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Arc-plasma spraying and suction-casting methods in magnetic materials manufacturing

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ABSTRACT

Purpose: The paper discusses two new technologies for producing magnetic materials which have been successfully developed in recent years at the Institute of Physics of the Czestochowa University of Technology and discusses properties of the materials obtained with the use of these methods.
Design/methodology/approach: In this research the arc-plasma deposition of $Nd_2Fe_{14}B$ powders onto a substrate either cooled with water or heated up to a temperature in the range from 773 to1023 K was applied. In the second method the suction of an arc-melted alloy to a water-cooled copper mould (the suction-casting method) was introduced. Moreover, microstructure, magnetic properties and domain structure of the produced samples were determined.
Findings: It has been found that thin $Nd_2Fe_{14}B$ strips obtained by the plasma method possess magnetic properties. It has also been demonstrated that the suction-casting method makes it possible to obtain both amorphous magnetically soft materials (e.g. Fe-Co-W-Zr-B), as well as magnetically hard nanocomposites (e.g. (Fe-Co)-(Pr-Dy)-B-Zr).
Research limitations/implications: The main problem in the suction-casting method is to reduce the critical cooling rate required for the production of amorphous alloys and to increase the geometrical dimensions of amorphous specimens.
Practical implications: Thin-layered Nd-Fe-B magnets produced by means of arc-plasma deposition can be applied directly onto the surface of electromagnetic equipment parts. Magnets with isotropic magnetic properties were obtained by applying layers onto the water-cooled copper substrate. Whereas, anisotropic magnets were obtained as a result of the arc-plasma deposition of powders onto the copper substrate heated up to 873 K. The most advantageous properties were achieved for the microcrystalline structure of a grain size close to the single-domain particle size (approx. 0.3 μm). Moreover, it has been demonstrated that the suction-casting method makes it possible to obtain bulk amorphous alloys of considerable sizes, such as rods of magnetically soft Fe-Co-W-Zr-B alloys of a diameter up to 2 mm, as well as Fe-Co-Pr-Zr-B tubes of a diameter up to 3 mm. It is also possible to produce magnetically hard nanocomposite materials of the (Fe-Co)-(Pr,Dy)-B-Zr type by annealing of metallic glasses.
Originality/value: Successfully introduced new methods of magnetic materials manufacturing.
Keywords: Technological devices and equipment; Arc-plasma spraying; Suction-casting; Bulk amorphous alloys

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1. Introduction

The progress which has occurred in the field of magnetic materials can be tracked on the example of magnetic hard materials used for the manufacture of magnets. Only over the past century, the value of maximum magnetic energy density, $(BH)_{max}$, which can be assumed as the parameter describing this progress, increased from approx. 1.6 kJ/m^3 for carbon steels (the beginning of the 20th century) to above 400 kJ/m^3 for alloys, in which the magnetic properties are determined by the phase $Nd_2Fe_{14}B$ or $Sm_2Fe_{17}N_3$ (the end of the 20th century).

As the production of magnetic hard phases which would be more perfect than $Nd_2Fe_{14}B$ and $Sm_2Fe_{17}N_3$ and would be characterized by high saturation magnetization, M_s, and a large magnetic anisotropy field, H_A, is difficult, therefore the further development in studies on magnets was targeted toward improving the microstructure. Thus, magnets of a nanocrystalline structure, both single- and two-phase (nanocomposites), were obtained.

The new magnetic materials required the development of new production technologies. New methods for producing magnetic materials have been successfully implemented in recent years at the Institute of Physics of the Czestochowa University of Technology, namely: plasma spraying of magnetically hard layers, and the suction-casting method for producing bulk metallic glasses. The present paper will discuss these technologies, as well as the materials obtained with the use of them.

2. Plasma spraying of layers

The miniaturization of magnetic circuits has entailed an increased interest in thin-layered magnets, which can also be applied directly onto the surfaces of magnetic equipment parts using the sputtering [1] and the plasma spraying [2] methods. In the case of the Nd-Fe-B compound, thin-layered magnets were produced by the sputtering method [3], as well as by plasma spraying of respective material [4,5]. In the latter method, powder was spread on a copper substrate either cooled with water or heated up in the temperature range from 773 to 1023 K using the arc-plasma spray layer application process (Fig. 1). Thus applied layers were up to 3 mm thick. These layers were then subjected to heat treatment in the temperature range from 773 to 1173 K for a duration from 0.5 to 2 hrs in a vacuum of about 0.01 Pa.

The layers applied on the water-cooled substrate had isotropic magnetic properties [5]. After the heat treatment for 0.5 h in the temperature range from 773 to 1023 K the sprayed material gained a coercivity of $_JH_c = 1.2$ MA/m, a remanence of $\mu_o M_r = 0.6$ T, and a magnetic energy density of $(B{\cdot}H)_{max} = 64$ kJ/m^3.

As was shown by X-ray phase analysis [5], the phase $Nd_2Fe_{14}B$ and slight amounts of the phases Nd_2O_3, NdB_2 and α-Fe are present in the Nd-Fe-B layers. Thus, the phase composition of the applied layers after heat treatment is close to the composition of bulk Nd-Fe-B magnets. While the grain size, as determined from X-ray line widening measurements, was 0.3 µm, which is approximately equal to the critical size of single-domain particles.

During the production of layers by arc-plasma spraying of Nd-Fe-B powders onto the copper substrate heated up to a temperature in the range from 773 to 1023 K, magnets with anisotropic magnetic properties were obtained [4]. Figure 2a shows a typical microstructure of a magnet produced, as viewed from the surface perpendicular to the direction of plasma beam application, while Figs. 2b-d show the cross-section. This microstructure is characterized by oblong grains. As indicated by examination carried out using an X-ray microanalyzer, the darker areas in the microstructure photos correspond to the locations of a lower neodymium content and a lower iron content. X-ray examinations, on the other hand, showed a favoured orientation of the grain axis c, that is perpendicular to the grain surface. This was also reflected in the image of the domain structure which consisted of small islets, whose magnetization vector is perpendicular to the layer surface. As the substrate temperature increases above 1023 K, a deviation in the magnetization vector from the direction perpendicular to the layer surface is observed, which is indicated e.g. by the formation of labyrinth domains and, in the extreme case, when the magnetization vector lies in the layer plane, domains with 180° Bloch walls (Fig. 3).

In Fig. 4, the microstructure (Fig. 4a) is compared with the domain structure (Fig.4b) of the plasma-sprayed magnets after heat treatment for 0.5 h at 1073 K. The microstructure with fine grains is visible (Spot A), as well as large grains (Spots B and C). The domain structure in the large grains consists of domains with 180^o Bloch walls (when easy direction of magnetization lies in the plane of the film; Spot B) or small domains in the form of islets (when the easy direction of magnetization is perpendicular to the film; Spot C).

The magnetization and demagnetization curves for the anisotropic Nd-Fe-B layers arc-plasma applied onto the Cu substrate heated up to a temperature of 873 K were measured. It should be emphasized that the rapid increase in the remanence $\mu_o M_r$ takes place within a narrow range of weak magnetic fields, much lower than the coercive field. Whereas, the curve for the primary magnetization of the thermally demagnetized magnet exhibits a fast increase in induction; thus, in the field of H<25 kA/m, the magnetization attains half of the maximum value. This fact of easy magnetization indicates the absence of effective domain wall pinning centres in the majority of grains. So, in accordance with the results of the work by Becker [6], such behaviour of the curve of primary magnetization versus the applied field confirms the fact that the basic mechanism enabling a high coercivity value to be obtained are processes associated with the inhibited nucleation of demagnetization domains. In work [4], the following magnetic properties of anisotropic Nd-Fe-B layers were obtained: $\mu_{oJ}H_c = 1.2$ MA/m, $\mu_o M_r = 0.9$ T and $(B{\cdot}H)_{max} = 180$ kJ/m^3. The above-mentioned work generally concludes that the magnetic properties of thin-layered magnets of the Nd-Fe-B type, as obtained by the plasma spraying method, are strongly dependent on the microstructure and domain structure. The best magnetic properties were obtained in magnets of a grain size close to the critical size of single-domain particles (i.e. approx. 0.3 µm). This microstructure corresponds to the domain structure of the layers investigated, which is composed of a network of small islets of a size below 1 µm, which is indicative of the fact that the domain walls are fixed (pinned) at the boundaries of grain, and the process of demagnetization of those grains involves the nucleation of domains in the direction opposite to the magnetization vector.

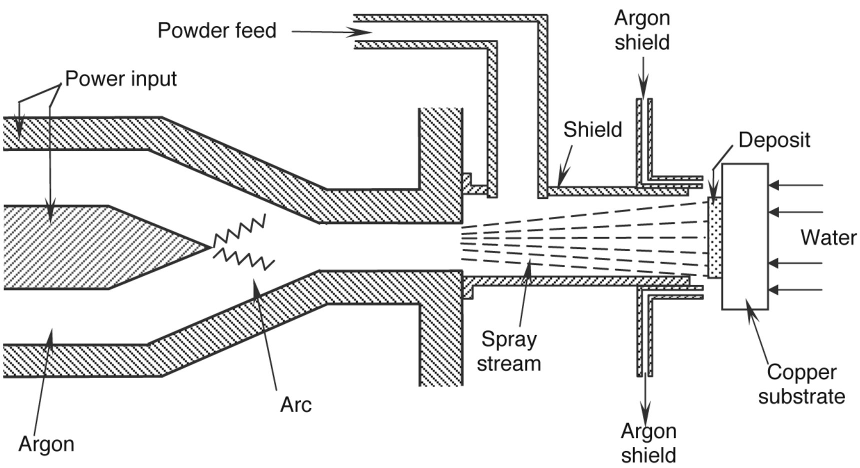

Fig. 1. Schematic sketch of the deposition of the Nd-Fe-B films by the arc-spraying technique

a) b) c) d)

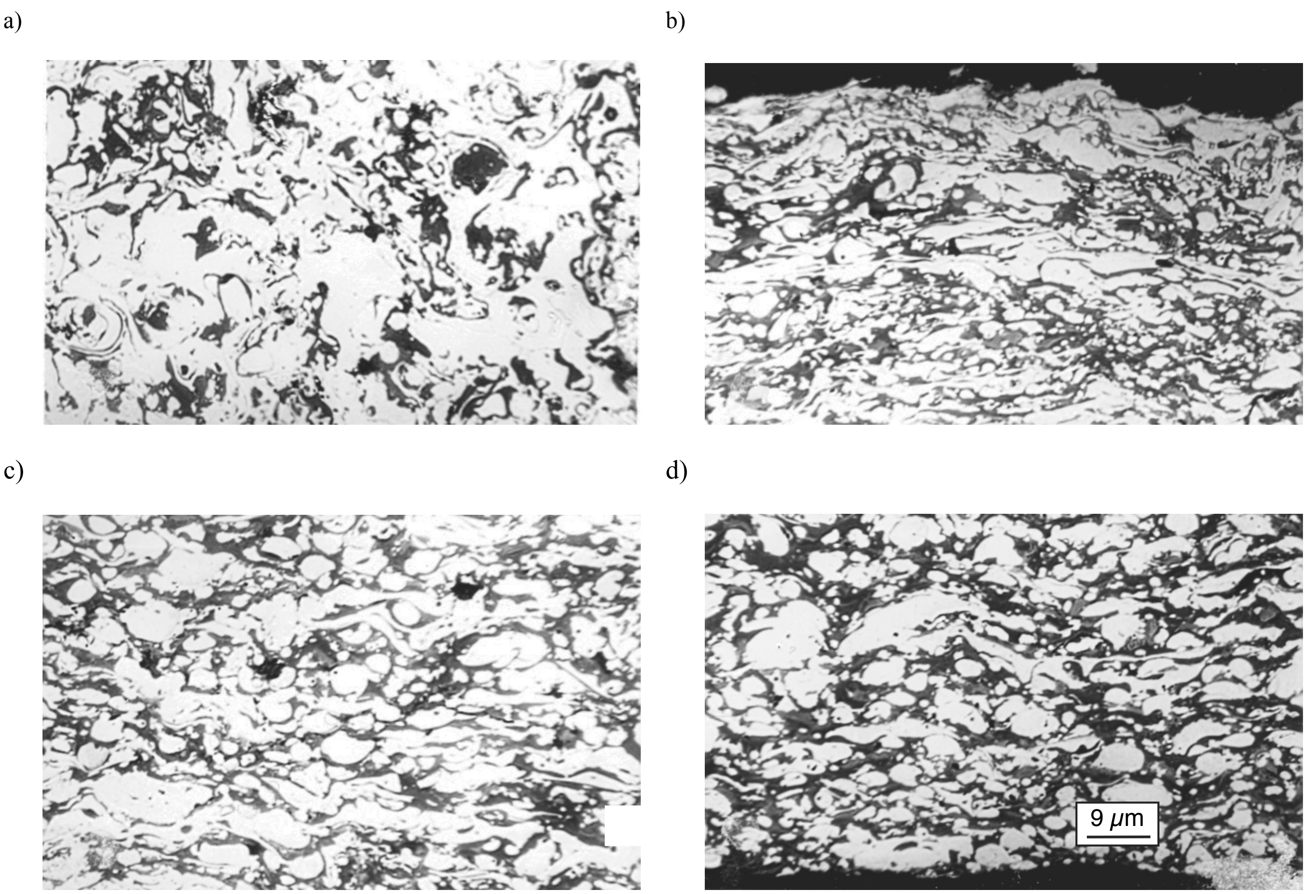

Fig. 2. Microstructure of plasma-sprayed $Nd_2Fe_{14}B$ films deposited onto substrate heated to 873K (a), cross section of the film (b-d)

The reduction of magnetic properties is associated with the increase in grain size and formation of 180° domain walls. The demagnetization process proceeds in that case more easily through the motion of domain walls and their pinning.

3. Bulk metallic glasses (the suction-casting method)

The technologies of production, as well as the studies of these materials constitute one of the fastest developing areas of materials engineering owing to the huge potential for applications. The main problem in the manufacture process of these materials is to reduce the critical cooling rate required for the production of amorphous alloys and to increase the geometrical dimensions of amorphous specimens.

Thus, amorphous zirconium-based alloys exhibiting exceptionally high mechanical elasticity, hardness and wear resistance have been successfully used for the commercially manufactured heads of golf clubs and baseball bats and for tennis racket frames [7]. Also the exceptional corrosion resistance and high biocompatibility of these materials have been utilized for the production of knee endoprosthesis elements. Moreover, bulk metallic glasses are used for the production of heart pacemaker casings, and their exceptional hardness has been taken advantage of for the production of scalpel blades, which is also associated with a more efficient technological process of their manufacture.

Amorphous materials based on iron have aroused great interest for many years. The low price of these materials has encouraged researchers to seek the compositions of alloys exhibiting enhanced abilities to form metallic glasses. Amorphous ribbons have also found broad application in electrical engineering as transformer cores showing exceptionally low magnetic energy losses in variable magnetic fields. Amorphous wires of a micrometric diameter, manufactured by the method of rapid cooling in a water bath, are used as the active elements of magnetic field sensors. Bulk amorphous iron alloys are characterized by considerably higher mechanical hardness compared to their crystalline counterparts, and possess soft magnetic properties. Moreover, some alloys containing rare-earth elements exhibit hard magnetic properties after appropriate heat treatment, which creates chances for the production of nano-composite magnets of the RE-Fe-B (RE = Nd, Pr, Dy) type with substantially higher corrosion resistance compared to the presently used magnets of this type. The process of manufacturing bulk iron-based metallic glasses places, however, greater demands on the apparatus, due to the much higher cooling rates of these alloys, compared to palladium or zirconium alloys [7]. A system designed for the production of bulk metallic glasses has been constructed at the Institute of Physics of the Czestochowa University of Technology. One of the authors (P.P.), who was involved in the carrying out of the programme "Research Training Network on Bulk Metallic Glasses" headed by Prof. H. Davies at the University of Sheffield in the years 2001-2003 within the 5th Framework EU Programme, is the chief designer and executor of this system.

The device designed for the production of bulk metallic glasses uses the suction-casting method that consists in sucking in an alloy arc-melted in an argon atmosphere to a water-cooled copper mould by means of a pressure difference between chambers integrated with the system [8]. The technological process requires prior evacuation of the system to approx. 10^{-6} Tr to avoid oxidation of the alloy. Grain nuclei formed on the interface between the arc-melted metal and the water-cooled copper mould, after being sucked in to the mould, provide the source of rapid grain growth and, as a consequence, the formation of a mixed structure containing a large fraction of crystalline phases grains in an amorphous matrix. To reduce the likelihood of grain nucleation, innovative technological solutions were adopted, which involved the use of a system for the thermal isolation of the copper mould from the molten metal, which, at the same time, markedly increases the temperature difference between the molten metal and the cooled mould. The increase of the temperature difference is a key factor contributing to improving the cooling rate attainable in the system. Additionally, in order to reduce the probability of grain nucleation, the copper block was subjected to vibration. The vibratory motion of the arc-melted metal results in a reduction of the thermal contact between the specimen and the mould.

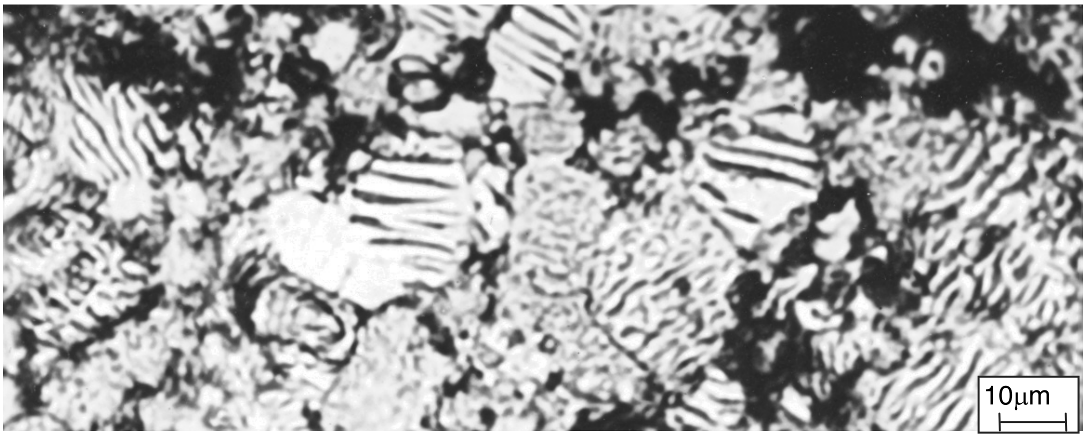

Fig. 3. Domain structure of the plasma-sprayed $Nd_2Fe_{14}B$ magnet. Powder pattern method

a) b)

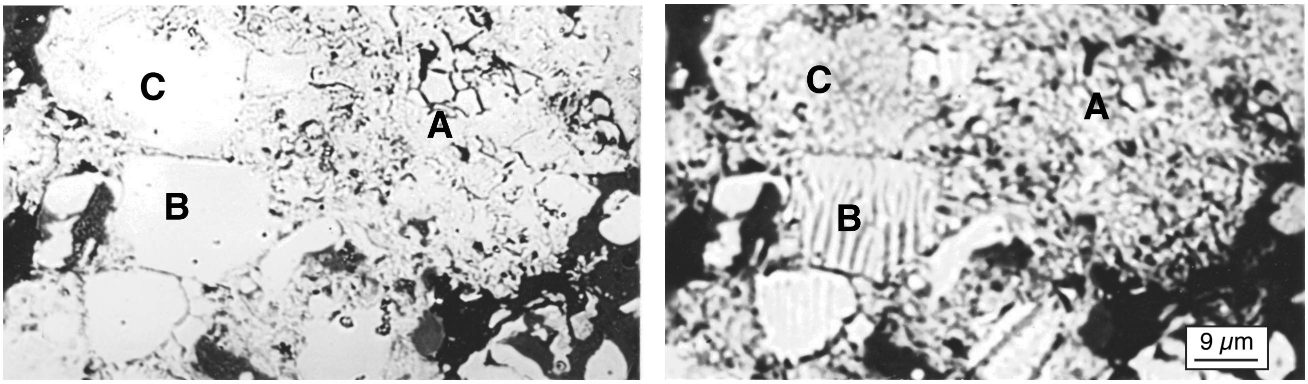

Fig. 4. Comparison of microstructure (a) with magnetic domain structure (b), of the plasma-sprayed isotropic Nd-Fe-B films after annealing for 0.5 h at 1073 K

a) b)

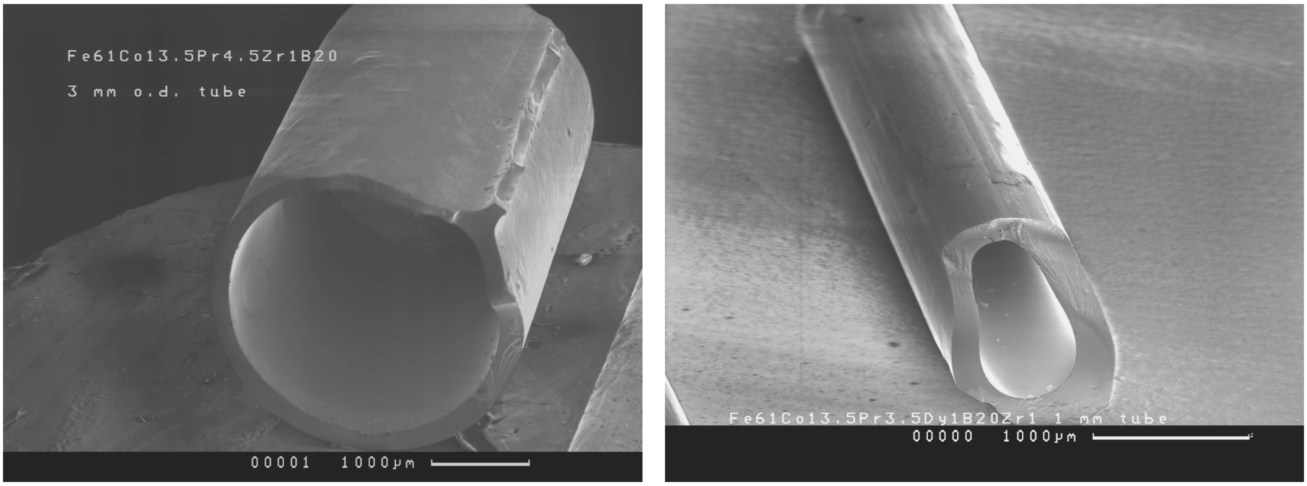

Fig. 5. SEM micrographs of the suction cast tube sample: a) $Fe_{61}Co_{13,5}Pr_{4,5}Zr_1B_{20}$, 3 mm diameter; b) $Fe_{61}Co_{13,5}Pr_{3,5}Zr_1Dy_1B_{20}$, 1 mm diameter

The most important results concerning bulk metallic glasses include the production of Fe-Co-Zr-W-B alloy specimens in the form of tubes of an outer diameter of 3 mm and rods of a maximum diameter of 2 mm using the built system [8-11]. The X-ray diffraction and Mössbauer spectroscopy of the test specimens revealed the existence of a fully amorphous structure of specimens with this diameter.

Moreover, the Institute of Physics, in collaboration with the Department of Engineering Materials of the University of Sheffield (the UK), has developed a technology for the production of state-of-the-art magnetically hard nanocomposites of the (Fe-Co)-(Pr, Dy)-B-Zr type by annealing of bulk metallic glasses in the form of tubes and rods of a variable diameter [12,13] (Fig. 5). The shortening of the technological process of nanocrystalline material manufacture and the improvement of the corrosion resistance of Pr-Fe-B alloys compared to magnetically hard nanocomposites of the RE-Fe-B (RE=Nd, Pr, Dy) type, as manufactured by conventional methods, create chances for these materials to be widely applied in industry - particularly for the production of miniature ring-type magnets to be used for the construction of stepper motors intended for electronic watches. The magnetic properties of magnetically hard nanocomposites of the (Fe-Co)-(Pr,Dy)-B-Zr type, as obtained by soaking of metallic glasses, are summarized in Table 1.

Bulk magnets of the Fe-Co-Pr-B-Zr-Ti type with a nanocrystalline structure, containing 9 at% of praseodymium, were also obtained by the suction-casting method using direct rapid cooling. Nanocrystalline magnets in the form of tubes for this type of alloys are characterized by an exceptionally high coercive field magnitude, reaching 1230 kA/m.

Table 1.
Magnetic properties of the nanocomposite hard magnetic (Fe-Co)-(Pr,Dy)-B-Zr alloys produced by annealing of bulk glassy precursors

Material and heat treatment	Magnetic properties		
	J_s [T]	$_JH_c$ [kA/m]	$(BH)_{max}$ [kJ/m^3]
$Fe_{61}Co_{13.5}Zr_1Pr_{4.5}B_{20}$ (903K/0.5 h)			
Tube; ϕ = 3 mm	1.45	133	14.6
$Fe_{61}Co_{13.5}Zr_1Pr_{3.5}Dy_1B_{20}$ (923K/0.5 h)			
Tube; ϕ = 3 mm	1.4	144	22.7

4. Conclusions

Thin-layered Nd-Fe-B magnets were produced by means of arc-plasma deposition of Nd-Fe-B powders. Magnets of this type can be applied directly onto the surface of electromagnetic equipment parts. Magnets with isotropic magnetic properties were obtained by applying layers onto the water-cooled copper substrate. The optimal magnetic properties of isotropic layers, i.e. a coercivity of $_MH_c$ = 1.2 MA/m, a remanence of μ_oM_r = 0.6 T and a magnetic energy density of $(B{\cdot}H)_{max}$ = 64 kJ/m^3 were attained after heat treatment for a duration of 0.5 h and at a temperature of 1023 K. Whereas, anisotropic magnets with optimal magnetic properties ($_MH_c$ =1.2 MA/m, μ_oM_r=0.9 T and $(B{\cdot}H)_{max}$=180 kJ/m^3) were obtained as a result of the arc-plasma deposition of powders onto the copper substrate heated up to 873 K. The most advantageous properties were achieved for the microcrystalline structure of a grain size close to the single-domain particle size (approx. 0.3 μm).

Moreover, a system designed for the production of materials by the method of sucking in an arc-melted alloy to a water-cooled copper mould (the suction-casting method) was constructed. It has been demonstrated that the suction-casting method makes it possible to obtain bulk amorphous alloys of considerable sizes, such as rods of magnetically soft Fe-Co-W-Zr-B alloys of a diameter up to 2 mm, as well as Fe-Co-Pr-Zr-B tubes of a diameter up to 3 mm. It is also possible to produce magnetically hard nanocomposite materials of the (Fe-Co)-(Pr,Dy)-B-Zr type by annealing of metallic glasses.

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