Crystal chemistry of anisotropy magnetic properties gas atomization powders of an alloy of the Fe-Nd-B system

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Abstract. The magnetic material of Fe-Nd-B alloys is widely used in science and technology due to the unique physical and chemical properties of borides based on it. The functional properties of the material significantly depend on the structural-phase state in the alloy. The transition on the Melt Quenching technology (MQ) for its production required additional theoretical and experimental studies of the regularities of the formation and stability of the structural-phase state in multicomponent REM-containing alloys under conditions of nonequilibrium crystallization and solidification of a highly supercooled melt. The implementation of the industrial MQ technology by the method of Gas Atomization (GA) of medium pressure imposes additional significant requirements for such studies. The paper comprehensively studies and summarizes the available results on the relationship between the conditions for obtaining powder materials of Fe-Nd-B alloys by the MQ GA method and the functional properties of materials based on them. It is proved that the anisotropy features of their magnetic properties are related to the existing inhomogeneities in the distribution and morphology of Fe14Nd2B phase grains in MQ GA powder materials. A crystal-chemical explanation of the occurrence of the identified features is proposed and the possibility of their practical application is shown.

1. Introduction

A number of mandatory requirements are imposed on the materials used for the production of high-energy permanent magnets: high residual induction; high coercive force; required temperature stability and corrosion resistance; sufficient mechanical properties; manufacturability of production and technical feasibility of subsequent processing; availability of raw materials; production cost and the cost of the finished product. Alloys of the Fe-Nd-B system and sintered powder magnets based on them have been invariably the most promising materials that meet the requirement for the price-property ratio over the past few decades [1-2]. During this long period, numerous targeted studies are being systematically conducted to develop new alloy compositions (alloying) and improve the technology for their production in order to increase the magnetic characteristics of the material and optimize the functional properties of the finished product (magnets and magnetic systems) [3-40]. It is generally accepted that the maximum magnetic properties of the material and the finished product are determined by the optimal structural-phase state of the alloy [1, 3, 6, 17, 19, 21, 24, 26]. The introduction of the liquid quenching (Melt Quenching; MQ) technology into the production of hard magnetic alloys of the
Fe-Nd-B system has significantly expanded the limits of the attainable level of magnetic characteristics of the material and the functionality of products [19, 20, 25, 32, 33, 35]. Especially with a combination of MQ technologies and hot plastic deformation [17, 18, 32, 40]. Of course, the design of magnetic systems, especially for special purposes, should be guided by the maximum magnetic characteristics of the material used. But this does not contradict another statement: for a given magnetic system (finished product), the magnetic properties of the material should not be maximum, but optimal. Moreover, taking into account the cost of the material and products from it. Such a method of MQ is undoubtedly the spraying of a melt jet by an inert gas stream (Gas Atomization; GA) or any other spraying medium that ensures the disintegration of the melt jet into droplets and guarantees the protection of the alloy from oxidation [18, 28].

The usage of MQ technology by the GA method allows us obtaining a powder material - a gas atomized powder (GAP) of a given chemical and fractional composition, which has increased corrosion resistance during long-term storage (up to 10 years) under natural conditions and at the same time retains its technological properties [28]. The use of the GAP for the production of magnets makes it possible to exclude the melting, crushing and grinding of the ingot from powder from the technological process, increases its manufacturability (reproducibility) and reduces the cost of producing a unit of production.

Academic discussion about the formation of high properties in magnets from GAP-alloys of the Fe-Nd-B system, arose from the moment of their preparation [4, 8, 17, 18, 19, 25, 28] and approbation for the production of magnets using standard powder technology [19]. Today, the main working theory is the model of recrystallization of non-equilibrium grains GAP-alloys during sintering by powder technology [42].

The grinding of a powder material of an average weighted fractional composition (+60, -640 microns) to particles (crystallites) with an optimal size (~6-12 microns) remains a mandatory technological operation in the production of magnets from GAP. But this only intensifies the process of recrystallization of grains in the alloy during sintering of powders due to an increase in the defect in the resulting crystallites. At the same time, the initial (weighted average) powder array always contains a certain number of Fe$_{14}$Nd$_2$B phase grains close to the optimal one. As a result, under the optimal grinding mode, this leads to the formation of the necessary and sufficient number of crystallites with the morphology and size necessary for optimal magnetic properties. It is these crystallites that become the basis (centers) of recrystallization of the sintered powder and ensure the formation of the necessary grain structure in the magnetic material.

This effect is significantly enhanced when the technological processes of mechanical grinding (in certain types of ball mills or disintegrators) are combined with the process of hydrogen treatment (sorption - desorption of hydrogen) [7, 29, 31], including the imposition of thermal cycling in the temperature range of phase magnetic (310 °C) or structural (510 °C) transitions [27]. It should be borne in mind that in the case of the MQ quenching technology by the GA method for alloys of the Fe-Nd-B system, depending on the dispersion of the resulting powder and the mechanisms of interaction of the drops with each other in the sputtering flow, cooling rates are realized and supercooling of the melt sufficient for its amorphous solidification is achieved [19, 25, 35, 37, 41]. Moreover, the alloy contains an amorphous state (AS) of two compositions: AS$_1$ - the composition of the alloy; AS$_2$ is a composition with a high content of neodymium [41, 42]. Crystallization of these components during the thermal treatment of GAP or the production of magnets can significantly affect the recrystallization process and the formation of the magnetic properties of the finished product [17, 19, 20, 25, 35, 41]. However, the presence of an amorphous component in MQ alloys of the Fe-Nd-B system opens up fundamentally new opportunities for improving known technologies [20, 31, 32, 40, 42] and allows considering the use of fundamentally new technologies for the production of sintered magnets, including selective fusion [34] or additive growing [43].

2. Research objective
Based on the statement that the GSP of alloys of the Fe-Nd-B system, obtained by MQ using GA technology, are promising materials for the manufacture of permanent magnets for general and special
purposes both according to traditional powder technology and innovative technologies of selective sintering, in work the research goal was formulated: to test the hypothesis that in each GAP powder of ternary and alloyed alloys, regardless of the fractional composition, there is always a dominant direction of grain orientation of the main magnetic phase - Fe\(_{14}\)Nd\(_2\)B. The indicated dominant direction is formed as a result of crystallization of a supercooled melt under conditions of rapid cooling and spherically symmetric heat removal of the drop during MQ by the GA method.

3. Materials and research methods

To achieve this goal, the following research methods were used: X-ray phase analysis (modernized DRON-3 device with Cu- and Co-irradiation); metallographic studies (scanning station based on the analyzer of fragments of microstructure of solids SIAMS-800 for panoramic applications, including metallographic microscope OLYMPUS BX-51 and SIAMS Drive System); scanning electron microscopy (JSM-6390LV with Oxford INCAEnergy energy dispersive analyzer); microhardness measurement (SHIMADZU HMV G21ST and PMT-3); differential thermal analysis (NETZSCH 204 F1 Phoenix); production of magnetoplastics (in the form of cubes with a size of 5 × 5 × 5 mm), including in magnetic fields of different magnitudes (up to 2 T); measurement of the magnetic field on the surface of magnetoplastics (magnetic induction meter ATE - 8702).

MQ-melt quenching GA was performed on the URZhMV-3 unit (UkrNIISpetstal, Zaporizhzhia) using energy carrier gas (technological argon with the addition of special gas passivating additives) of medium pressure (≤ 1.2 MPa or 12 atm.) And spray nozzles of the "Nozzle Laval". The melt (weighing up to 30 kg) was obtained by induction melting in a rammed (lining based on corundum and oxides of rare-earth elements) overturning crucible (Leibold-Gereus furnace, Germany) with a capacity of up to 45 kg.

As charge materials used: technically pure iron grade 005ZhR (TU 14-1-2033-77) with a total impurity content of up to 0.15 wt. %, neodymium grade NM-1 (TU 48-4-271-91); ferroboron FB - 17.6 produced by JSC Zaporizhzhia Abrasive Plant (GOST14021.1-78).

Substances belonging to the "chemically pure" type were used as alloying elements.

The paper considers two main GSP compositions (stoichiometry in at. %): ternary alloy Fe\(_{78}\)Nd\(_{15}\)B\(_{7}\) and alloy Fe\(_{73}\)Nd\(_{15}\)B\(_{8}\)Co\(_{0.5}\)Al\(_{1.0}\)Mо\(_{1.5}\)(Dy, Тв)\(_{1.0}\).

Fractional composition of GSP was made using measuring sieves with numbers: 0.020; 0.056; 0.100; 0.160; 0.400 and 0.630 mm (GOST 18318–94).

The hysteresis properties of the powders were measured on a VSM-250 vibration magnetometer in fields with an intensity of up to 2 T at room temperature (NUST MISIS). The accuracy of determining the specific magnetization did not exceed 0.003 A·m\(^2\)/kg, and the coercive force did not exceed 0.005 kA/m.

The hysteresis properties of magnetoplastics and sintered anisotropic powder magnets were measured on a hysteriograf in a closed magnetic flux with two differential (compensated) coils in a field up to 1.4 T in a 5.0 mm gap (Federal State Unitary Enterprise Research and Experimental Institute of Automotive Electronics and electrical equipment).

4. Results and discussion

The paper presents the results of comprehensive studies of the structural-phase state in the material and the functional properties of magnetoplastics from the initial and annealed (argon and / or vacuum) MQ-melt quenching GSP alloys of the Fe - Nd - B system of different chemical and fractional compositions. This choice of the samples under study is due to the following known facts obtained in our earlier works [19, 26–30, 35, 37, 41–42]:

1) The alloying elements used are surface active additives to the alloy and affect the physicochemical properties of the solidifying supercooled melt, including the last solidifying liquid phase component in the MQ GAP alloy (neodymium-based ternary eutectic), which separates (isolates) the grains the main phase and provides predominant mass transfer during their recrystallization under isothermal annealing conditions above the temperature of the eutectic transformation (≥ 510 ° C)
2) Within the framework of the accepted modern mineralogical terminology [44], the processes of grain growth of the Fe$_{14}$Nd$_2$B phase can be considered as recrystallization processes in the presence of a liquid-phase component in the alloy.

3) The physicochemical properties of the liquid-phase component are determined by the chemical and fractional compositions of the MQ GAP of the investigated alloys.

4) During MQ by the GA method of alloys of the Fe-Nd-B system, GAP is formed, which has a fractional distribution depending on its chemical composition (content of neodymium, boron and alloying elements) and the parameters of the technological process, first of all: the type of nozzle; type, pressure and consumption of energy carrier gas; temperature and time of draining; heating temperature of the intermediate tank; the size of the injection hole; the shape and speed of the melt jet.

5) GAP with fractional composition from 1 to 800 microns under the conditions of the realized GA process is cooled at a rate from $10^5$ to 10 K/s.

6) Smaller GAPs (captured by a cyclone-type cleaning system) can be cooled at a rate of more than 105 K/s. Its amount indicates the fluidity of the melt and the role of the surface energy of the melt in the dispersion of the melt jet by an inert gas flow.

7) Supercooling of the melt in solidifying GAP droplets depends on their size both due to the attainable cooling rate ($V_{\text{cool}} \sim d_m^{-3/2}$) and a decrease in the proportion of heterogeneous crystallization in smaller droplets due to a decrease in the likelihood of impurities (crystallization centers) into drops of small volume.

8) The grain structure of GAP in the first approximation is determined by the chemical composition of the alloy, the droplet size and the crystallization mechanism (homogeneous or heterogeneous).

Second-order effects (dendritic shape of grains and interfaces caused by grain dispersion) are associated with heat release at the initial stages of crystallization of the supercooled melt and the forming concentration overcooling at the crystallization front.

The size of the formed particles is determined by the ratio between the flow rate of the melt and the flow rate of the gas, the Weber number, the ratio between the critical viscosity of the melt and the kinetic viscosity of the gas. In this case, there is an equation that characterizes the deviation of the particle size $D_1$ from its average size $D_m$ [45]:

$$\frac{D_m}{D_1} = A * K^B$$

where $A$, $B$ are constants depending on the process conditions;

$$K = \frac{M_L v_{\text{L}} 1}{M_g v_{\text{g}} W_e \gamma}$$

where $M_L$ is the melt flow rate (kg/s); $M_g$ – gas consumption (kg/s); $v_{\text{L}}$, $v_{\text{g}}$ – kinetic viscosity of melt and gas (m$^2$/s); $\gamma$ – specific heat ratio; $\gamma = C_L/C_g$; $W_e$ – Weber’s number.

The achieved supercooling determines the rate of nucleation and growth of crystals and affects the solidification of the supercooled melt.

Figures 1 and 2 (respectively) show a schematic diagram of the spraying unit URZhMV-3 and the differential curves of the distribution density of the studied hydraulic fracturing by size $n(d) = \frac{d\Delta M}{M \Delta d}$ [46].

The appearance of GAP and the shape of an individual powder are shown in figure 3. The characteristic features of their metallographic structure are shown in figure 4.
Figure 1. Diagram of the installation for spraying a stream of melt with an inert gas flow (URZHMV-3). 1 - induction furnace; 2 - spray chamber (with a diameter of 1.88 m and a height of 7 m with forced water cooling); 3 (10) - powder receiver with a vacuum seal; 4 - heated metal receptacle; 5 - unit for spraying liquid melt with an inert gas flow under pressure up to 2.5 MPa; 6 - inert gas supply system to the spraying unit; 7 - "Cyclone" - a system for capturing super fine powder from the discharged gas stream; 8 (9) - vacuum system with a vacuum seal.

Figure 2. Differential distribution density curve of hydraulic fracturing by size, where 1 (3, 4) - ternary alloy with different charge content of boron; 2 - alloyed alloy.

Figure 3. Appearance of GAP ternary alloy (a) and the shape of its separate powder (b).

The paper investigated the effect of isothermal annealing (1, 2 and 3 hours 600 ° C, vacuum ~ 10\(^{-3}\) Pa) on the microstructure of GAP alloy. The obtained results of the digital optical metallography data set of the images of thin sections GAP were statistically processed using the SIAMS Drive System program, summarized depending on the alloying and are shown in figure 5.

There is a clear tendency that for the alloyed alloy (in contrast to the ternary alloy), upon isothermal annealing, an increase in the average maximum grain size of the Fe\(_{14}\)Nd\(_2\)B phase is observed. As can be seen from figure 4, such a dependence may be due to the presence of multiple contacts of grain boundaries (not separated by a ternary eutectic) of the Fe\(_{14}\)Nd\(_2\)B phase with each other and their coalescence (growth) by the recrystallization mechanism.
Figure 4. Metallographic structure of GAP of fraction (+ 120–460) µm of ternary (top) and alloyed (bottom) alloy, where the lower left photo is an enlarged image of the particle periphery shown on the right.

Figure 5. Influence of the time of isothermal annealing (600 °C, vacuum ~ 10^{-3} Pa) on the average maximum grain size of the Fe_{14}Nd_{2}B phase for the MQ GAP alloy of the fraction (+ 120–460) µm.

This is confirmed by metallographic images (figure 6) of the initial and annealed GSP of ternary and alloyed alloys.
Figure 6. Microstructure of the initial and annealed GAP of (a) ternary and (b) alloyed alloys.

Attention is also drawn to the fact that, upon annealing of ternary GAP, the processes of fusion (recrystallization) of Fe$_{14}$Nd$_2$B grains also proceed, but are leveled by the processes of grain refinement of the Fe$_{14}$Nd$_2$B phase at an early stage of annealing and therefore become noticeable only upon prolonged annealing (more than 2 hours). The grain refinement of the Fe$_{14}$Nd$_2$B GAP phase of the ternary alloy at the early stages of annealing is primarily due to magnetostrictive effects [27]. As a consequence, in figure 5, there is a tendency for the average maximum grain size of Fe$_{14}$Nd$_2$B to grow during isothermal annealing at 600 °C for more than 2 hours GAP ternary alloy. In alloyed GAPs of a given fractional composition, already in the initial state, there is a reduced value of the average maximum grain size of the Fe$_{14}$Nd$_2$B phase (in comparison with the ternary alloy) and, therefore, its growth is realized immediately from the early stages of annealing. At the same time, there is an increased (in comparison with the unalloyed ternary alloy) tendency of an increase in the number of pores on the metallographic section GAP. It is most likely to associate the observed result with an increased content of additional intermediate phases (intermetallic compounds) based on alloying elements and rare earth elements in the alloy doped with GAP. Such inclusions are always predominantly concentrated in the intergranular space (ternary eutectic enriched in neodymium) [25, 47–49]. As a rule, during standard sample preparation of a GAP metallographic section (mechanical polishing and subsequent chemical etching), selective extraction (precipitation) from the processed surface of the section of solid inclusions will inevitably be present.

For the manufacture of magnetoplastics, we used a standard plasticizer - a two-component epoxy resin. Three schemes have been implemented. According to the first: a previously prepared homogeneous mixture of powder of the fraction (+120 - 240) microns and resin in a ratio of 10:1 was loaded into a rectangular mold, which was placed on the surface of a magnetic plate (permanent magnet with a field on the surface of up to 0.6 T); the workpiece was compacted using a screw press with a force of up to 1 MPa (0.1 t/cm$^2$) and held under pressure until the resin was completely solidified; a briquette (magnetoplast) with a size of (5 × 5 × 5) mm was obtained; the sample was magnetized (in the direction of the initial pressing field) in a closed magnetic system of an electromagnet in a gap of 5 mm at an induction of up to 2.2 T (figure 7). For a magnetoplast (using an ATE-8702 device), the field (induction) was measured on different surfaces along (S, N) and across (Sn, Nn) of the pressing field (in the center of the face) of a magnetized (square) sample, and thus its anisotropy was estimated. Properties. The surface with the maximum properties (S) corresponds to the surface of the minimum distance with the magnetic plate when making a briquette. Accordingly, the surface opposite to it is (N). The difference in magnetic induction on the S and N - surfaces of such magnetoplastics is associated with the topological (inhomogeneity of the packing density) and approximate (inhomogeneity of rotation in
a magnetic field) of the magnet of anisotropic GAP. The difference in magnetic induction on the S and Sn (N and Nn) surfaces is mainly determined by the magnetic anisotropy of the GAP. The results are summarized in table 1.

The second scheme for the manufacture of magnetoplastics: a pre-prepared sample of a given mass in the form of a homogeneous mixture of GAP fraction (+120 –240) µm and resin in a ratio of 10:1 was loaded into a rectangular demountable mold made of A316L stainless steel with a wall thickness of 3 mm; the mold was placed in a magnetic system based on an electromagnet with a closed core and special tips made of alloy grade K49F2 (“permendur”); the total gap between the tips during compaction did not exceed 11.0 ± 0.1 mm; induction in the gap during compaction is not less than 1.2 T; compacting of the briquette is performed using a hydraulic press with a force of up to 5 MPa (0.5 t/cm²); the briquette was kept under pressure until completely solidified (but not less than 3 hours); received a square sample with a size of 5 × 5 × 5 mm; the sample was magnetized (in the direction of the initial pressing field) in a closed magnetic system of the same electromagnet in a 5 mm gap at an induction of 2.4 T (figure 7); then the measurements of the anisotropy of the magnetic properties of the magnetoplast are made, as in Scheme 1. The measurement results are listed in table 1.

Table 1. Values of magnetic induction at the center of the surface of cubic samples (5 × 5 × 5 mm) of the investigated magnetized magnetoplastics (S, N - faces perpendicular to the field, Sn, Nn - parallel to the compaction field).

| GAP condition in magnetoplast | Induction measurement surface | Scheme 1 | Scheme 2 |
|-------------------------------|-------------------------------|----------|----------|
|                              |                               | doped    | doped    | undoped  |
| Original                     | S/S₀                          | 37/4     | 65/7     | 55/6     |
|                              | N/N₀                          | 37/4     | 65/6     | 55/6     |
| 1                             | S/S₀                          | 34/4     | 61/6     | 57/6     |
|                              | N/N₀                          | 33/3     | 60/6     | 57/5     |
| Isothermal annealing in vacuum, hour | S/S₀ | 39/4 | 67/5 | 60/5 |
| 2                             | N/N₀                          | 42/4     | 68/5     | 60/5     |
| 3                             | S/S₀                          | 60/6     | 71/4     | 62/4     |
|                              | N/N₀                          | 60/6     | 72/5     | 63/4     |

The first scheme for the manufacture of magnetoplastics (compaction in an open magnetic field) leads to an inhomogeneous distribution of GAP over the volume and insufficient orientation along the direction of the magnetic field during compaction. The orientation of the particles in the GAP magnetic field occurs due to the average magnetic anisotropy existing in them, related to the average
inhomogeneity of the grain size of the Fe$_{14}$Nd$_2$B phase in a separate powder (see figure 6) and, as a consequence, in the bulk of the magnetoplast as a whole. The values of the magnetic induction on the surface of such a magnetoplast do not exceed 40 ± 5 mT.

The transition to schemes (2) and (3) for the manufacture of magnetoplasts and the use of compaction in a closed magnetic field make the magnetoplast more uniform in the distribution of GAP in the sample volume and make it possible to orient a larger number of powder particles along the direction of the magnetic field, including those with a weakly expressed structural magnetic anisotropy. This makes it possible to achieve a magnetic induction at the center of the GSP on the surface (perpendicular to the compaction field) of the magnetized GAP sample in the initial state of more than 55 ± 5 mT. This corresponds to an increase in this value by more than 30% in comparison with magnetoplastics manufactured according to the scheme (1).

The performed measurements of the anisotropy of the magnetic properties of magnetoplastics (measurement of the magnetic induction on mutually perpendicular faces along and across the compaction field) convincingly prove that in the initial state in the GAP of ternary and doped alloys, a structural-phase state (inhomogeneity of the grain structure of the Fe$_{14}$Nd$_2$B phase) on average provides a certain magnetic anisotropy of each powder and anisotropic properties of the magnetoplast as a whole.

During isothermal annealing at 600 °C, structural-phase changes occur in the GAP alloy, increasing their average magnetic anisotropy. As a consequence, the functional properties of the magnetoplast made of such GAP (magnetic field induction on the surface) are improved. Moreover, in the alloyed alloy, the increase in properties with optimal annealing is ~ 15% greater than in the ternary alloy.

The legitimately identified changes are associated with the observed process of fusion (recrystallization) of grains of the Fe$_{14}$Nd$_2$B phase, which is more pronounced in the GAP of the alloyed alloy (see figure 6).

In figure 8 shows the results of differential thermal analysis (DTA) of the investigated undoped (a) and doped (b) GAP alloys with fractional composition (+ 120–240) µm. The analysis was carried out in an atmosphere of technical argon at a speed of 20 K / min in a standard Al crucible. The mass of the investigated powder was (2.0 ± 0.1) g. Analysis shows that the calorimetric effects of thermal absorption begin immediately upon the annealing of the GAP and experience additional features in the region of the magnetic phase transition (280 ÷ 350 °C) and melting of the ternary eutectic (510 ÷ 560 °C).

![Figure 8. DTA (20 K / min, argon) GAP (weight 2.0 g) fractions (+ 120–240) µm of undoped (a) and doped (b) alloys.](image)

To optimize the properties (to achieve the maximum value of the induction on the surface) of the magnetoplast, the third scheme of their production was implemented in the work: the mass fraction of the plasticizer was reduced to 3 wt%; pressing pressure increased to 10 MPa (1 t / cm$^2$); the bulk density of GAP in the powder mixture is increased due to the mixing of the powder of three fractions, the sizes of which are close to the requirements of the closest packing of balls, for example, in the fcc lattice,
taking into account the presence of voids in the form of octa \((R_2)\) and tetra \((R_3)\) pores. According to the size and ratio of the number of octa \((N_{R2})\) and tetra \((N_{R3})\) pores per ball \((N_{R1} = 1)\) of unit size \((R_1)\), such a package has the following ratios: \(R_1:R_2:R_3 = 1:0.41:0.22\); \(N_{R1}:N_{R2}:N_{R3} = 1:1:2\) [52]. A simple recalculation of the number and size of pores per mass fraction in a mixture of a fraction of the appropriate size (for a constant density of the powder material and the existing discrete set of fractional composition) gives the following ratios for a charge charge with a mass of \((20.0 \pm 1.0)\) g: \(m_1\) (fraction +400 - 640 microns): \(m_2\) (fractions +120 - 240 microns): \(m_3\) (fractions + 56 - 120 microns) = 5: 5: 10. This mass corresponds to the optimal volume of the mixture in the manufacture of a minimum experimental batch of magnetoplastic samples of a given size (at least 20 pieces with a size of \(5 \times 5 \times 5\) mm).

To control the nature of the distribution of GAP particles in the volume of the magnetoplast, metallographic sections were made with a surface along the direction of the magnetic field during compaction (perpendicular to the direction of compaction). A typical example of a metallographic image for a magnetoplast obtained according to the 2-scheme from the initial GAP doped fraction (+120–240) \(\mu\)m is shown in figure 9 (a). Alongside are the data of scanning electron microscopy on the morphology of the used GAP (9 b).

![Figure 9](image_url)

Figure 9. Magnetoplastic made according to scheme 2 (a) and the morphology of the used GAP (b).

Metallographic images of other studied samples of magnetoplastics (Scheme 3, from the initial and annealed GAP) are shown in figure 10. The nature and parameters of the distribution of GAP on the cross-sectional area of the magnetoplast section were made by digital metallography (Olympus BX-30 microscope) using the SIAMS Drive System software of the SIAMS-800 solid body image analysis station. The results obtained for all investigated samples are summarized in table 2.

To verify the results on the existence of structural (grain) magnetic anisotropy in hydraulic fracturing, obtained in the study of magnetoplastic samples, the magnetic properties of GAP were measured on a VSM-250 vibration magnetometer in fields with an intensity of up to 2.4 T at room temperature. The magnetometer was calibrated using a reference sample of metallic Pd with a known value of the magnetic moment. The error in determining the specific magnetization \((S_s)\) did not exceed 0.003 \(A^2m^2/kg\), and the coercive force \((H_C)\) did not exceed 0.005 kA/m.
Table 2. The results of the analysis of the distribution of GAP particles on the surface of the section of the metallographic section of the magnetoplastic samples, depending on the method of their preparation.

| Analyzed image parameters of a metallographic section | Magnetoplast Original | After annealing 600 °C 3 hours |
|------------------------------------------------------|-----------------------|---------------------------------|
|                                                      | doped Scheme 2 | undoped Scheme 3 | doped Scheme 3 | undoped Scheme 3 |
| Analyzed section area (sq. microns)                  | 82781084 | 98462648 | 54687649 | 57575586 | 68476800 |
| Number of particles (pcs.)                           | 17824 | 13047 | 5690 | 8418 | 10416 |
| Particle cross-sectional area (sq. microns)           | 27905008 | 44452564 | 35979964 | 36134614 | 39058655 |
| Fraction of particles in the area of a thin section (%)| 34.0±1.8 | 45.0±0.9 | 62.1±1.4 | 62.8±1.2 | 57.0±1.2 |
| Average distance between particles on a thin section (μm) | 49.0±2.0 | 61.0±1.0 | 60.4±1.6 | 49.0±1.1 | 44.6±1.2 |

Figure 10. Image of metallographic sections of magnetoplastics obtained according to scheme 3. a - from the original undoped GAP; b - from the original doped GAP; c - from annealed (600 °C, 3 hours) undoped GAP; d - from annealed (600 °C, 3 hours) alloy doped GAP.

The measurements were carried out on GSP of the fraction (+120–240) μm in the initial state. The mass of the powder sample was 500 ± 10 mg. The measurement results are shown in figure 11 for undoped (a) and doped (b) GAP. In both cases, the studied GAP has a magnetic rigidity, which is
determined by remanent magnetization ($S_r$), coercive force ($H_C$) and the shape of the demagnetization loop. These parameters are also shown in figure 10 (a, b). For doped and undoped hydraulic fracturing, the indicated values are respectively equal: $S_r = 31.19$ and $38.69$ A·m$^2$/kg; $H_C = 224.1$ and $233.4$ kA/m or $2.816$ and $2.933$ kOe.

Figure 11. Demagnetizing branch of the hysteresis loop of GAP of the fraction (+ 120-240) μm in the initial state for undoped (a) and doped (b) alloys.

Annealing of GAP at 600 °C does not lead to complete recrystallization of grains of the Fe$_{14}$Nd$_2$B phase, but the processes occurring in alloys of the Fe-Nd-B system during the manufacture of powder anisotropic sintered magnets using standard technology [1, 9-16]: vacuum induction melting of an ingot (from 0.5 to 45 kg); crushing to particles with a size of 5 ÷ 50 mm; mechanical grinding in a ball mill in a protective liquid medium to a fineness of 1 ÷ 10 microns; wet pressing (compaction) of samples in a
magnetic field with an induction above 1.2 T; sintering in vacuum at ~ 1050 °C for 1 hour; cooling with a furnace up to 600 ÷ 800 °C and accelerated cooling (quenching) by an inert gas flow to room temperature.

To implement the complete recrystallization of the studied GAP and to prove that anisotropic magnets with properties similar to those of a magnet with a similar chemical composition obtained by the standard technology are obtained from GAP (using a technology close to the standard), anisotropic sintered samples were prepared from GAP. The following technological features were implemented: a mixture of different GAP fractions was used; the mixing algorithm was similar to the 3rd scheme - the production of magnetoplastics (the condition for the most dense filling of the space with spherical powders of different sizes); a GAP mixture with a mass of 100 ± 2 g was ground in a PM-100 planetary ball mill to particles with a size of 1 ÷ 10 microns; further, according to the modes of standard powder technology [1, 9-16], taking into account the data obtained in [32, 33, 36, 38, 39], anisotropic sintered magnets (10 × 10 × 10) mm in size were manufactured. From them, by the method of plane-parallel grinding, square specimens with dimensions (5 × 5 × 5) mm were made. The samples were magnetized to saturation in a pulsed magnetization apparatus in a field with an induction of up to 10 T. Their magnetic properties were measured by demagnetization in the gap of an electromagnet in a field with an induction of up to 2.2 T. The hysteresis loop used a measurement circuit with two differential compensated coils. The demagnetization rate did not exceed 0.5 T/minute. Standardized SmCo5 reference samples were used to calibrate the measuring system. The results of measurements of demagnetization of anisotropic sintered magnets from undoped (alloy No. 1) and doped (alloy No. 2) GAP of anisotropic sintered magnets magnetized to saturation are shown in figure 12 (a). The same figure (b) shows a typical image of a metallographic structure (in the plane of a microsection parallel to the compaction magnetic field) that forms in the material during sintering (for example, alloy No. 2).

Figure 12. Magnetic properties (a) and metallographic structure (b) of anisotropic sintered magnets from unalloyed (alloy No. 1) and doped (alloy No. 2) GAP: demagnetization curves of samples magnetized to saturation (a); image of the metallographic structure formed during sintering by the example of alloy No. 2 (b).

The obtained structural-phase state in the sintered material ensures its good magnetic properties: for alloys No. 1 and No. 2 (respectively) the rectangularity of the demagnetization loop exceeds 85% and 80% (in area); residual induction (Br) reaches 1.050 ± 0.005 and 1.025 ± 0.005 T; coercive force (\(H_C\)) - 10.2 ± 0.1 and 12.8 ± 0.1 kOe. The results achieved are comparable with similar data for anisotropic sintered magnets of the same composition, manufactured using traditional powder technology [5, 9–12, 17, 33].

5. Conclusions and discussion
The performed studies and the presented results concretize and expand the existing understanding of the formation of magnetic properties in the material of alloys of the Fe-Nd-B system, manufactured by the
MQ method [1, 2, 22, 25]. At least, the results obtained prove that ternary and alloyed alloys of the Fe-Nd-B system in the MQ GAP with a fractional composition of (+120, −640) μm, with their subsequent processing into anisotropic sintered magnets by grinding to particles with dispersion of (+1, −10) μm and sintering (1050 °C, 1 hour), complete recrystallization of the initial grain structure of the Fe14Nd2B phase occurs and the formation of a relatively homogeneous microstructure with an average size along (parallel to the crystallographic axis "c") and across (parallel to the crystallographic axis "a") grains of the main magnetic phase: 10 ± 5 μm and 5 ± 2 μm, respectively. In this case, the grain boundary has a size approaching 1 μm and is filled with a ternary eutectic (based on neodymium and a mixture of borides Fe14Nd2B + Fe4Nd14B4) with single inclusions of non-metallic phases (slags) [3] and intermetallic compounds such as Laves phases, μ, σ and others Frank-Kasper related compounds [21-25, 36, 47-51].

It should be especially noted that in the sintered compact obtained by grinding GAP to granules with an average size of ~ 10 μm, there are always grains of the Fe14Nd2B phase with a size significantly less than the specified size (up to 1.0 μm and possibly less). However, during sintering, a pronounced grain structure of the main magnetic phase is formed with a size comparable to the size of particles in a compact (briquette). And this means that when manufacturing anisotropic sintered magnets, it is necessary and sufficient to form a compact, in which only a certain (minimum sufficient) number of single-grain oriented (by pressing in a magnetic field) granules with a size close to optimal (6 ÷ 10 μm) should be present. In the future, if the necessary thermodynamic and kinetic conditions are created, then by the recrystallization mechanism in all sintered particles of the compact, single-grain structures will be formed.

The boundary (surface) of the compaction particles simultaneously plays two roles. First, it is a barrier to the recrystallization interaction of grains from different granules. Secondly, it is the main volume where the liquid-phase component of the sintered material is concentrated. Thirdly, it is a sink and a source of technological impurities, including non-metallic (oxygen, nitrogen, hydrogen). The first component predominantly determines the optimal (final) grain macrostructure of the sintered material. The second component determines the formation of the grain boundary, the diffusion of the main components and technological impurities between the sintered volumes (granules), the formation of micro- and nano-structures inside the granules and at their boundaries. The third component affects both of the first. Moreover, it can both enhance their course, and still stabilize, for example, by the mechanism of concentration hypothesia (see figure 4, upper pictures). The cumulative result of these three processes occurring simultaneously is the structural-phase state of the sintered material, which determines the entire complex of its magnetic properties. Moreover, the dominant component of this complex process is the process of recrystallization in the MQ GAP alloys at temperatures when the material contains an insignificant amount (up to 6 vol. %) Of the liquid-phase component. The relevance of this issue is multiplying in connection with the introduction of additive technologies in the production of micromagnetic systems based on the alloy. Fe-Nd-B [43].

The presented results prove that when analyzing the magnetic anisotropy of magnetoplastics from GAP, it is legitimate to use the following model [37, 41]: the magnetic anisotropy of GAP is formed by inhomogeneities (in shape and size) of the grain structure of the Fe14Nd2B phase in the alloy of a powder (micro-ingot). These features are associated with the chemical composition of the alloy (alloying) and the conditions of its solidification (crystallization) during quenching from a liquid state (Melt Quenching) by spraying a melt jet with an inert gas flow (Gas Atomization) of medium pressure (up to 1.2 MPa).

Upon annealing above the melting point of the neodymium-based ternary eutectic (above 510 °C), which is present in a certain amount (up to 5 vol. %) In all industrial magnetically hard alloys of the Fe-Nd-B system, the process of recrystallization of grains of the Fe14Nd2B phase occurs. The kinetics of this process for a fixed chemical composition depends on the initial grain structure of the alloy and the annealing temperature.
The initial grain structure of the GAP alloy can be controlled by the technological parameters of spraying (drain temperature, metal consumption, nozzle design, type and pressure of energy carrier gas) and fractional composition.

The more dispersed structure of the alloy is more sensitive to annealing. In such GAP, as a rule, the initial stages of alloy recrystallization are realized faster.

The maximum (optimal) properties of the magnetoplast are formed upon recrystallization of grains of the $\text{Fe}_{14}\text{Nd}_2\text{B}$ phase with a size of up to 6 μm (along the crystallographic axis "c"). The temperature and duration of isothermal annealing of hydraulic fracturing in the manufacture of magnetoplastics from them should not lead to significant growth of grains of the base phase (over 10 μm).

The technology of quenching from a liquid state (MQ) by the method of gas atomization (Gas Atomization) of a melt jet by a flow of an inert gas of medium pressure (up to 1.2 MPa) makes it possible to obtain a powder material (GAP), which has functional properties and cost indicators promising for its use in production sintered anisotropic magnets, magnetoplastics and magnetic systems, including additive technologies.

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