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Preliminary Quality Control of Magnetic Materials for applications in Restorative Medicine - Quantitative Analysis of Structural Homogeneity of RE-M-B /Polymer Composites

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The properties of bonded magnetic materials (RE-M-B /polymer magnetic composites) depend not only on the magnetic properties of powder, but also on the parameters of the consolidation process and the type of binder. Increasing the binder content in RE-M-B /polymer composites could be very beneficial from the corrosion resistance point of view, which, unfortunately, is not conducive to the magnetic properties improvement. Therefore, a compromise between both trends is necessary to obtain a material with adequate corrosion resistance with an acceptable decrease in magnetic properties. In the paper the results of research under $Nd_{12}Fe_{77}Co_5B$ / biotolerant-polymer composites with different binder content have been presented. The research has been carried out on $Nd_{12}Fe_{77}Co_5B$ / biotolerant-polymer composites with 20 and 10 wt. % of binder. Due to the possibility of using the magnetic material in restorative medicine, as a binder the bio-tolerable polymeric material has been used (acrylate). All results has been compared to previously determined measurements for composite with a binder content about 3 % wt.. It has been found that the content of 10 % wt. bio-tolerable polymeric material in the magnetic composite is the most favorable (optimal) - the binder material is evenly distributed throughout the composite volume.

Keywords: quality control, bonded magnets, quantitative analysis, composite structure

1 Introduction

The RE-M-B magnetic materials (where RE - rare earth element, M - transition metal) have a number of indisputable advantages, which makes them a very promising material for designers, and the scope of their applications is constantly growing. These materials are unrivaled in terms of BH_{max} value, high remanence value and the fact that the volume of material needed to create a specific magnetic field strength is much smaller than that of other materials [1–4]. The applicability of RE-M-B magnetic materials depends not only on the magnetic properties, but also on their mechanical and thermal properties as well as chemical resistance to the destructive effects of the usage environment. Although, according to estimates, Nd-Fe-B sintered magnets account for 90 % of the magnet market, but the attractiveness of bonded magnets increases with the simplification of their technology [5]. The essential part of the technological process of the bonded magnetic materials producing consists of simple plastics processing operations - which can be done by small entrprises [5, 6]. Bonded magnets are usually obtained from high-density powders obtained in the process of rapid cooling from the liquid state (melt spinning), HDDR, spraying the liquid phase (spray atomizing) and by grinding alloys or pure elements. But the surface oxidation is a serious obstacle in the process of obtaining RE-M-B powders. Powders have a much higher degree of oxidation than their solid counterparts [3, 4, 7].

The high content of the active rare earth element makes the surface of powder particles easily covered with oxidation products in the presence of insignificant amounts of oxygen and moisture. The presence of oxide phases on the powder particles surface is a significant limitation in the consolidation process. First, the presence of oxides and hydrated metal oxides on the powder particles surface reduces the adhesion of the binder material to the metallic surface, which consequently leads to a decrease in the consistency of the finished RE-M-B magnetic composites. Secondly, the oxidation of metals included in the magnetic alloy causes degradation of the ferromagnetic phase (which is responsible for the unique magnetic properties of RE-M-B materials) and in turn leads to a drastic deterioration in magnetic properties [8]. According to the literature review [9, 10], the research under the possibility of protecting magnetic powder particles based on RE-M-B alloy against the negative effects of the atmosphere are carried out. The coating methods are becoming increasingly popular and two methods are used for this purpose: the encapsulation and biencapsulation method [10–13].

Another problem in the use of materials containing rare earth elements is their high susceptibility to corrosion - especially sintered materials, which in environments with reduced pH are strongly degraded [14]. In this case, also bonded magnetic materials based on RE-M-B powder (RE-M-B/polymer magnetic composites) are irreplaceable, because in aggressive substances they show greater durability than their counterparts [15]. The RE-M-B/polymer magnetic composites also owe their corrosion resistance to the isolation of powder particles with polymeric binder material. Therefore, the binding material, apart from its basic function, is a protective material - it isolates individual powder particles and reduces the penetration of aggressive corrosive media into the interior of the material. Therefore, increasing the binder content in bonded RE-M-B composites is desirable from the corrosion resistance viewpoint, but it is not desirable because of the magnetic properties. In order to increase the magnetic properties of RE-M-B bonded materials, the binder content should rather be limited. It is necessary to search for a compromise between both trends, to obtain a material with adequate corrosion resistance and acceptable magnetic properties.

Due to the technical application of magnetic composites, the most commonly used binding materials include thermo- and chemically-setting epoxy or polyester resins. However, the presence of toxic resins excludes the use of RE-M-B / polymer magnetic materials from use in restorative medicine - which is a potential area of application for magnetic materials. The possibility of using RE-M-B / polymer bonded composites in restorative medicine, as magnetic retention systems, or epithelial abutments, results in the search for new binder materials for this group of magnetic composites [16, 17].

In medical applications, there is no need to use magnets with the highest magnetic properties, so bonded materials with slightly worse properties are sufficient here. However, it must be biotolerable/biotolerant and resistant to degradation in the body's fluids.

The main goal of the research presented in this work is to evaluate the microstructure homogeneity of magnetic composites based on quantitative analysis of metallographic images. The presented research are the basic method of initial (though destructive) quality control of new magnetic materials. Regardless of the type of industry, quality control as well as qualitative and quantitative analyzes are the basis for implementing changes in technological processes - hence the great emphasis on the implementation of various methods of analysis and assessment [18–20].

2 Experimental

The material for the research presented in this work was a group of magnetic composites whose main purpose is the use of dental prosthetics (or in restorative medicine). The discussed group of magnetic composites is based on high coercive magnetic powder based on Nd- (Fe,Co)-B alloy, which is consolidated with polymeric materials for biomedical applications (biotolerant-polymer - a group of acrylates). In the research commercial magnetic powder (*Magnequench*) with the chemical formula $Nd_{12}Fe_{77}Co_5B_6$ has been used (subscripts represent the atomic percentage) (Fig.1). This powder is characterized by an irregular shape - the shape of the plaque, lamellas or flakes.

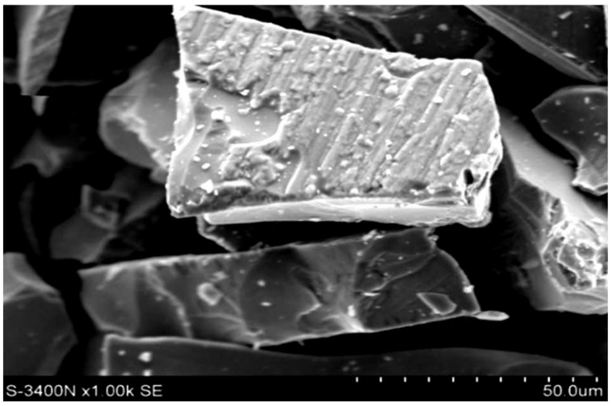


Fig.1 *SEM image of $Nd_{12}Fe_{77}Co_5B_6$ magnetic powder - magnification × 500 / × 1.00k*

Lack of proportions in the spatial dimensions of powder particles can contribute to significant fragmentation and powders crushing during the manufacturing process of magnetic composites - mixing / homogenization of powder compositions, initial molding, pressing.Commercial powder is also characterized by diverse fragmentation (according to sieve analysis, the particle size in the range of 0 ÷ 250 μm). The particle size of the powder effect on the magnetic interactions, therefore it is crucial to select such a fraction that will not reduce the magnetic properties of the material. According to the literature, a smaller particle size of powder (25 ÷ 75 μm) contributes to the demagnetization process of the material. Whereas, the larger fraction, the better the magnetic properties [10, 21–23]. Due to the fact that the technology for the production of the tested magnetic composites ($Nd_{12}Fe_{77}Co_5B$ / biotolerant-polymer) is to be used in practice in prosthetic laboratories, therefore ready-made mixtures of thermosetting acrylate masses have been used for consolidation (table 1).

Three powders compositions have been selected for the tests. It has been assumed that the increase in binder content could cause a decrease in magnetic properties and an increase in corrosion resistance. Therefore, in order to provide a compromise between these trends, the content 10 and 20 % wt. of biotolerant-polymer were used - the samples have been marked accordingly: sample 2 and sample 3. The reference sample contains abaut 3 % wt. of binder (it is the lowest possible binder content [29]) and has been marked as sample 2.

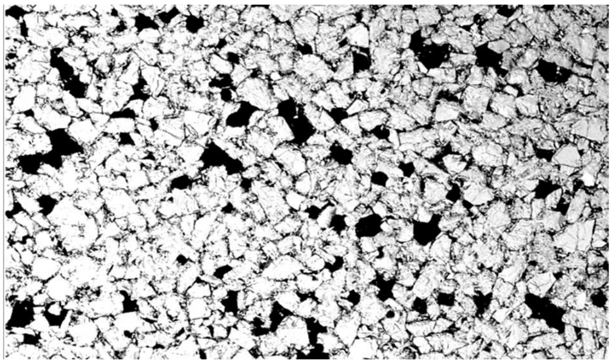
***Tab. 1** Characteristics of thermosetting acrylic polymer*

COMPOSITION	
	Polymer binder, of which the main component is PMMA
APPLICATION	
	Material used to prepare prosthetic restorations (or denture repair)
POLYMERIZATION PROCESS	
	Material obtained in the process of low temperature polymerization Process temperature: ≈ 40 ° C Polymerization time: 25 min.

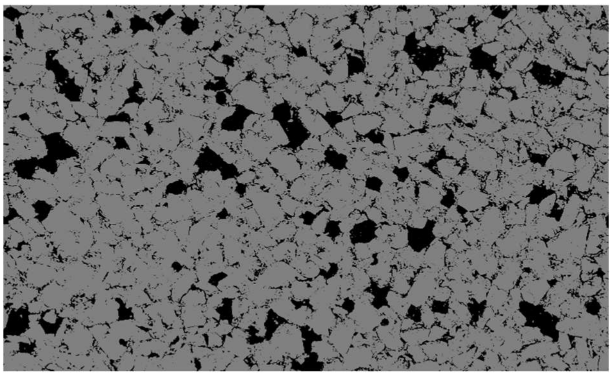
The main goal of the research presented in this work is to evaluate the microstructure homogeneity of magnetic ($Nd_{12}Fe_{77}Co_5B$ / biotolerant polymer) composites. For this purpose, microscopic images of the structure have been taken. Based on the obtained digital images for samples 1, 2 and 3, a quantitative analysis has been performed using the MeTilo program.

3 Results and discussion

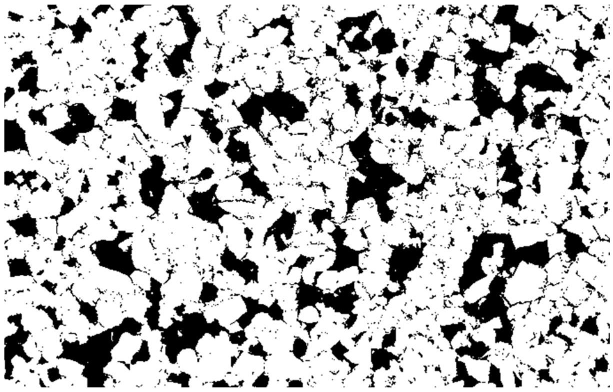
In Figures 2 a, c, e real images of magnetic composite structures have been presented. The images of $Nd_{12}Fe_{77}Co_5B$ / biotolerant-polymer composites structures were the basis for further quantitative analysis. For the needs of quantitative analysis, binary images were also generated (Fig 2 b, d, f).



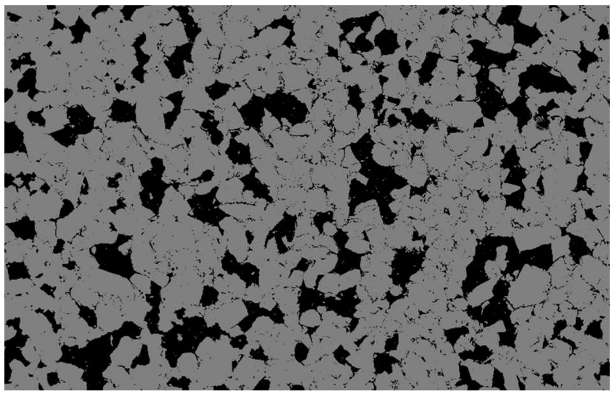
a)



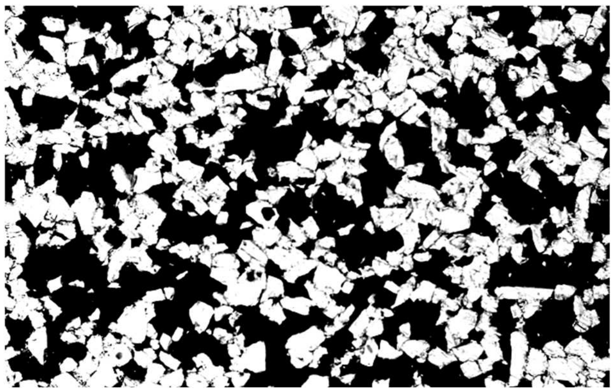
b)



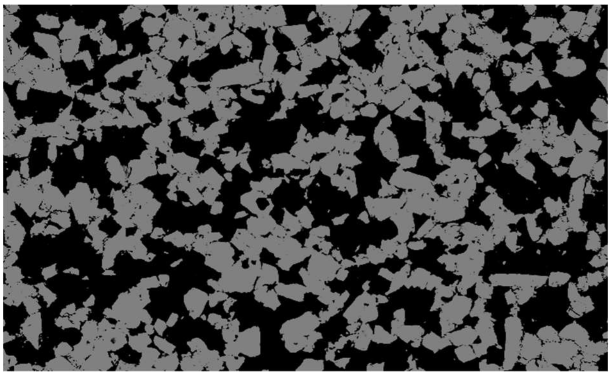
c)



d)



e)



f)

Fig. 5 *Microstructure images for the $Nd_{12}Fe_{77}Co_5B$ / biotolerant-polymer composites. Image obtained with the use of an optical microscope (a, c, e), digital images after binarization (b, d, f): a, b) sample 1 - magnetic powder consollidated with 3 % wt. of biotolerant polymer; c, d) sample 2 - magnetic powder consollidated with 10 % wt. of biotolerant polymer; e, f) sample 3 - magnetic powder consollidated with 20 % wt. of biotolerant polymer*

On binary images the areas corresponding to the occurrence of magnetic powder have been marked in grey, while the areas of occurrence of both the binder as well as voids and pores (which are characteristic for this type of materials) are marked in black. The characteristic values for the observed composite structures are given in Table 2.

Quantitative analysis using the standard (surface) method showed the volume fraction of the binder in the tested composites. According to the assumption, the smallest share (%) of binder is demonstrated for sample 1 (3 % wt. of biotolerant polymer), and the largest for sample 3 (20 % wt. of biotolerant polymer). In sample 1 (3 % wt. of biotolerant polymer, the magnetic powder particles are in close contact.

Based on the values presented in Table 2 and binary images of the structure (Fig. 2) obtained for sample 2 (10 % wt. of biotolerant polymer), it can be concluded that the distribution of magnetic powder particles and areas of binder occurrence is even in the structure of this composite.

Tab. 2 *Results of a quantitative analysis for the $Nd_{12}Fe_{77}Co_5B$ / biotolerant polymer magnetic composite - analysis using the MeTilo program for the entire area of the structure (Fig 2)*

Sample	$Nd_{12}Fe_{77}Co_5B$ / biotolerant polymer		
	area share of magnetic material (grey area), %	area share of binder material (black area), %	distanceof binder agglomerates*, mm
1 3 % mas. biotolerant polymer	81.60	18.40	0.05 - 0.30
2 10 % biotolerant polymer	73.70	26.30	0.10 - 0.30
3 20 % biotolerant polymer	51.40	48.60	0.30 - 0.80

* distance of the nearest objects

However, for sample 3 (20 % wt. of biotolerant polymer) large binder agglomerates can be observed, distributed throughout the material volume. Probably already at the stage of preparing the powder composition (magnetic powders and biotolerant-polymer components), the lower content of metal powder did not allow for sufficient binder dispersion in the entire volume. Variable distribution of adjacent agglomerates of binder allows to conclude about their uneven distribution in sample 3. Such distribution of the binder reduces the durability of the material, because the action of adhesive forces is limited to small areas.

The average percentage of magnetic powder particles in the volume of the composite has been determined based the large area of composites metallographic images - representative results of the analysis are presented in Figure 3.

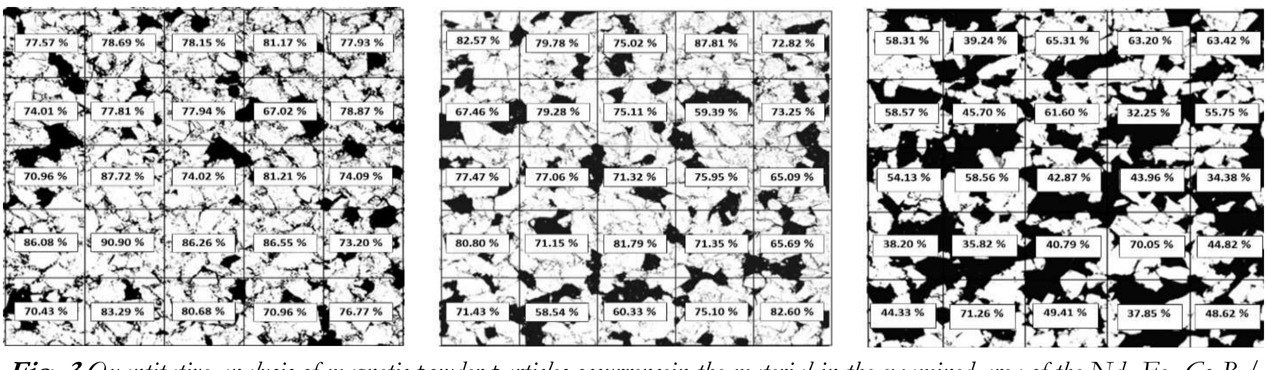


Fig. 3 *Quantitative analysis of magnetic powder particles occurrencein the material in the examined area of the $Nd_{12}Fe_{77}Co_5B$ / biotolerant-polymer composites*

To determine the distribution of powder particles in the polymer matrix, the entire metallographic image was divided into 25 square-shaped areas. Quantitative analysis using a standard (surface) method for designated areas in the microstructure image enabled the presentation of diversity in the distribution of powder particles and binder in the composite. The values given in Figure 3 correspond to the percentage of the surface occupied by the metallic powder (bright area). The obtained results indicate that the distribution of powder particles in the material is the most homogeneous for sample 2 (10 % wt. of biotolerant polymer).

The presented analysis shows that the amount of binder used significantly affects the distribution of powder particles in the $Nd_{12}Fe_{77}Co_5B$ / biotolerant-polymer composite. In sample 1, the binder is distributed fragmentarily and unevenly, and its content is not sufficient to fill all spaces between the particles. The distribution of powder particles and binder in sample 2 is the most advantageous, the distances between the particles of magnetic powder are small, and the spaces between them are evenly filled with binder. In contrast, sample 3 contains large binder agglomerates distributed throughout the volume of material. Thus, the content of 10 % binder in the tested material ensures the highest homogeneity of the $Nd_{12}Fe_{77}Co_5B$ / biotolerant-polymer composite.

However, in the case of sample 3, one of the partial technological processes - the process of components mixing (random arrangement of particles) caused the formation of different sizes of binder agglomerates. Surface topography studies revealed that the binder did not fill all the spaces between the magnetic powder particles, and the isolation of individual magnetic particles is is not complete - as it is also presented in the work [24]. The increase in binder content should increase the corrosion resistance of the composit but uneven distribution of the binder and magnetic particles can lead to increased penetration of the corrosive solution deep into the composite structure. The corrosive analysis will be the subject of subsequent team studies.

4 Conclusions

Based on quantitative analysis using binarization of metallographic images of the $Nd_{12}Fe_{77}Co_5B$ / biotolerant-polymer composite structure the conclusions have been stated:

1. The binder material content has a positive effect on the coherence of the $Nd_{12}Fe_{77}Co_5B$ / biotolerant-polymer composite structure.
2. The content of only 3 % wt. of binder is not sufficient to ensure proper consistency of the $Nd_{12}Fe_{77}Co_5B$ / biotolerant-polymer composite structure.
3. About 20 % wt. binder content does not appear to meet the quality requirements for tested magnetic composites - this binder content does not promote homogenised structure in the entire volume, resulting in large binder agglomerate in the composite.
4. 10 % binder content is the most favorable (optimal) for the $Nd_{12}Fe_{77}Co_5B$ / biotolerant-polymer composite - based on quantitative analysis and microstructure observation, it has been found that the binder material is evenly distributed throughout the composite volume.

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