Archives of Materials Science and Engineering

Volume 52
Issue 2
December 2011
Pages 74-81

International Scientific Journal published monthly by the World Academy of Materials and Manufacturing Engineering

Properties and structure of the functional composite materials - Nd-Fe-Co-B powder bonded with polymer

B. Ziębowicz*, M. Dziekońska, L.A. Dobrzański
Division of Materials Processing Technology, Management and Computer Techniques in Materials Science, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
* Corresponding author: E-mail address: boguslaw.ziebowicz@polsl.pl

Received 03.09.2011; published in revised form 01.12.2011

ABSTRACT

Purpose: This paper presents the material and technological solution which makes it possible obtaining functional composite materials based on the nanocrystalline Nd-Fe-Co-B powder with polymer matrix and shows the possibility of application in different branches of the techniques.

Design/methodology/approach: For fabrication of composite materials: Nd-Fe-Co-B powder obtained by rapid quenched technique and for matrix - high density pressureless polyethylene (PEHD) and polyamide (PA12) (2.5 % wt.) were used. Composite materials were compacted by the one-sided uniaxial pressing. The complex relationships among the manufacturing technology of these materials, their microstructure, as well as their mechanical and physical properties were evaluated. Materialographic examination of the structure of composite materials and fractures after decohesion were made.

Findings: The main purpose of obtaining this kind of composite materials is broadening possibilities of nanocrystalline magnetic materials application that influence on the miniaturization, simplification and lowering the costs of devices. Composite materials show regular distribution of magnetic powder in polymer matrix. Examination of mechanical properties show that these materials have satisfactory compression strength.

Practical implications: The manufacturing of composite materials Nd-Fe-Co-B powder – polymer greatly expand the applicable possibilities of nanocrystalline powders of magnetically hard materials however further examination to obtain improved properties of magnetic composite materials and investigations of constructions of new machines and devices with these materials elements are still needed.

Originality/value: Manufacturing processes of functional composite materials obtaining Nd-Fe-Co-B – polymer matrix and determination of their mechanical properties. Results are the base for further investigations such composite materials.

Keywords: Composites; Functional materials; Nanomaterials; Nanomagnetics; Nanocrystalline powder; Polymer; Polyethylene; Polyamide

Reference to this paper should be given in the following way:

B. Ziębowicz, M. Dziekońska, L.A. Dobrzański, Properties and structure of the functional composite materials - Nd-Fe-Co-B powder bonded with polymer, Archives of Materials Science and Engineering 52/2 (2011) 74-81.

MATERIALS

1. Introduction

One of the base factor of civilization evolution is Materials Engineering. New materials investigations are conditioned by technological progress. At the turn of the XX and XXI century Materials Engineering attained a phase of modern designing and manufacturing materials with unique mechanical and physical properties. It conducted among others things to obtain metallic materials with amorphous microstructure, and nanocrystalline as a further consequence. These materials started a nanotechnology epoch in materials engineering and thanks to their excellent magnetic properties resulting wide application possibilities got opinion “future materials”. Nanotechnology is the approach to the most straightforward production control of small and big structures with complex properties; this is the path to the future, the precise method for the controlled fabrication within the environmentally friendly Manufacturing By Design framework [1-4].

Nanomagnetics (nanocrystalline magnets) with specific magnetic properties, in comparison to the others magnetic materials, are quite new materials, discovered in 70thies of XX century. The interest of scientists of these materials is caused by better magnetic and mechanical properties in comparison with conventional one. Nanocrystalline magnetic alloys have properties being a combination of the best properties of other conventional materials used so far. Nanocrystalline magnets is the group of magnetic materials which properties comes from not the features of some concrete alloy but from special ultracrystalline structure. Suitable chemical composition and structure depending on the parameters of technological process, conducted to invent unconventional manufacturing methods, which allows to obtain materials with phase compositions impossible to achieve by traditional methods [5-8].

In spite of high technological development and new, very precise investigation methods of nanocrystalline alloys with special magnetic properties, they are still an investigation purpose for many scientists in the whole world.

Nanocrystalline materials with specific hard magnetic properties (nanomagnetics) today play a very important role in many life field, and their meaning is still growing (Fig. 1) [9-15]

Hard magnetic composite materials can be included to functional materials. There is no generally accepted definition of functional materials. They are characterized by unique feature - under external factors can change in wide range their physical properties. Functional materials are materials which nature directly condition fulfilling special functions. These materials have special electronic, optical, magnetic or smart properties.

They can be (taking into consideration the function) divided into:

- materials for electronic and eletrotechnique,
- materials for optic, optoelectronic and photonic,
- smart materials.

The main purpose of the paper is to present the mechanical properties of functional composite materials: hard magnetic powder - thermoplastic polymer.

2. Nanocrystalline materials

Nanocrystalline materials (nanomaterials) are polycrystalline solid body in which the grain size or the thickness of deposited or created layer is in the range from 1 to 100 nm, at least in one direction (sometimes this range is extended up to 200 nm). Overflowing this boundary in materials new and commonly surprising properties. Volume portion of grain boundaries in nanocrystalline material with grains up to 5 nm is 50%, 10 nm – 5%, and 100 nm – 3%, respectively. Their structure is unequilibrium with higher interaction energy. Annealing commonly leads to the grain growth, so the manufacturing of nanocrystalline materials should be made in conditions which make it impossible, or supply of external energy causes bigger grains fragmentation [1-4].

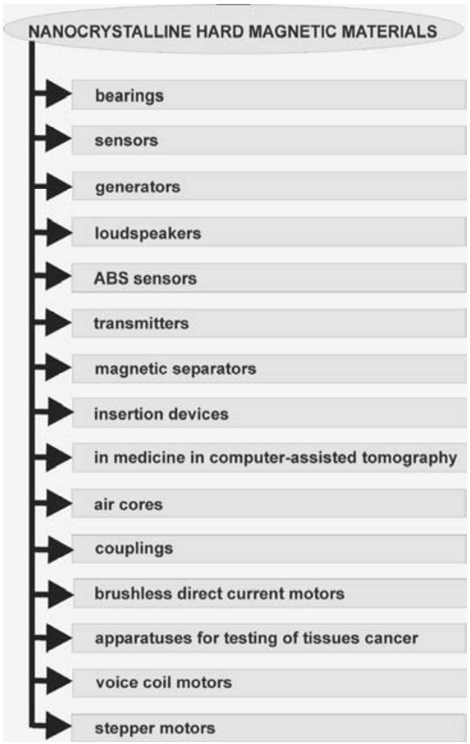

Fig 1. Fields of nanocrystalline hard magnetic materials applications [9-15]

Nanocrystalline materials can be also obtained in a crystallization process of amorphous materials, in which during very rapid cooling the structure of overcooled liquid is “frozen”. To nanostructural materials can be included quant dots and bars, grains, nanotubes, nanobars, nanofibres, nanofoams, nanocrystals, nanoprecise and selforganising thin films, metals, intermetallic phases, semiconductors, minerals, ferromagnetics, dielectrics, nanocomposites, alloys, blendes, organic materials, organo-minerals, biominerals, biomoleculs, polymers, functional structures and devices [7, 11-14].

Nanomaterials are manufactured in scientific laboratories among the others as powders, thin films or isolated (nanometric) particles by the use of mechanical, physical and chemical methods:

- based on the generation of big number of crystalline structure defects (dislocations, grain boundaries) in policrystalline materials as a result of high degree of plastic deformation.

It includes processes of mechanical synthesis and high energy ball milling, squeezing, shearing or high energy radiation,
- crystallization from metastable and unstable condensed phases - crystallization from overcooled liquids by rapid quenching, crystallization of amorphous materials or precipitation from supersaturated solid solutions,
- atoms or particles deposition in PVD (Physical Vapour Deposition) or CVD (Chemical Vapour Deposition) techniques,
- sol-gel,
- deposition isolated particles from gas phase, decomposition of chemical compounds or extraction form solutions.

During manufacturing of nanocrystalline materials the following criteria should be fulfilled:
- multistage crystallization process,
- presence of uniform nucleation places in amorphous phase,
- reduction of growth reaction, caused by segregation of dissolved compound, with low diffusion coefficient near the separation surface of nanocrystalline/amorphous phases,
- high thermal stability of residual amorphous phase enriched in elements dissolved during primary crystallization [5-7].

The hard magnetic powders can be obtained, among others, with the HD (Hydrogenation Disproportionation) technologies, with the HDDR (Hydrogenation, Disproportionation, Desorption, Recombination) method, by Mechanical Alloying (MA), and by Melt Quenching (MQ). The most often used method is Melt Quenching, which consists in spraying the molten alloy with the relevant chemical composition onto the chill roll rotating at a high rotational speed. Rare earth alloys are very prone to oxidation so the process should be made in protective atmosphere. Alloy is melted in quartz inductive melting pot in the protective gas (argon or vacuum) than is sprayed onto the chill roll rotating. Alloy solidify as thin tape or flakes (Fig. 2) [5, 16].

a) b)

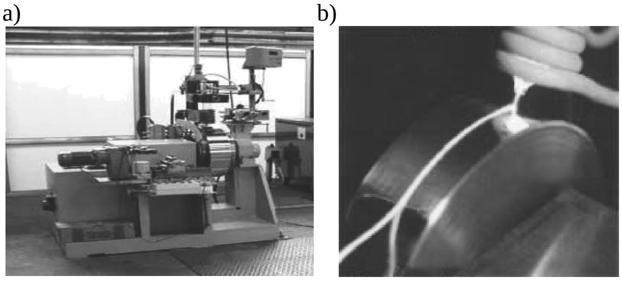

Fig. 2. Manufacturing of nanomaterials by melt quenching method a) general view, b) melting pot, spraying the molten alloy onto the chill roll rotating [5-7]

The tape made in this way is further mechanically milled in high energy ball mills or in Hydrogenation Disproportionation method and the obtained powder may be mixed with the chemo or heat-hardening polymer and further hot or cold formed to obtain composite materials with required shape [17-18].

During the consolidation process it is very important to give attention to the metastable structure of powders. Plastic forming, hot working, metallurgy powder is in many cases disadvantageous because big deformation and high temperature influence grain growth and loss of nanocrystalline structure. Manufacturing of composite materials nanocrystalline powder - polymer considerably increases application possibilities of these materials (Fig. 3) [19-27].

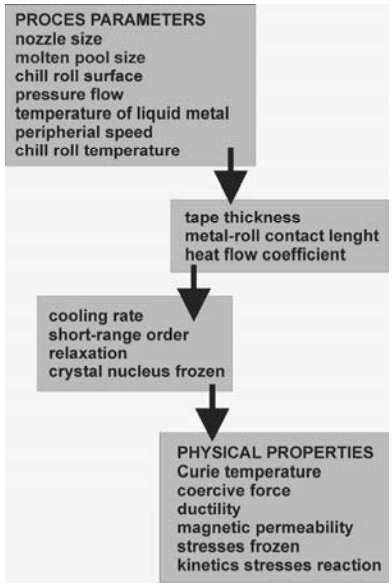

Fig. 3. Schema of relationship between process parameters and physical properties of materials obtained in melt quenching method

3. Materials and technology

The experiments were made with the polymer matrix functional composite materials reinforced with particles of the powdered rapid quenched Nd-Fe-Co-B strip bonded with the high density pressureless polyethylene (PEHD) and polyamide (PA12). The amount of polymer matrix was 2.5% wt.

Advanced composite materials were compacted by the one-sided uniaxial pressing. Portion of the matrix, compacting pressure as well the temperature and curing time of the polymer materials decide the technological conditions of magnets manufacturing.

The selection of the method of obtaining composites determines the following criteria:
- enables to make any elements with sophisticated shapes,
- the process of compacting has been executed at the temperature which take into account the metastable structure of powders,
- during the compacting process the powder particles get closer to each other what increases their contact area and causes their mechanical meshing. That is the reason why the shape of particles has great influence on mechanical properties of obtained composite materials because the connection of their elements is made by the adhesion forces,
- this method is a simple and not costly.

Schematic diagram of the technological operations for manufacturing functional composite materials based on the nanocrystalline Nd-Fe-Co-B powder with polymer matrix is presented in Figure 4. Base parameters of composite materials obtaining are shown in Table 1.

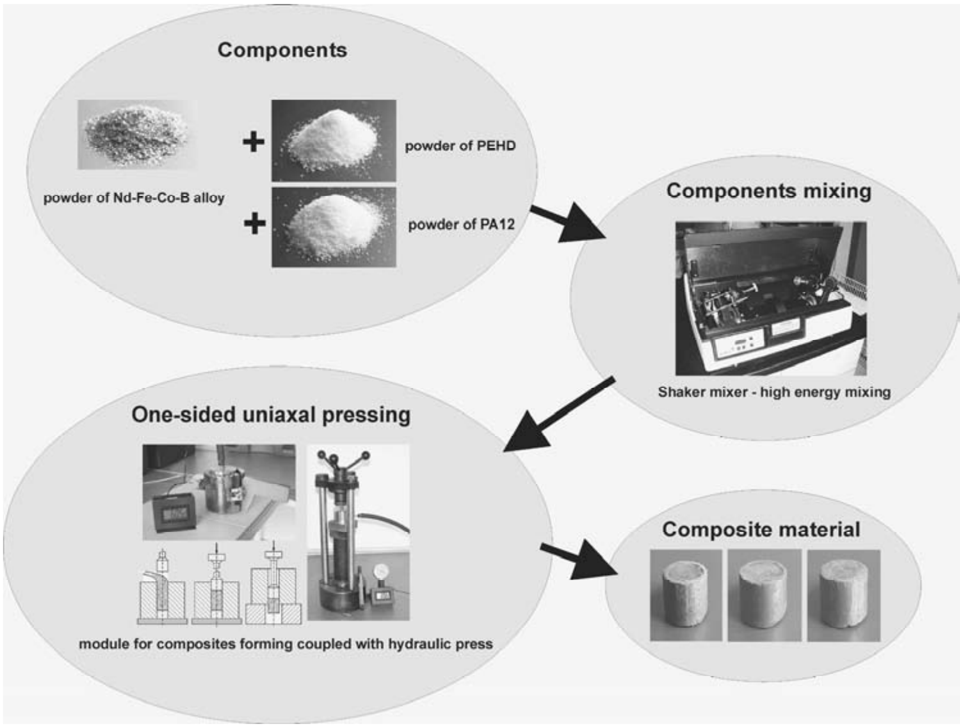

Fig. 4. Schematic diagram of the technological operations for manufacturing functional composite materials of nanocrystalline Nd-Fe-Co-B powder with polymer matrix

Table 1.
Base parameters of obtaining composite materials

Components	
Reinforcement	powder of Nd-Fe-Co-B alloy - chemical composition [concentration at.%] Nd14.8 Fe76.0 Co4.95 B4.25 mean grain size 95 μm - flaky shape
Matrix	- powder of high density polyethylene (PEHD) - 2.5% wt., mean grain size 80 μm - powder of polyamide (PA12) - mean grain size 100 μm
Parameters of one - sided uniaxial pressing	
Components mixing time	0.25 h
Pressure	500 MPa, 1000 MPa
Temperature	120°C - PEHD, 170°C - PA12
Pressing time	0.25 h
Atmosphere	free air

4. Methodology

Topography of the surface after compression test were made on the ZEISS Discovery V12 light microscope equipped with the computer image analysis system at the magnification of 75x.

Observations of fractures after decohesion were made on the ZEISS Supra 25 scanning electron microscope at the maximum magnification of 100x, 500x and 2000x using the secondary electron detection at the 20 kV accelerating voltage.

The density of the composite materials was evaluated by determining the test piece mass using the analytical balance with the accuracy of $\pm 10^{-4}$ g and its volume basing on the apparent mass loss by immersing in water according to the standard PN-ISO 33769:2010.

Compression tests were made on the ZWICK Z100 all-purpose testing machine. The tests were carried out at room temperature with compression rate 5 mm/min. The following properties were evaluated: Young's module E, compression strength R_C, unit shortening A.

Hardness measurements were made on Vickers FM-700 microhardness tester. To minimize errors for each sample 100 measurements were made.

5. Results and discussion

Figure 5 shows topography of composite observed in light microscopy. Occurrence of the small portion of pores was observed in the manufactured composite material.

Figures 6 and 7 show fractures of composite materials after compression test. On the base of microscopic observation it can be seen that as a result of uniaxial, one-sided pressing the powders' particles get closer to each what increased their contact area and caused their mechanical meshing. On the fractures it can be observed polymer clusters, so the polymer distribution is non-uniform and can influence on decrease of composite materials mechanical properties.

Results of density measurements are shown in Table 2. Real density is smaller than theoretical one what is caused by the pores between particles of pressed composite materials. Density of composite materials compacted under the pressure of 1000MPa is higher than under 500MPa. The ratio of density to theoretical density is in the range of 75.7% for composite material PEHD 2,5%-Nd-Fe-Co-B compacted under the pressure of 500MPa up to 83.7% for composite material PA12 2.5%-Nd-Fe-Co-B compacted under 1000MPa. Compacting pressure influences the density of composite materials - the higher pressure, the higher density. Real density for composite material PEHD 2,5%-Nd-Fe-Co-B compacted under the pressure of 500MPa is in the range from 4.925 g/cm^3 up to 5.524 g/cm^3 for PA12 2,5%-Nd-Fe-Co-B composite materials compacted under the pressure of 1000 MPa.

a) b)

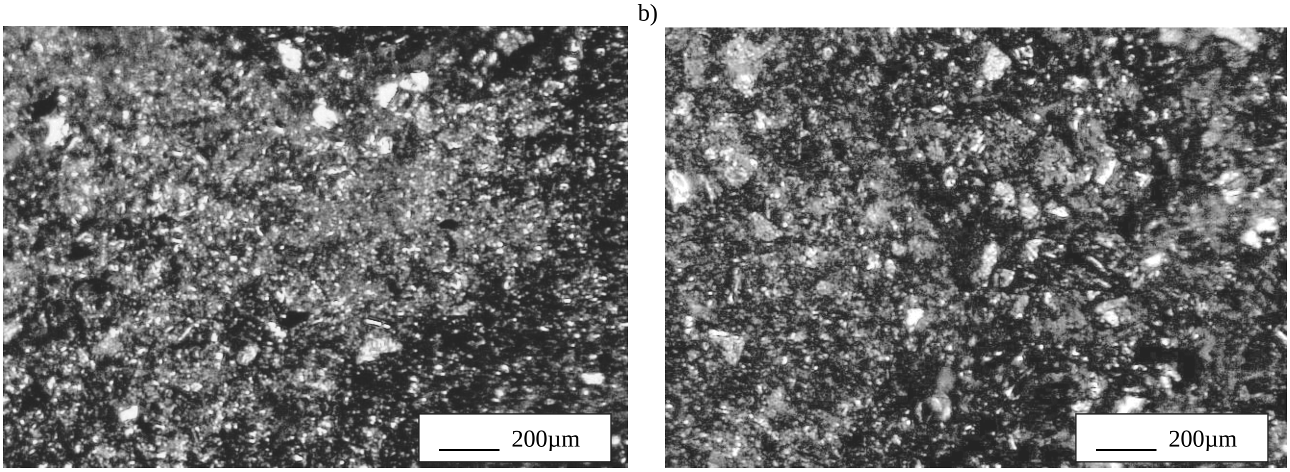

Fig. 5. Topography of the surface of composite materials: a) PEHD 2.5% + Nd-Fe-Co-B, b) PA12 2.5% + Nd-Fe-Co-B

Table 2.
Comparison of composite materials density

Material	Pressing pressure [MPa]	Density [g/cm^3]	Theoretical density [g/cm^3]	Ratio of density to theoretical density [%]
PEHD 2.5% + Nd-Fe-Co-B	500	4.925	6.509	75.7
PEHD 2.5% + Nd-Fe-Co-B	1000	4.956	6.509	76.1
PA12 2.5% + Nd-Fe-Co-B	500	5.286	6.596	80.1
PA12 2.5% + Nd-Fe-Co-B	1000	5.524	6.596	83.7

Table 3.
Comparison of mechanical properties of composite materials

Material	Pressing pressure [MPa]	Young's module E [MPa]	Compressive strength R_c [MPa]	Unit shortening A [%]	Microhardness $HV_{0.1}$
PEHD 2.5% + Nd-Fe-Co-B	500	122.83	20.28	16.51	45.75
PEHD 2.5% + Nd-Fe-Co-B	1000	127.25	21.57	16.95	103.25
PA12 2.5% + Nd-Fe-Co-B	500	230.96	35.36	15.31	78.92
PA12 2.5% + Nd-Fe-Co-B	1000	425.16	70.79	16.65	95.42

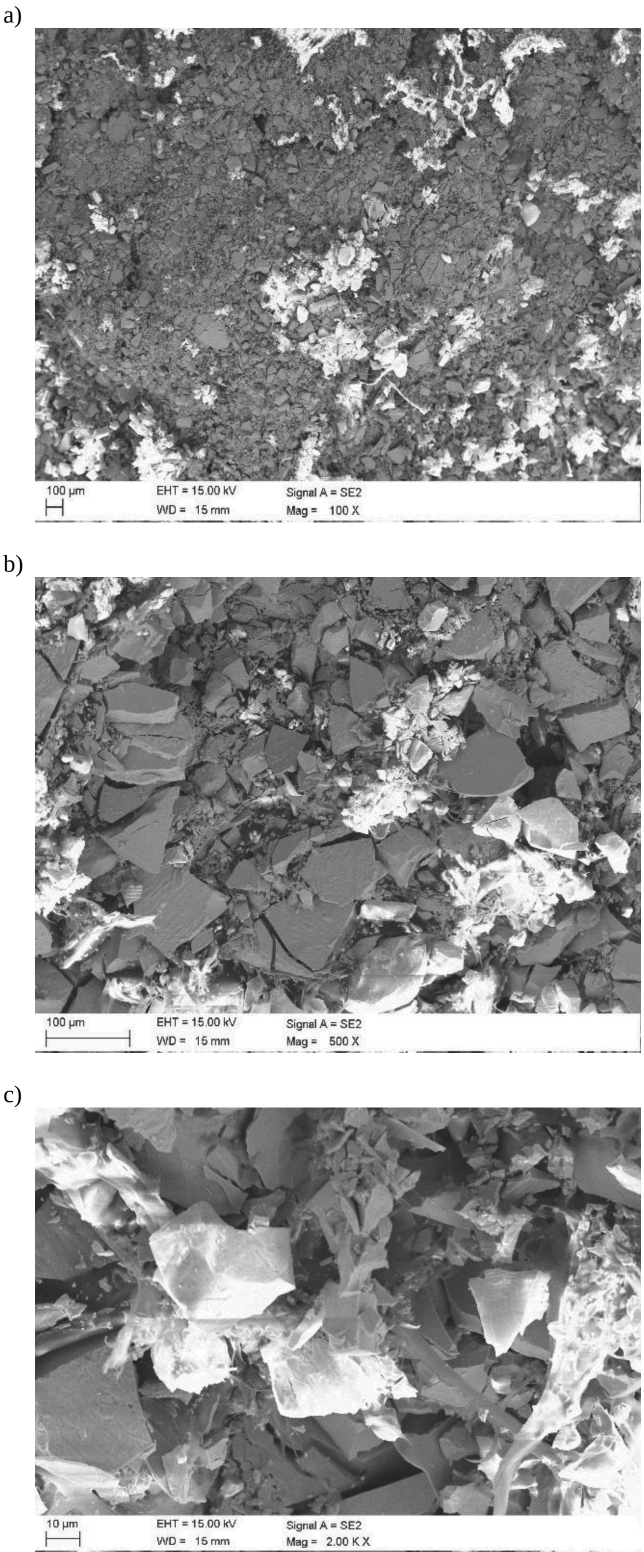

Fig. 6. The SEM images of composite material PEHD12 2.5% + Nd-Fe-Co-B fractures obtained after decohesion in the compression test

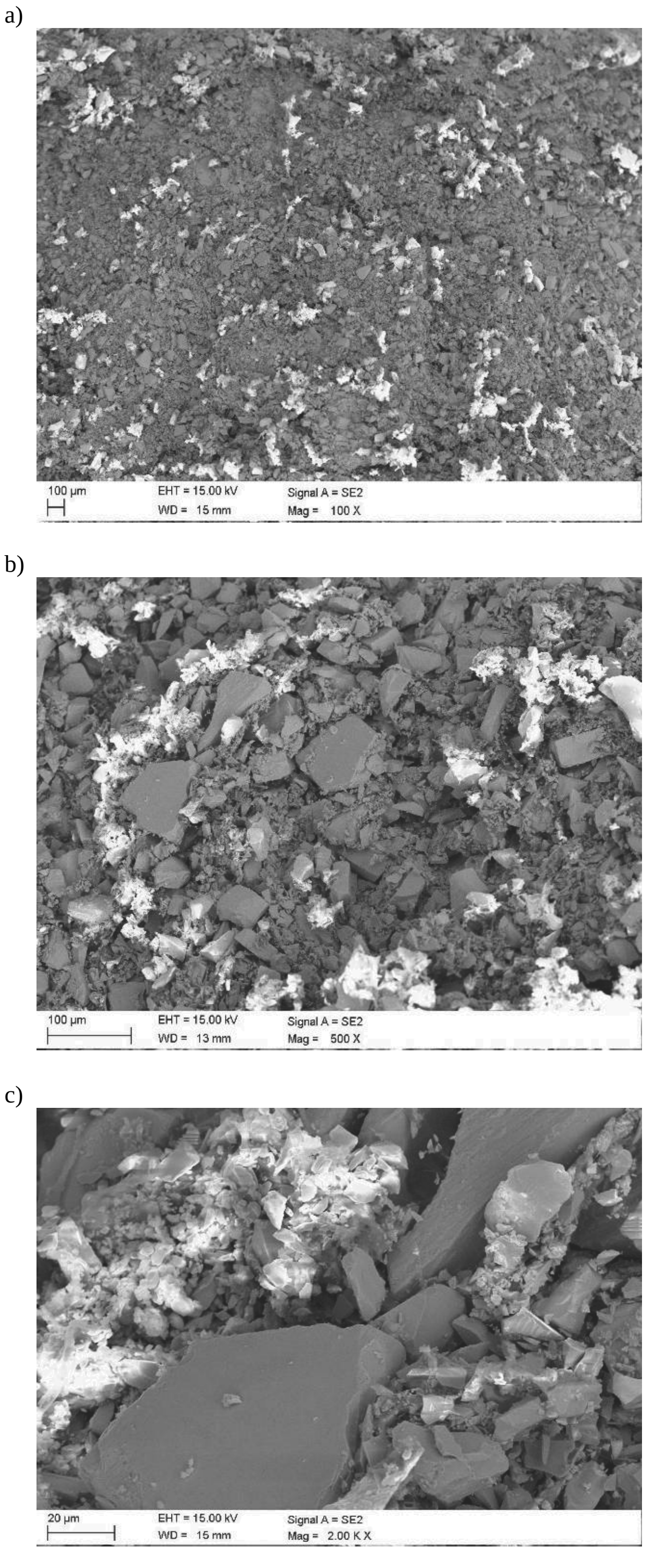

Fig. 7. The SEM images of composite material PA12 2.5% + Nd-Fe-Co-B fractures obtained after decohesion in the compression test

Table 3 shows comparison of mechanical properties of obtained composite materials. Polymer portion was experimentally determined. At first investigations were made on composite materials with polymer matrix 2.5%, 5.0%, 7.5% and 10.0%.

On the base of that investigations composite materials with 7.5% and 10.0% matrix were rejected because polymer overflows the die during compacting process. The optimal polymer portion was determined to be 2.5% because obtained composite materials show the best mechanical properties. Composite materials with PA12 matrix have better compression strength and hardness in comparison with composite materials with PEHD matrix.

Higher compacting pressure causes improvement of composite materials mechanical properties. Compressive strength is in the range from 20.3 MPa for composite material PEHD 2.5%-Nd-Fe-Co-B compacted under the pressure of 500 MPa up to 70.8 MPa for composite material compacted under the pressure of 1000 MPa. Hardness increases for composite material PEHD 2.5%-Nd-Fe-Co-B compacted under the pressure of 500 MPa from 45.7 up to 95.4 for composite material PA12 2.5%-Nd-Fe-Co-B compacted under 1000 MPa.

Hard magnetic composite materials with 2.5% of polymer matrix will be subjected the next investigations. Among the others will be measured the magnetic properties and the resistivity on corrosion in different environments to evaluate the correlation between mechanical, magnetic and other properties of obtained composite materials.

6. Summary

Functional materials with specific magnetic properties can be today commonly meeted. They can find practical application in every field of human live, from toys, clothing industry, automotive industry, electrical industry, to complicated medical apparatus and advanced space devices.

The development of Materials Science is so quick that materials which few years ago were found only in space devices can be meted now in our houses.

Tendency to miniaturization - to manufacturing materials with the least possible mass and size, simultaneously with the best mechanical properties leads to functional materials among the others to composite materials with specific magnetic properties.

The selection of composite components is made in respect of its advisable features. The new material with new, planned properties is created.

The main direction of miniaturization in modern world are show in Fig. 8.

Currently the best hard magnetic properties show nanocrystalline alloys. Its manufacturing process allows only to obtain thin tapes, bars or after mechanical treatment - nanocrystalline powder. There is no possibility to obtain bigger elements with complicated shape with nanocrystalline structure.

The best way of manufacturing elements from nanocrystalline magnetic powder is compacting then into a composite materials in which magnetic powder is a reinforcement while polymer is a matrix. Polymers show satisfies mechanical properties and do not have any chemical reaction with nanocrystalline magnetic powder. The temperature of polymer processing do not influence the loss of nanocrystalline structure in hard magnetic materials.

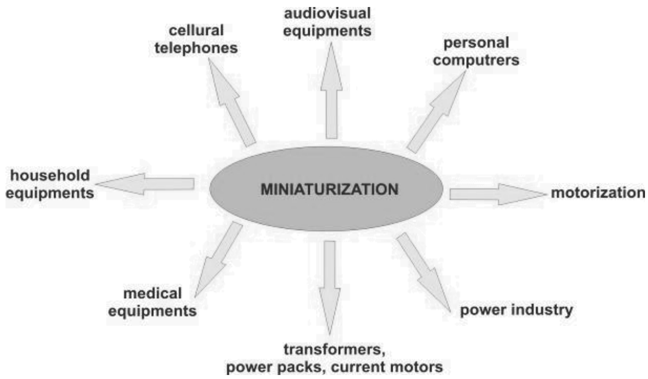

Fig. 8. The main direction of miniaturization in modern world

Composite materials are usually obtained during pressing process of mixed component in the temperature higher than polymer processing temperature.

One-sided unaxial pressing is the simplest pressing method. In spite of disadvantages like non-uniform pressure distribution in material during pressing process resulting differences of moulding density this method is sufficient to manufacture small element with sophisticate shapes. The difference of density increase with increase of the distance between stamps but for small distance the differences are not so much meaningful.

The main advantageous of this method is its accessibility, simplicity, facility and low costs.

Investigations made show the influence of the compacting pressure, portion and kind of polymer matrix on the mechanical and physical properties of composite materials reinforced by nanocrystalline hard magnetic powder. The best mechanical properties show PA12%-Nd-Fe-Co-B composite material pressed under the pressure of 1000MPa.

Investigations allows to optimize technological operation and material choice to obtain composite material with the best possible mechanical properties. This optimization can be a base for different technological modification which allows to choose operation taking into consideration expected magnetic and mechanical properties of hard magnetic composite materials.

The conducted investigations are important taking into considerations complex approach to the manufactured materials. Nowadays, the modern materials requires not only the typical properties connected with their main function but also they need to fulfill complex function connected mainly with the specific applications of these materials both in different environments and operating conditions. Only the set of all these properties give full opportunity to the optimal use of the materials manufactured. The studies complete knowledge of hard magnetic composite materials bonded polymer concerning their mechanical properties and structure.

References

[1] G. Cao, Nanostructures and nanomaterials: synthesis, properties and applications, Imperial College Press, London, 2004.

[2] H. Brune, H. Ernst, G. Schmid, Nanotechnology: assessment and perspectives, Springer, 2006.
[3] M. Karkare, Nanotechnology: fundamentals and applications, I.K. International Pvt. Ltd., 2008.
[4] H. Hosno, Y. Mishima, H. Takezoe, K.J.D. Mackenzie, Nanomaterials - from research to applications, Elsever, 2007.
[5] M. Leonowicz, Noncrystalline magnetic materials, Warsaw, WNT, 2005 (in Polish).
[6] R.C. O'Handley, Modern magnetic materials, Principles and applications, Wiley, New York, 2000.
[7] M. Leonowicz, J. Wysłocki, Contemporary magnets: technologies, mechanism of coercive, applications, Warsaw, WNT, 2005 (in Polish).
[8] H. Kronmüller, S. Parkin, Handbook of magnetism and advanced magnetic materials, Jon Wiley and Sons, 2007.
[9] J.M.D. Coey, Magnetic materials, Journal of Alloys and Compounds 326 (2001) 2-6.
[10] D.C. Jiles, C.C.H. Lo, The role of new materials in the development of magnetic sensors and actuators, Sensors and Actuators A 106 (2003) 3-7.
[11] B.M. Ma, J.W. Herchenroeder, B. Smith, M. Suda, D.N. Brown, Z. Chen, Recent development in bonded Nd-Fe-B magnet, Journal of Magnetism and Magnetic Materials 239 (2002) 418-423.
[12] H.J. Fastenau, E.J. Loenen, Aplication of rare earth permament magnets, Journal of Magnetism and Magnetic Materials 157-158 (1996) 1-6.
[13] M. Soiński, Magnetic materials in engineering, NOSiW SEP, Warsaw, 2001 (in Polish).
[14] B. Ślusarek, Dielectromagnets, Wrocław, 2001 (in Polish).
[15] J.F. Gieras, Advancements in electric machines, Springer, 2008.
[16] D.C. Jiles, Recent advances and direction in magnetic materials, Acta Materialia 51 (2003) 5907-5939.
[17] R. Nowosielski, R. Babilas, Preparation and properties of Fe-based bulk metallic glasses, Journal of Achievements in Materials and Manufacturing Engineering 40/2 (2010) 123-130.
[18] D. Chung, Composite materials: functional materials for modern technologies, Springer, 2010.
[19] D. Gay, S. Hoa, Composite materials: design and applications, CRC Press, 2007.
[20] D. Szewieczek, L.A. Dobrzański, B. Ziębowicz, Structure and magnetic properties of nanocomposites of nanocrystalline powder - polymer, Journal of Materials Processing Technology 157-158 (2004) 765-770.
[21] B. Ziębowicz, D. Szewieczek, L.A. Dobrzański, Magnetic properties and structure of nanocomposites of powder $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy - polymer type, Journal of Materials Processing Technology 157-158 (2004) 776-780.
[22] A. Baron, D. Szewieczek, R. Nowosielski, Selected manufacturing techniques of nanomaterials, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 83-86.
[23] P. Gramatyka, R. Nowosielski, P. Sakiewicz, Magnetic properties of polymer bonded nanocrystalline powder, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 115-118.
[24] L.A. Dobrzański, M. Drak, Hard magnetic composite materials Nd-Fe-B with additions of iron and X2CrNiMo-17-12-2 steel, Journal of Alloys and Compounds 449/1/2 (2005) 88-92
[25] M Drak, LA Dobrzański, Corrosion of Nd-Fe-B permanent magnets, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 239-241
[26] D. Plusa, M. Dospial, U. Kotlarczyk, B. Ślusarek, T. Mydlarz, Study of reversible and irreversible magnetization components in hybrid Nd-Fe-B/Ferrite/Alnico resin bonded magnets, Archives of Metallurgy and Materials 53 (2008) 867-873.
[27] L.A. Dobrzański, A. Wydrzyńska, O. Iesenchuk, Intelligent epoxy matrix composite materials consisting of $Tb_{0.3}Dy_{0.7}Fe_{1.9}$ magnetostrictive particulates, Archives of Materials Science and Engineering 35/1 (2009) 33-38.