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Magnetic properties, microstructures and domain structures of arc-plasma sprayed Nd–Fe–B permanent magnet

J. J. WYSŁOCKI
Institute of Physics, Technical University, Al. Armü Krajowej 19, 42-200 Częstochowa, Poland

Thin Nd–Fe–B films prepared by arc-plasma spraying at different substrate temperatures were investigated for their magnetic and structural properties. The isotropic magnets with the best magnetic properties (${}_{M}H_c = 1.2\ \mathrm{MA\,m^{-1}}$, $\mu_0 M_r = 0.6$ T, $(BH)_{max} = 64\ \mathrm{kJ\,m^{-3}}$), were obtained after plasma spraying the Nd–Fe–B powders on water-cooled copper substrates and subsequently annealing the films for 0.5 h at 750 °C. The optimum magnetic properties of the anisotropic Nd–Fe–B films, i.e. ${}_{M}H_c = 1.2\ \mathrm{MA\,m^{-1}}$, $\mu_0 M_r = 0.9$ T and $(BH)_{max} = 180\ \mathrm{kJ\,m^{-3}}$, were obtained in films sprayed on to heated to 600 °C substrates. The magnetic properties of the sprayed films were strongly influenced by the microstructure. The domain structure of these films is also presented.

1. Introduction

New permanent magnet materials based on the intermetallic compound $Nd_2Fe_{14}B$ with energy products $(BH)_{max}$ of at least $3 \times 10^5\ \mathrm{J\,m^{-3}}$ and coercivities of the order of $10^6\ \mathrm{A\,m^{-1}}$, are produced mainly by two techniques: rapid quenching [1] and conventional powder metallurgy [2].

Recently, miniaturization of the magnetic circuits has stimulated growing interest in thin film magnets which also may be deposited directly on to the surface of the electromagnetic devices using sputtering [3] or plasma spraying techniques [4]. However, in the case of the Nd–Fe–B compounds, thin films have only been obtained using sputtering as the preparation technique [5]. So far there are few papers dealing with successfully plasma-sprayed Nd–Fe–B thin films. Therefore, fabrication of the Nd–Fe–B thin films by plasma spraying, as well investigation of their magnetic properties, microstructures and domain structures, were the main aim of the present work.

2. Experimental procedure

In Fig. 1, a schematic sketch of the arc-plasma spray process of the Nd–Fe–B thin films is shown. A ceramic shield for the spray stream and also a stream of argon directed on to the substrate (Fig. 1) were applied to reduce oxidation of the powder feed of the plasma spraying process. The plasma-sprayed deposits were synthesized on the copper substrates which were water-cooled or heated in the temperature range 500–800 °C. The deposited films were prepared with thicknesses up to 3 mm. Comparison of the chemical composition of the powder feed and the arc-plasma-sprayed magnets has shown the smallest loss of boron (1.03–0.98 wt %) and the highest change in neodymium concentration due to evaporation and, possibly, oxidation. The deposited films were annealed in the temperature range 500–900 °C for 0.5–2 h under a vacuum of ~ 0.01 Pa. Phase analysis and crystallographic investigation were done by X-ray diffraction using CrK_α radiation. The microstructure was investigated by both optical and scanning microscopy and the surface distribution of the neodymium and iron elements was determined by X-ray microanalysis. Magnetic properties, i.e. magnetization and demagnetization curves, were measured in the parallel and perpendicular directions to the deposited magnet with a vibrating sample magnetometer in a $2\ \mathrm{MA\,m^{-1}}$ (maximum) magnetic field. The domain structure was observed by metallographic microscopy using the powder pattern method.

3. Results and discussion

3.1. Magnets with isotropic magnetic properties

As-sprayed deposits with thicknesses between 50 and 2000 μm formed on water-cooled substrates possess isotropic magnetic properties. The coercivity, ${}_{M}H_c$, of these films is low, reaching $50\ \mathrm{kA\,m^{-1}}$. The heat treatment of as-sprayed magnets for 0.5 h at temperatures between 500 and 750 °C causes an increase in ${}_{M}H_c$ up to $1.2\ \mathrm{MA\,m^{-1}}$. On further increasing the heat-treatment temperature, coercivity decreases (Fig. 2). However, remanence, $\mu_0 M_r$, does not change in the range of applied temperatures, remaining at the value of 0.6 T.

From X-ray phase analysis results, the $Nd_2Fe_{14}B$ phase is seen to form after the optimum heat treatment (for 0.5 h at 750 °C) of the as-sprayed Nd–Fe–B films and small amounts of Nd_2O_3, NdB_2 and α-Fe phase are present. Thus the crystallographic structure

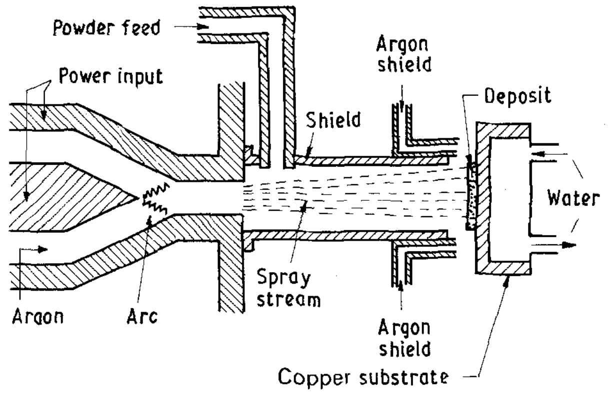


Figure 1 Schematic sketch of the deposition of the Nd–Fe–B films by the arc-spraying technique.

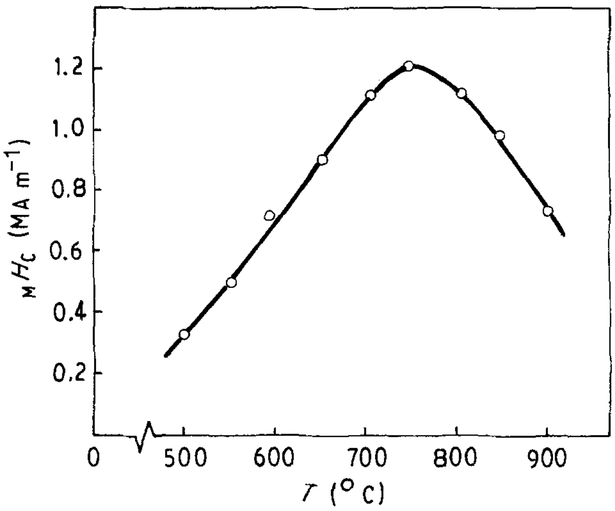


Figure 2 Dependence of the $_MH_c$ values of the plasma-sprayed isotropic Nd–Fe–B films on the annealing temperature.

of the heat-treated isotropic Nd–Fe–B sprayed magnets is similar to the structure of bulk permanent magnets prepared from this material. The common features of the crystallographic structure of the plasma-sprayed and sintered Nd–Fe–B magnets offer evidence for a similar magnetization process mechanism, which is mainly based on the nucleation of the domains with reverse magnetization vector [6]. As mentioned above, the obtained films are crystalline and magnetically isotropic. This was confirmed by both the X-ray diffraction patterns and the similarity in magnetization and demagnetization curves measured in the plane of the deposits and across their width. However, from X-ray line-broadening measurements, it was found that after optimum heat treatment, the films have a grain size of 0.3 μm, which is approximately equal to the critical size of the single domain particle [7]. This was also confirmed by observation of the magnetic domain structure presented in Fig. 3. This domain structure consists of a network of small islets of a size less than 1 μm.

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 800 °C. The microstructure with fine grains is visible (Spot A), as well as large grains (Spots B and C). The

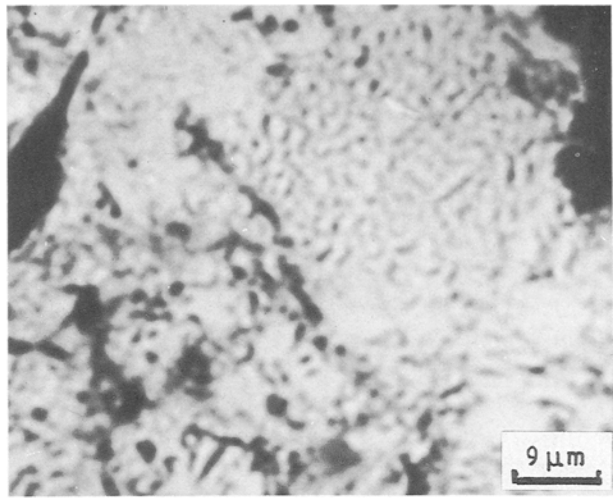


Figure 3 Domain structure of the plasma-sprayed isotropic Nd–Fe–B films after optimum annealing (for 0.5 h at 750 °C).

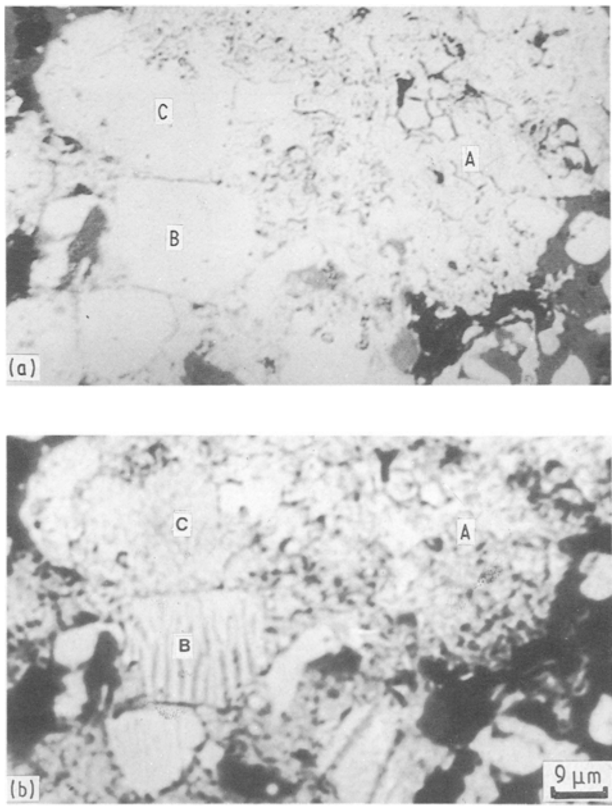


Figure 4 Comparison of (a) microstructure with (b) magnetic domain structure, of the plasma-sprayed isotropic Nd–Fe–B films after annealing for 0.5 h at 800 °C.

domain structure in the large grains consists of domains with 180° Bloch walls (when the 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). Increase in the heat-treatment temperature up to 850 °C causes further growth in grain size. The domain structure of these large grains consists of domains with 180° domain walls or aggregates of small islets (Fig. 5).

Thus in amorphous arc-plasma-sprayed Nd–Fe–B films deposited on water-cooled copper substrates and

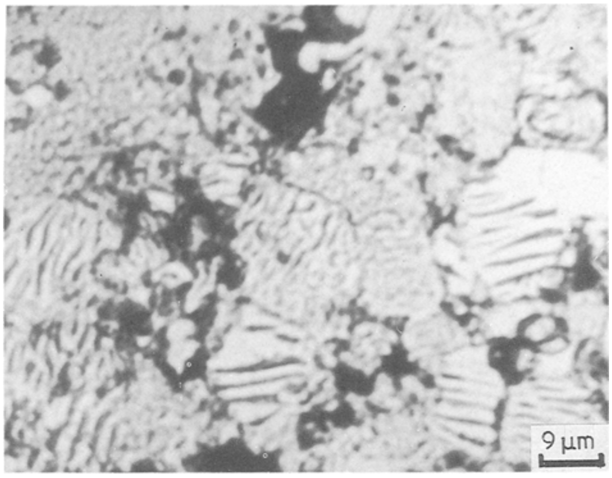


Figure 5 Domain structure of the plasma-sprayed isotropic Nd–Fe–B films after annealing for 0.5 h at 850 °C.

then crystallized into isotropic magnets, coercivity is determined by the grain size.

On the basis of the above study the best magnetic properties have been obtained in the isotropic arc-plasma-sprayed Nd–Fe–B films after heat treatment for 0.5 h at 750 °C: ${}_{M}H_c = 1.2$ MA m^{-1}, $\mu_0 M_r = 0.6$ T, $(BH)_{max} = 64$ kJ m^{-3}. A relatively low value of energy product, in comparison with sintered magnets, is due to the low value of remanence, $\mu_0 M_r$, in isotropically plasma-sprayed magnets. It is expected that this value of energy product may be increased by producing a crystallographic texture, e.g. by applying heat treatment in a magnetic field.

3.2. Magnets with anisotropic magnetic properties

Arc-plasma-sprayed Nd–Fe–B films deposited on to copper substrates heated in the temperature range 500–750 °C possess anisotropic magnetic properties. Fig. 6 shows the typical microstructure of this magnet taken from the surface of the deposit (Fig. 6a) and Fig. 6b, c and d present cross-sections of the films. As shown in Fig. 6, magnets are characterized by a layered pancake-type microstructure, which results from flattening of the molten particles as they impact the substrate. This is seen particularly clearly in the pictures of cross-sections of the magnets (Fig. 6b, c and d).

From the X-ray microanalysis and from a comparison between the microstructure (Fig. 6) and the surface distribution of neodymium and iron (Fig. 7), dark spots in the pictures of the microstructure (Fig. 6) correspond to the regions with higher neodymium and lower iron concentrations (Fig. 7b and c).

The X-ray diffraction data confirmed that preferred orientation of the *c*-axis (easy axis of magnetization) is perpendicular to the plane of the deposited film. This is consistent with the domain structure observations as shown in Fig. 8a, where domains are in the form of islets with the magnetization vector perpendicular to the plane of the deposited film. However, at higher deposition temperatures (above 750 °C), the *c*-axis alignment begins to switch from perpendicular to parallel to the plane direction. This is confirmed by changes in the type of domain structure leading to formation of a labyrinth-like domain structure and

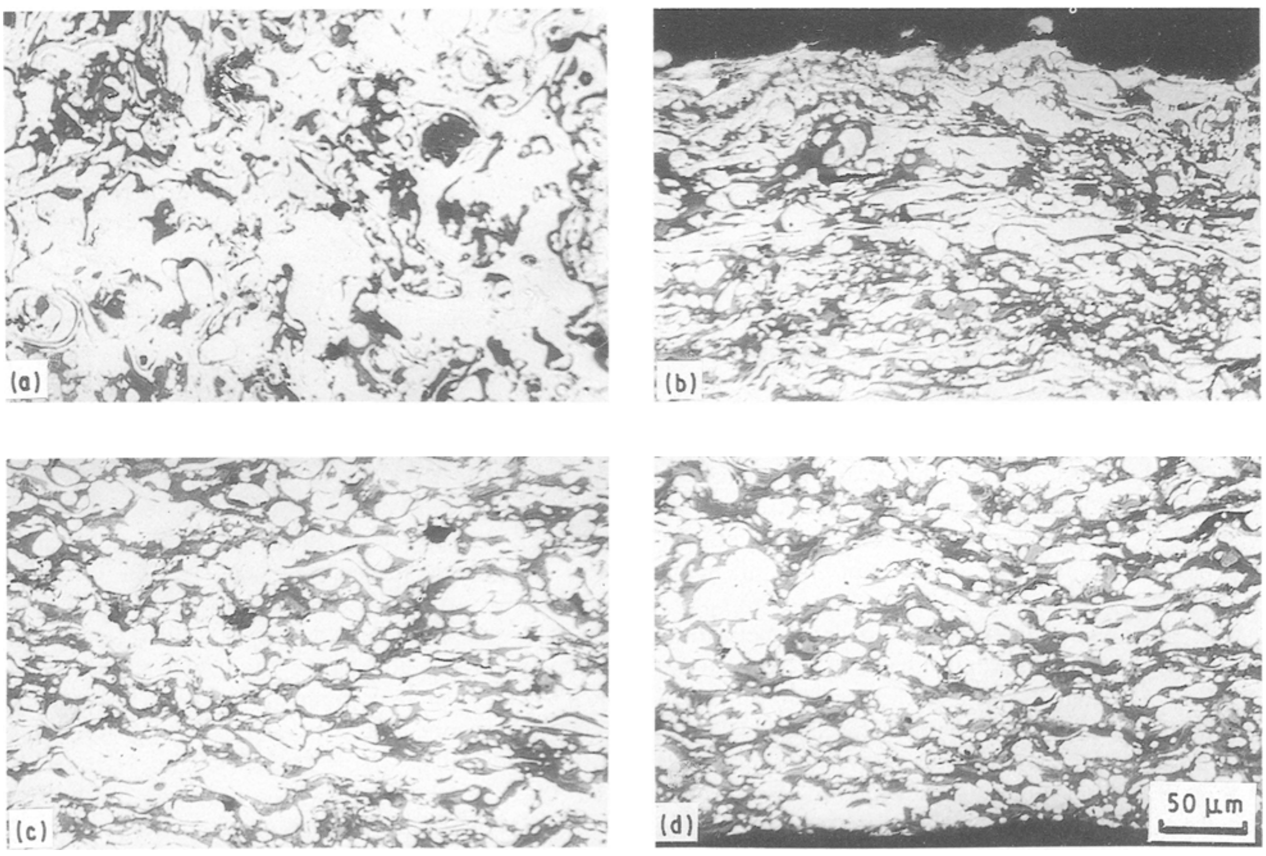
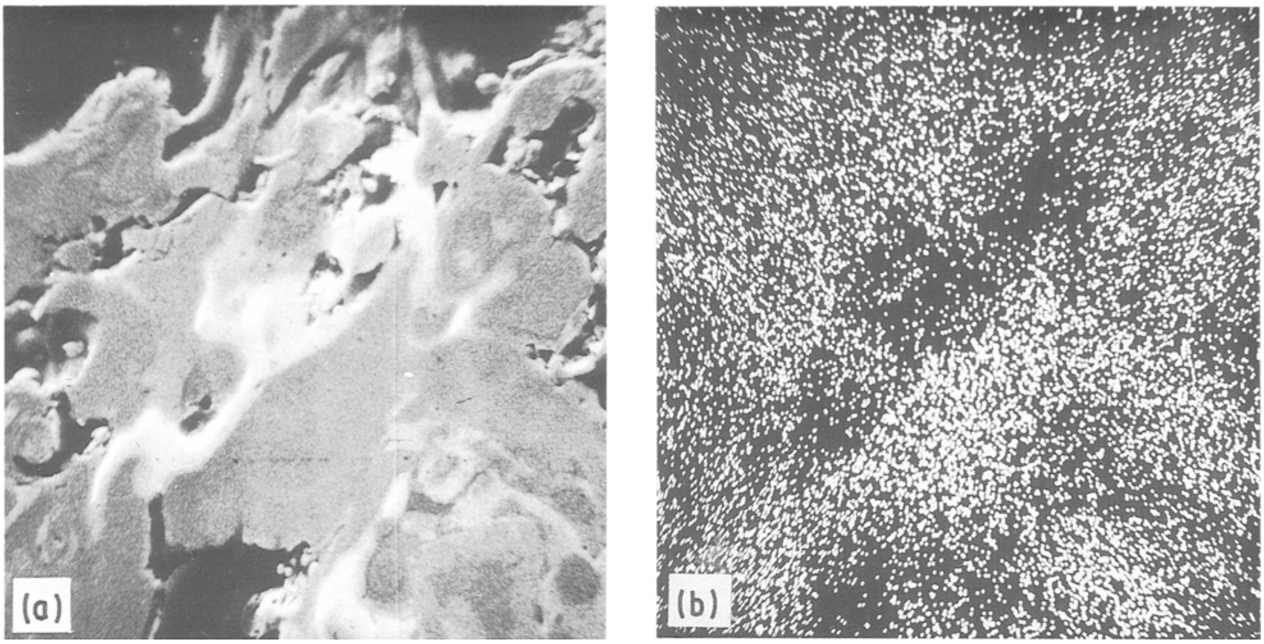


Figure 6 Microstructure of the plasma-sprayed anisotropic Nd–Fe–B films deposited on to a substrate heated to 600 °C, (a) surface of the deposit; (b–d) cross-sections of the films taken from the top, middle and bottom part, respectively.



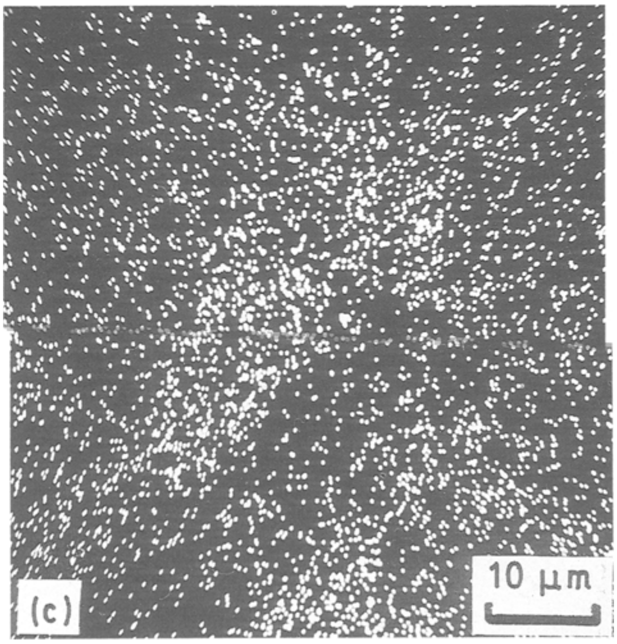


Figure 7 Surface distribution of elements in the plasma-sprayed anisotropic Nd–Fe–B films deposited on to a substrate heated to 600 °C (a) top, (b) iron and (c) neodymium.

finally domains with 180° domain walls when the c-axis lies in the plane of the film (Fig. 8b).

It should be emphasized that immediately after the arc-plasma-spraying process, anisotropic films deposited on to heated substrates exhibit very high magnetic properties in comparison with films deposited on to water-cooled substrates which need heat treatment after plasma spraying to achieve optimum magnetic properties.

Fig. 9 shows magnetization and demagnetization curves (1) as well as the dependence of the coercivity, ${}_{M}H_c$, and remanence, $\mu_o M_r$, on the applied field measured perpendicular to the film plane (parallel to the c-axis) of the arc-plasma-sprayed anisotropic Nd–Fe–B magnet directly crystallized at 600 °C. Also shown in Fig. 9, is the demagnetization curve (2) measured in the plane (normal to the c-axis) of this magnet. It should be noted that rapid growth of the remanence occurs in the narrow range of the low (far lower than coercivity) magnetic field. This range of magnetic field dependence of the ${}_{M}H_c$ values on the applied field, is characterized by a linear growth (Fig. 9). However, the virgin curve of the thermally demagnetized magnet shows a rapid growth of magnetic induction, and thus in the field $H < 25\ \mathrm{kA\,m^{-1}}$ magnetization reaches half its maximum value. This effect of effortless magnetization of the magnet is indicative of the absence of the domain wall attaching (pinning) effective centres in most grains. Thus, according to Becker [8], such a dependence of the virgin curve on the applied field allows us to conclude that the essential mechanism which makes it possible to achieve a high value of coercivity is related to the difficulty of reverse domain nucleation.

The optimum magnetic properties obtained for the arc-plasma-sprayed Nd–Fe–B anisotropic magnets directly crystallized at 600 °C are as follows: ${}_{M}H_c = 1.2\ \mathrm{MA\,m^{-1}}$, $\mu_o M_r = 0.9\mathrm{T}$, $(BH)_{max} = 180\ \mathrm{kJ\,m^{-3}}$.

4. Conclusions

As a result of arc-plasma-spraying of the Nd–Fe–B powders, isotropic and anisotropic permanent magnets have been successfully deposited in thin-film form. The isotropic magnets were formed after plasma spraying on water-cooled copper substrates. These magnets possess low coercivity which is equal to $50\ \mathrm{kA\,m^{-1}}$. The best magnetic properties were obtained after annealing the as-sprayed isotropic films for 0.5 h at 750 °C: ${}_{M}H_c = 1.2\ \mathrm{MA\,m^{-1}}$, $\mu_o M_r = 0.6\ \mathrm{T}$, $(BH)_{max} = 64\ \mathrm{kJ\,m^{-3}}$.

The magnets with anisotropic magnetic properties were prepared by arc-plasma spraying the Nd–Fe–B powders on to substrates heated in the temperature range 500–800 °C. The optimum magnetic properties

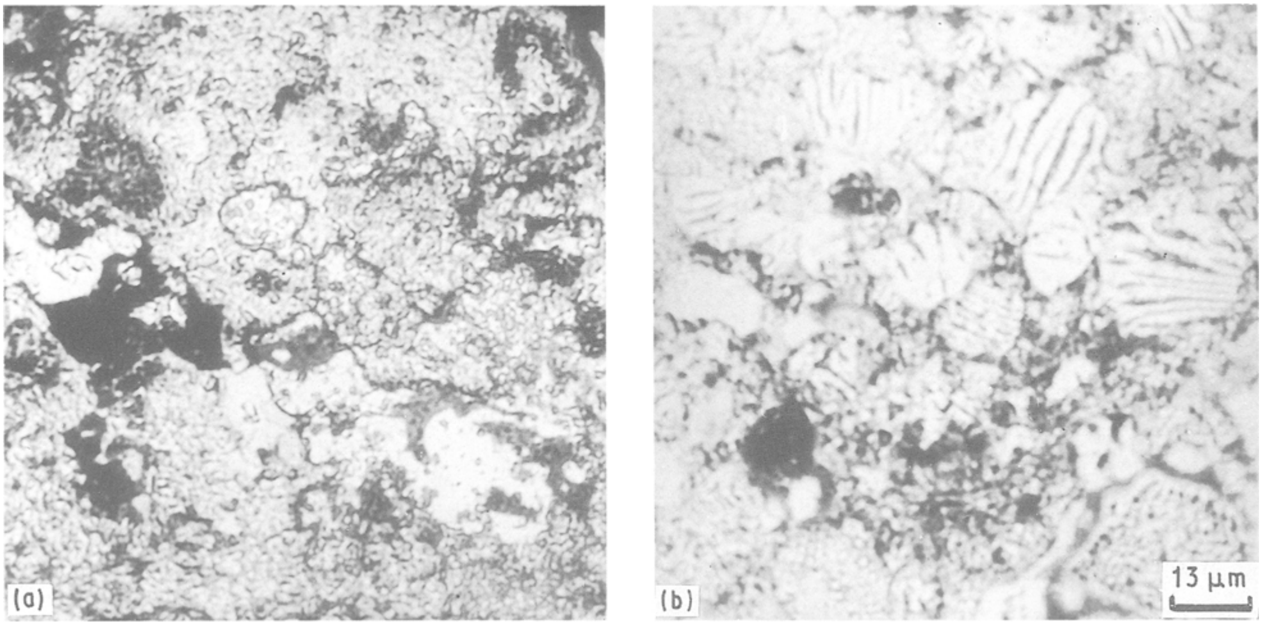


Figure 8 Domain structure of the plasma-sprayed anisotropic Nd–Fe–B films deposited on to substrates heated to (a) 600 °C and (b) 750 °C.

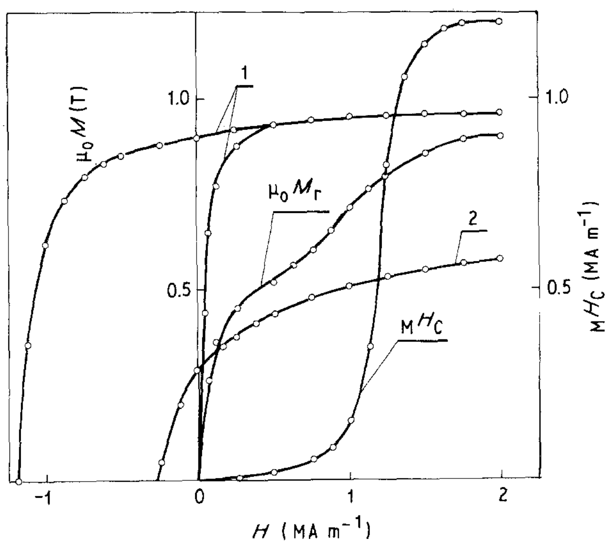


Figure 9 Magnetization and demagnetization curves (1), as well as the dependence of the coercivity, $_MH_c$, and remanence, $\mu_0 M_r$, on the applied field measured perpendicular to the film plane (parallel to the *c*-axis) of the arc-plasma-sprayed anisotropic Nd–Fe–B magnet directly crystallized at 600 °C. The demagnetization curve (2) measured in the plane (normal to the *c*-axis) of this magnet is also shown.

of the as-sprayed anisotropic Nd–Fe–B magnets directly crystallized at 600 °C are: $_MH_c = 1.2$ MA m^{-1}, $\mu_0 M_r = 0.9$ T, $(BH)_{max} = 180$ kJ m^{-3}.

The magnetic properties of the sprayed Nd–Fe–B magnets are mainly influenced by the microstructure. The best magnetic properties were achieved in magnets with a grain size which is close to the critical size of the single domain particle (about 0.3 μm). This microstructure corresponds to the domain structure which consists of a network of small islets of a size less than 1 μm, indicating that domain walls are attached (pinned) to the grain boundaries and the magnetization process in these grains takes place by the reverse domain nucleation. The decrease in magnetic properties is related to the grain growth and is followed by formation of the 180° domain walls. The magnetization reversal process can then take place more easily by domain wall motion and pinning.

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