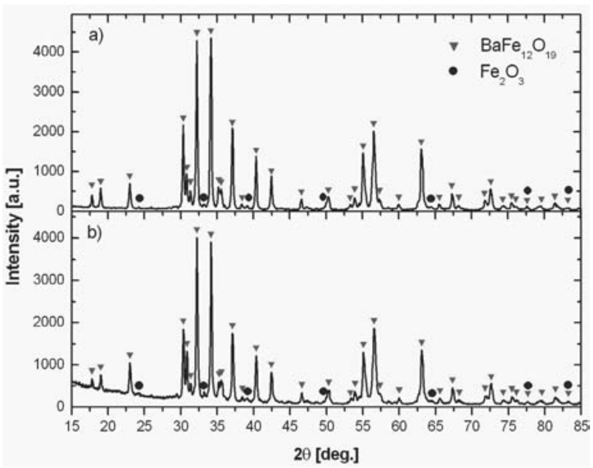

Fig. 3. XRD pattern of the tested material: a) powder sample, b) composite sample with polymer matrix

The Rietveld refinement plot of the powder sample is presented in Figure 4. The values of fitting parameters: R_{wp}, R_{exp}, and goodness-of-fit S obtained for powder and composite samples are quite similar and are in the range of: R_{wp}=7.95–8.36%, R_{exp}=5.03–5.19%, goodness-of-fit S=1.58–1.61.

Table 2.
Lattice parameters and the contents of sample components

Phase	Space group	Lattice parameters [nm] Rietveld Powder	Rietveld Ribbon	ICDD	Contents [wt.%]
$BaFe_{12}O_{19}$	$P6_3/mmc$	a_0 = 0.58910(9)	a_0 = 0.58907(9)	a_0 = 0.58920(1)	97.8
		c_0 = 2.3213(2)	c_0 = 2.3210(2)	c_0 = 2.3183(1)	
Fe_2O_3	$R\bar{3}c$	a_0 = 0.50343(8)	a_0 = 0.50346(8)	a_0 = 0.5034	2.2
		c_0 = 1.37607(2)	c_0 = 1.37605(2)	c_0 = 1.3747	

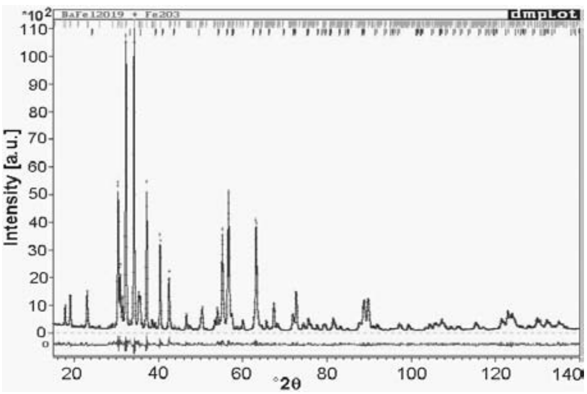

Fig. 4. Rietveld output of X-ray diffraction pattern for powder sample

The crystallite size (D) of $BaFe_{12}O_{19}$ phase is above 100 nm and the lattice strain ($<\Delta a/a>$) is 0.033%.

Analysis of obtain lattice parameters of tested phase ($BaFe_{12}O_{19}$) in examined material and lattice parameters from the International Centre for Diffraction Data (ICDD) for model materials allow to formulate that the elementary cell is elongated in a direction of Z axis and shortened in a direction of X and Y axis.

Comparison of a fragment of X-ray diffraction patterns for phase of barium ferrite in form of powder and composite material allows to find a difference in the intensity of (008) (2θ = 30.830) diffraction line for composite and powder (Fig. 5).

The difference induced axial texture on direction [001] in composite material, which is an effect of forming the tested composite by mixing of polymer with powders of barium ferrite and next by rolling to form of a ribbon. The intensity change of the other diffraction lines is not observed. Above conclusion was veryfied by Rietveld refinement analysis.

Figure 6 shows the morphology of barium ferrite powder. Moreover, the morphology of a fracture of the tested composite with powders of $BaFe_{12}O_{19}$ is presented in the Figure 7. The sizes of tested powder and their statistical means are presented in Table 3.

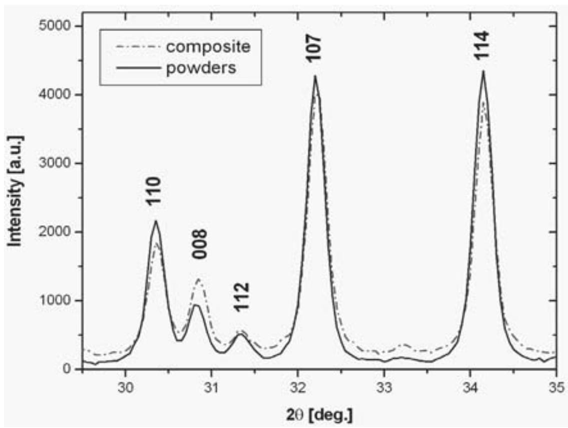

Fig. 5. Comparison of XRD patterns for powders of barium ferrite and a composite material

From morphology images of $BaFe_{12}O_{19}$ powder and surface fractures of the composite with powders of barium ferrite and polymer matrix the broad size distribution of $BaFe_{12}O_{19}$ powder can be concluded.

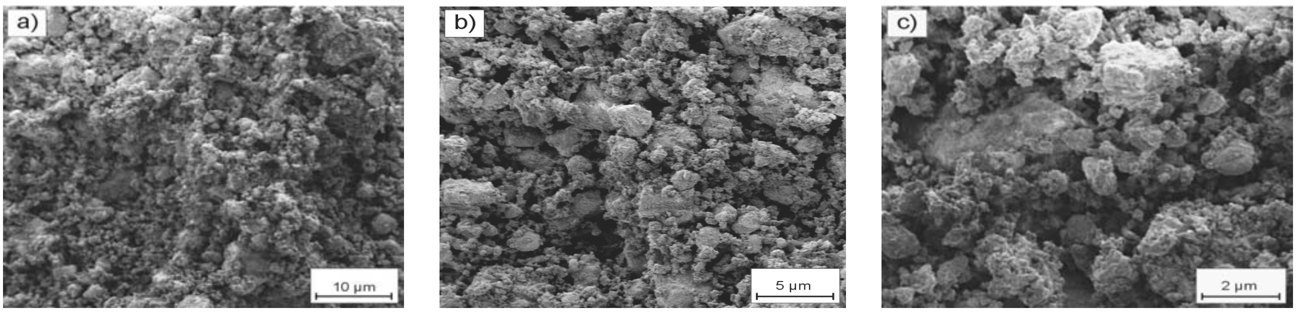

Fig. 6. SEM images of $BaFe_{12}O_{19}$ powder sample

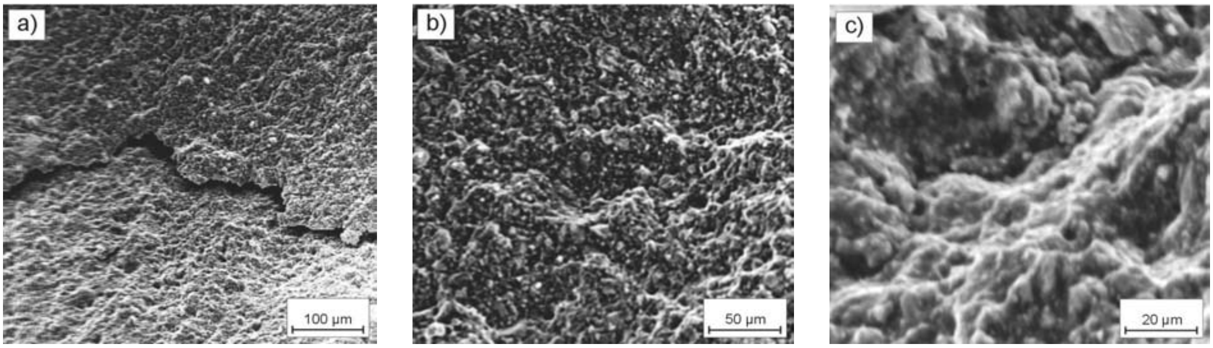

Fig. 7. Morphology of a fracture surface of the composite material

Table 3.
Statistical means and diameter sizes of $BaFe_{12}O_{19}$ powder bounded with polyvinyl chloride in tested composite

No.	Powder size	Value [μm]
1.	Arithmetic mean diameter	10.3
2.	Geometric mean diameter	8.5
3.	Quadratic square mean diameter	11.8
4.	Harmonic mean diameter	5.9
5.	Minimum diameter	0.2
6.	Maximum diameter	40.5
7.	Mode	10.6
8.	Median	9.4

The population of examined barium ferrite powders is contained in range from 0.2 μm (minimum diameter) to 40.5 μm (maximum diameter). The arithmetic mean diameter of whole population of $BaFe_{12}O_{19}$ powders is 10.3 μm. The size of powders, which are often presented in studied population (mode) is 10.6 μm. The representative diameter of examined powders (median) has a value of 9.4 μm. What is more, the shape of powder particles is irregular.

4. Conclusions

The investigations of the barium ferrite powders and tested composite material allowed to formulate the following statements:

- The X-ray diffraction investigations enabled the identification of two phases: $BaFe_{12}O_{19}$ (97.8 wt.%) and Fe_2O_3 (2.2 wt.%) in examined material.
- Good agreement of lattice parameters determined by Rietveld refinement method and these from ICDD files was obtained for all involved phases.
- The lattice parameters of the barium ferrite phase for powder sample are a_0 = 0.58910(9) nm, c_0 = 2.3213(2) nm and ribbon sample are a_0 = 0.58907(9) nm, c_0 = 2.3210(2) nm.
- The crystallite size of $BaFe_{12}O_{19}$ phase in studied material lies above nanoscale.
- Scanning electron microscopy images reveal that the shape and size of barium ferrite powder particles is irregular.
- The population of studied $BaFe_{12}O_{19}$ powders is contained in range from 0.2 μm to 40.5 μm.

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References

[1] O. Carp, R. Barjega, E. Segal, M. Brezeanu, Nonconventional methods for obtaining hexaferrites, Thermochimica Acta 318 (1998) 57-62.

[2] G. Dercz, B. Formanek, K. Prusik, L. Pająk, Microstructure of Ni(Cr)-TiC-Cr_3C_2-Cr_7C_3 composite powder, Journal of Materials Processing Technology 162-163 (2005) 15-19.

[3] G. Dercz, B. Formanek, K. Prusik, L. Pająk, Microstructure of Ni(Cr)-TiC-Cr_3C_2-Cr_7C_3 composite powder, Proceedings of the 13th Scientific International Conference "Achievments in Mechanical and Materials Engineering" AMME'2005, Gliwice−Wisła, 2005, 99-102.

[4] G. Dercz, L. Pająk, B. Formanek, Dispersion analysis of NiAl-TiC-Al_2O_3 composite powder ground in high-energy attritorial mill, Journal of Materials Processing Technology 175 (2006) 334-337.

[5] G. Dercz, K. Prusik, L. Pająk, Structure investigations of commercial zirconia ceramic powder, Journal of Achievements in Materials and Manufacturing Engineering 18 (2006) 259-262.

[6] G. Dercz, K. Prusik, B. Formanek, L. Pajak, Structure investigations of the ground FeAl(Cr)-Cr_3C_2-Cr_7C_3-TiC composite powder prepared by SHS process, Proceedings of the 11th International Scientific Conference "Contemporary Achievements in Mechanics, Manufacturing and Materials Science" CAM3S'2005, Gliwice−Zakopane, 2005, 167-170 (CD-ROM).

[7] G. Dercz, K. Prusik, T. Goryczka, L. Pająk, B. Formanek, X-ray studies on NiAl-Cr_3C_2-Al_2O_3 composite powder with nanocrystalline NiAl phase, Journal Alloys and Compounds 423/1-2 (2006) 112-115.
[8] J. Ding, W.F. Miao, P.G. McCormick, R. Street, High-coercivity ferrite magnets prepared by mechanical alloying, Journal of Alloys and Compounds 281 (1998) 32-36.
[9] L.A. Dobrzański, Fundamentals of materials science and physical metallurgy, Engineering materials with fundamentals of materials design, WNT, Warsaw, 2006 (in Polish).
[10] L.A. Dobrzański, M. Drak, B. Ziębowicz, Materials with specific magnetic properties, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 37-40.
[11] Y.P. Fu, Ch.H. Lin, K.Y. Pan, Barium ferrite powders prepared by microwave-induced combustion process and some of their properties, Journal of Alloys and Compounds 364 (2004) 221-224.
[12] P.E. Garcia-Casillas, A.M. Beesley, D. Bueno, J.A. Matutes-Aquino, C.A. Martinez, Remanence properties of barium hexaferrite, Journal of Alloys and Compounds 369 (2004) 185-189.
[13] R.J. Hill, C.J. Howard, Quantitative phase analysis from neutron powder diffracton data using the Rietveld method, Journal of Applied Crystallography 20 (1987) 467-474.
[14] D.B. Hovis, K.T. Faber, Textured microstructures in barium hexaferrite by magnetic field assisted gelcasting and templated grain growth, Scripta Materialia 44 (2001) 2525-2529.
[15] P. Kerschl, R. Grossinger, C. Kussbach, R. Sato-Turtelli, K.H. Muller, L. Schultz, Magnetic properties of nanocrystalline barium ferrite at high temperatures, Journal of Magnetism and Magnetic Materials 242-245 (2002) 1468-1470.
[16] M. Leonowicz, Modern hard magnetic materials, Published by Warsaw University of Technology, Warsaw, 1996 (in Polish).
[17] M. Leonowicz, Nanocrystalline magnetic materials, WNT, Warsaw, 1998 (in Polish).
[18] M.H. Makled, T. Matsui, H. Tsuda, H. Mabuchi, M.K. El-Mansy, K. Morii, Magnetic and dynamic mechanical properties of barium ferrite-natural rubber composites, Journal of Materials Processing Technology 160 (2005) 229-233.
[19] A. Mali, A. Ataie, Structural characterization of nanocrystalline $BaFe_{12}O_{19}$ powders synthesized by sol-gel combustion route, Scripta Materialia 53 (2005) 1065-1070.
[20] R. Nowosielski, R. Babilas, G. Dercz, L. Pająk, Microstructure of composite material with powders of barium ferrite, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 117-120.
[21] R Nowosielski, R. Babilas, J. Wrona, Microstrure and magnetic properties of commercial barium ferrite powders, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 307-310.
[22] L. Pająk, G. Dercz, B. Formanek, Rietveld analysis of intermetallic phases from Ni-Al system, Proceedings of the 11th Scientific International Conference "Achievments in Mechanical and Materials Engineering" AMME'2002, Gliwice−Zakopane, 2002, 405-408.
[23] L. Pająk, G. Dercz, B. Formanek, Dispersion analysis of composite FeAl-Fe_xAl_y powders ground in high-energy mills, Proceednigs of the 19th Conference "Applied Crystallography", Cracow, 2003, 221-224.
[24] L. Pająk, B. Formanek, G. Dercz, Dispersion analysis of NiAl-TiC-Al_2O_3 composite powder, Proceedings of the 12th Scientific International Conference "Achievements in Mechanical and Materials Engineering" AMME'2003, Gliwice−Zakopane, 2003, 723-726.
[25] L.S. Pinchuk, L.V. Markova, Yu. V. Gromyko, Polymeric magnetic fibrous filters, Journal of Materials Processing Technology 55 (1995) 345-350.
[26] J. Qiu, M. Gu, Magnetic nanocomposite thin films of $BaFe_{12}O_{19}$ and TiO_2 prepared by sol-gel method, Applied Surface Science 252 (2005) 888-892.
[27] J. Qiu, H. Shen, M. Gu, Microwave absorption of nanosized barium ferrite particles prepared using high-energy ball milling, Powder Technology 154 (2005) 116-119.
[28] N. Shams, X. Liu, M. Matsumoto, A. Morisako, Manipulation of crystal orientation and microstructure of barium ferrite thin film, Journal of Magnetism and Magnetic Materials 290-291 (2005) 138-140.
[29] R.L. Snyder, J. Fiala, H.J. Bunge, Defects and microstructure analysis by diffraction, IUCr Monogrphs on Crystallography 10, Oxford University Press, New York, 1999.
[30] M. Soiński, Magnetic material in technics, COSiW SEP, Warsaw, 2001 (in Polish).
[31] H. Toraya, Array type universal profile function for powder pattern fitting, Journal of Applied Crystallography 19 (1986) 485-491.
[32] G.K. Williamson, W.H. Hall, X-ray line broadening from filed aluminium and wolfram, Acta Metallurgica 1 (1953) 22-31.
[33] R.A. Young, D.B. Wiles, Application of the Rietveld methods for structure refinement with powder diffraction data, Advances in X-Ray Analysis 24 (1980) 1-23.
[34] R.W. Young, The Rietveld method, IUCr Monograph on Crystallography, Oxford Science Publishing, 1993.
[35] X.Y. Zhang, C.K. Ong, S.Y. Xu, Z. Yang, Barium ferrite films with in-plane orientation grown on silicon by pulsed laser deposition, Journal of Magnetism and Magnetic Materials 190 (1998) 171-175.
[36] B. Ziębowicz, D. Szewieczek, L.A. Dobrzański, New possibilities of application of composite materials with soft magnetic properties, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 207-210.