SURFACE MODIFICATION OF Nd-Fe-B BASED MATERIALS WITH PULSED HELIUM PLASMA STREAMS

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X-ray amorphous $Nd_2Fe_{23}B_3$ phase have been synthesized under the interaction of accelerated helium plasma with $Nd_8Fe_{87}B_5$ and $Nd_{4,5}Fe_{77}B_{18,5}$ alloys. Microstructure and composition of modified layer have been examined.

PACS: 52.40.Hf

1. INTRODUCTION

Nd-Fe-B permanent magnets manufactured by traditional powder technology possess record magnetic characteristics [1]. But such magnets have insufficient corrosion resistance. With purpose of increasing corrosion resistance Nd-Fe-B magnets were treated by nitrogen plasma [2]. It was obtained that in the range of constant composition the microstructure became X-ray amorphous with specific non-uniform phase and elements redistribution.

It was shown previously that irradiation of structural steels with powerful plasma streams, generated by pulsed plasma accelerators, led to hardening of their surface and increasing the wear resistance of steel samples [3,4,5]. Such surface modification is realized due to the combination of the heating and structure-phase transformation in solid state, decay of the solid solutions, melting, decomposition of the chemical agents, diffusion of the plasma stream atoms into the depth of material being in liquid state and high speed cooling-quenching (10^7-10^8 K/s) due to a heat sink to the inner layers of the materials. As a result of these processes the creation of the amorphous or quasi-amorphous layer with increased wear resistance and corrosion tolerance takes place.

The pulsed plasma technologies can be a principally new way for modification of the surface layers of magnetic materials with the aim of improvement of the permanent magnets corrosion properties. Investigations of the formation of a metastable structure of magnetic alloys under an influence of the high energy plasma streams are of great interest for the determination of patterns of structure formation under the ultra-speed crystallization that can lead to changing the mechanical and magnetic properties.

2. EXPERIMENTAL

Alloys of $Nd_8Fe_{87}B_5$ and $Nd_{4,5}Fe_{77}B_{18,5}$ were prepared by arc-melting desired elements (Fe purity 99%, Nd purity 99% and ferro boron FeB_{20}). The surfaces of the samples were polished and then irradiated by pulsed plasma streams with pulse length of an order 2-3 μs. Energy density of plasma streams was 35 J/cm^2. The energy of accelerated ions achieved 2 keV. The numbers of pulses were 5 and 10 for $Nd_8Fe_{87}B_5$ and $Nd_{4,5}Fe_{77}B_{18,5}$ accordingly. Microstructure of treated surfaces and cross-sections of samples were examined with optical microscope MMR-4 and scanning electron microscopy JEOL with X-ray analyzer LINK. The crystal structure was studied with XRD.

3. RESULTS AND DISCUSSION

Synthesis of $Nd_2Fe_{23}B_3$ magnetic phase in the $Nd_8Fe_{87}B_5$ alloy under helium plasma treatment

Fig. 1 shows microstructure of initial $Nd_8Fe_{87}B_5$ alloy. The structure of bulk alloy consists of $Nd_2Fe_{14}B$ phase between α-Fe dendrites (peritectic equilibrium). Moreover grains of $NdFe_4B_4$ phase can be observed. It means that alloy is placed in following equilibrium triangle:

$$Fe - Nd_2Fe_{14}B - NdFe_4B_4 - Fe$$

The optical microscope photo of a cross-section of the $Nd_8Fe_{87}B_5$ sample irradiated by plasma streams is shown in Fig. 2. Plasma stream impact leads to the formation of modified layer with a thickness of ~4 microns. Content of metal elements in cross-section of modified layer is almost like local content in "matrix" surface (Fig. 3 and Table 1). This content differs from integral content of elements on the surface of modified layer and it associates with not uniform elements distribution. Nd-rich inclusions of oval and spherical forms (2-3 microns) and meshes of more fine Nd-rich inclusions (< 1 micron) have been observed on the irradiated surface (Fig. 3). Hence after plasma treatment integral content of elements have not been changed actually and it matches to nominal content of alloy. However element's distribution in the modified layer is not homogenous and there are Nd-rich and Nd-lean inclusions with ratio Fe/Nd about 12.

Source of excess of Nd atoms which forms Nd-rich inclusions can be $Nd_2Fe_{14}B$ phase: $3Nd_2Fe_{14}B(4P)t \rightarrow 1Nd_2Fe_{23}B_3(4I)c+4Nd+19Fe$ (at T> 717 C).

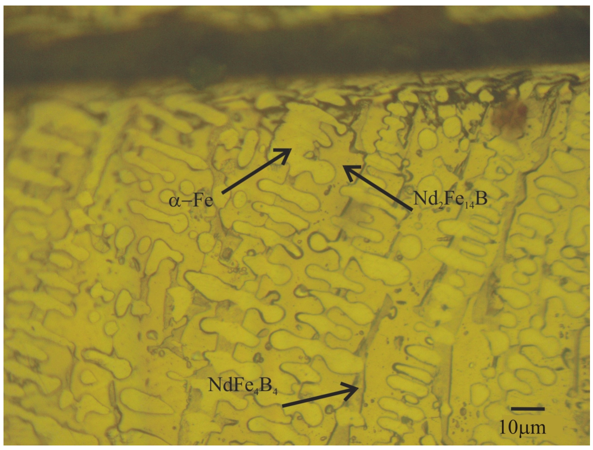

Fig. 1. Microstructure of initial $Nd_8Fe_{87}B_5$ alloy

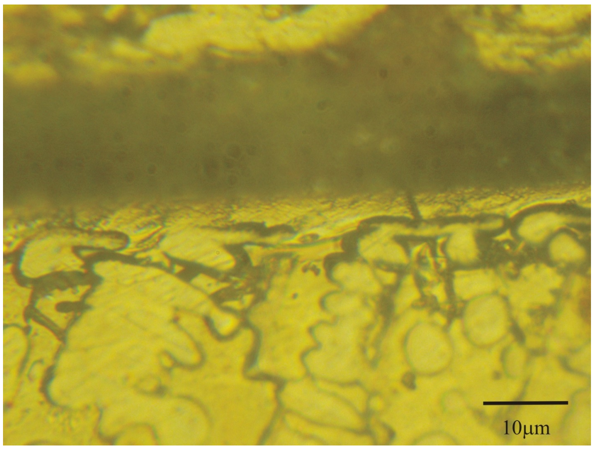

Fig. 2. Cross-section of treated $Nd_8Fe_{87}B_5$ sample

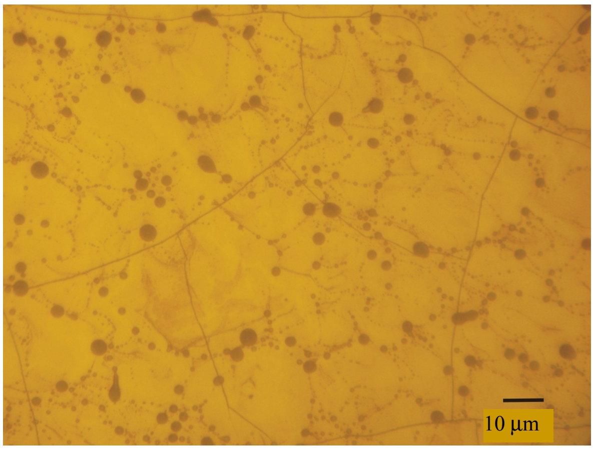

Fig. 3. Surface of $Nd_8Fe_{87}B_5$ sample after plasma treatment

Table 1. Content of elements in modified layers of $Nd_8Fe_{87}B_5$ alloy after 5 pulses

Name	Fe	Nd	Fe/Nd
a) cross-section Fig. 2			
integral content of modified layer	92,5	7,5	12,4
field between grains of α-Fe phase	87,9	12,1	7,3
b) on the surface Fig. 3			
integral content	91,3	8,7	10,5
matrix	92,2	7,8	11,8
inclusions	4,2	95,8	-

X-ray analysis of initial sample revealed that as-cast sample consists of α-Fe and $Nd_2Fe_{14}B$ phases. All angles of diffraction peaks which fitted to a=0,28665(5) nm lattice constant matched with calculated intensities for α-Fe phase. The rest of diffraction peaks were indexed as tetragonal lattice constants a=0,8802(2) nm, c=1,2119(6) nm (volume 0,9389(6) nm^3). The phase was indexed as $Nd_2Fe_{14}B$(4P)t with known atomic structure and a=0,8792(1) nm, c=1,2190(1) nm [6] lattice constants. Intensity of (311), (410), (411) diffraction peaks matched to powder diffraction data (I=585, 100, 640 accordingly) but (124) diffraction with I=877 have not been detected at all.

Fig. 4 shows XRD pattern of treated $Nd_8Fe_{87}B_5$ sample. There is a halo in the interval of angles 25 – 60^0 and singles peaks which matches to body centered cube structure with a=0,286(5) nm lattice constant. Rest of peaks fitted to $Nd_2Fe_{23}B_3$(4I) phase with known atomic structure and lattice constant a=1,4161(1) nm [7].

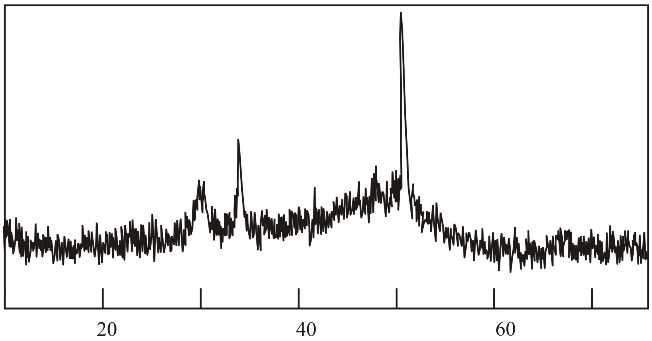

Fig. 4. X-ray diffraction patterns of $Nd_8Fe_{77}B_5$ sample, after plasma treatment (3 microseconds, 5 impulses)

The $Nd_2Fe_{23}B_3$ phase locates at the periphery of the easy glass-forming region where it's easier to form metastable states from the amorphous alloys [8]. Wang et al also pointed out that a sharp concentration gradient of Nd atoms developed by the initial nucleation and growth of α-Fe during the crystallization reduces or even eliminates the thermodynamic driving force for compound nucleation, and thus the metastable $Nd_2Fe_{23}B_3$, phase with small curvature of free energy curve is more suitable to form prior to the $Nd_2Fe_{14}B$.

Structural and phase changes in modified layer of $Nd_{4.5}Fe_{77}B_{18.5}$ alloy

Fig. 5 shows microstructure of initial $Nd_{4.5}Fe_{77}B_{18.5}$ alloy. The structure of bulk alloy is tetragonal boride Fe_2B phase with accurate grain boundaries, $Nd_2Fe_{14}B$ phase (peritectic equilibrium with Fe_2B phase) and Fe-rich eutectic (etched). So phase content of alloy means that one is placed in following equilibrium triangle

Fe – $Nd_2Fe_{14}B$ – Fe_2B – Fe

and differs from known in literature [9].

Table 2. Content of elements in modified layers of $Nd_{4.5}Fe_{77}B_{18.5}$ alloy after 10 pulses

Name	Fe	Nd	Fe/Nd
a) cross-section (Fig.6)			
integral content of modified layer	95,92	4,08	23,5
$Nd_2Fe_{14}B$ phase	87,7	12,3	7,1
boride (Fe_2B)	99,00		
b) on the surface (Fig. 7)			
integral content	93,82	6,18	15,2
matrix	92,2	7,8	11,8
inclusions	8,24	91,76	-

The optical microscope photo of a cross-section of the $Nd_{4.5}Fe_{77}B_{18.5}$ sample irradiated by plasma streams is shown in Fig.6. Plasma treatment of the sample's surface leads to the formation of modified layer with a thickness of ~4 microns. Surface of treated sample (Fig. 7) covered with cracks and cavities, the possible way of its formation is crystallization of Fe-rich eutectic during plasma impact.

Content of metal elements in cross-section of modified layer is almost like local content in "matrix" surface (Fig. 7 and Table 2).

Nd-rich inclusions have been observed too on the irradiated surface. There are Nd-rich inclusions with ratio Fe/Nd ~ 12.

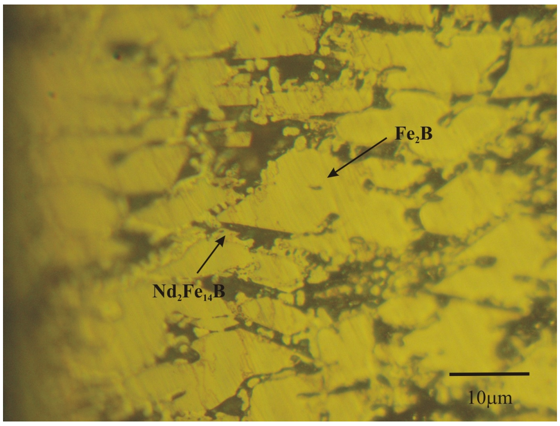

Fig. 5 Microstructure of initial $Nd_{4.5}Fe_{77}B_{18.5}$ alloy

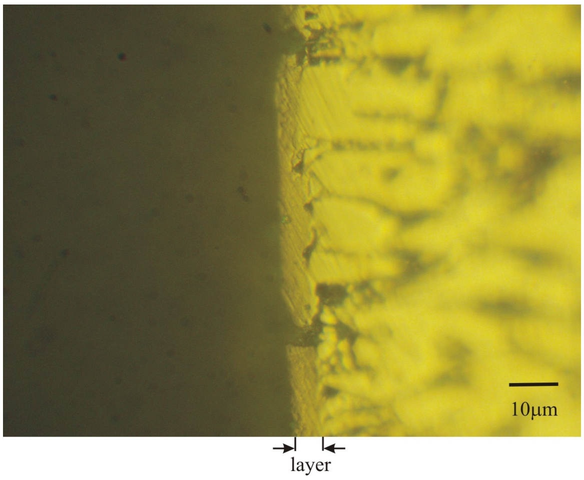

Fig. 6 Cross-section of treated $Nd_{4.5}Fe_{77}B_{18.5}$ sample

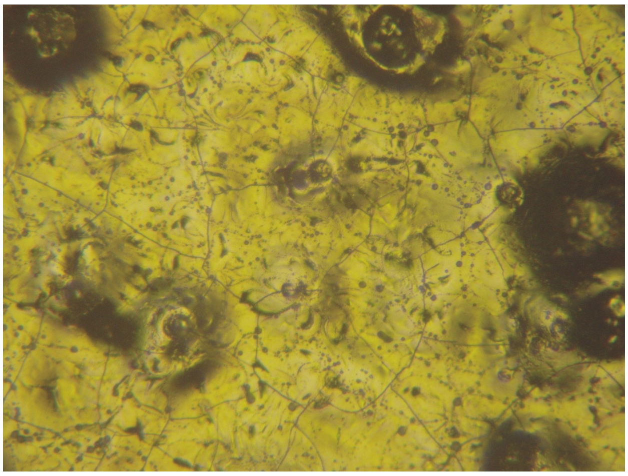

Fig. 7 Surface of $Nd_{4.5}Fe_{77}B_{18.5}$ sample after plasma treatment. Magnification Ч127

Fig. 8 shows XRD pattern of treated $Nd_{4.5}Fe_{77}B_{18.5}$ sample. As can be seen in the XRD pattern the modified layer consists of a mixture of α-Fe, Fe_2B and $Nd_2Fe_{23}B_3$. Intensities of α-Fe phase peaks correlate with calculated intensities. For Fe_2B phase (124) diffraction peak with I=877 have not been detected at all. Texture apparently took place after plasma treatment. Rest of diffraction peaks fitted to cubic a=1,4139(1) nm lattice constant matched with $Nd_2Fe_{23}B_3$(4I) phase with known atomic structure. It should be noted that Fe_3B phase haven't been observed after plasma treatment. Though nuclei of Fe3B phase always have been observed after melt-spinning process and crystallized during appropriate heat treatment [10].

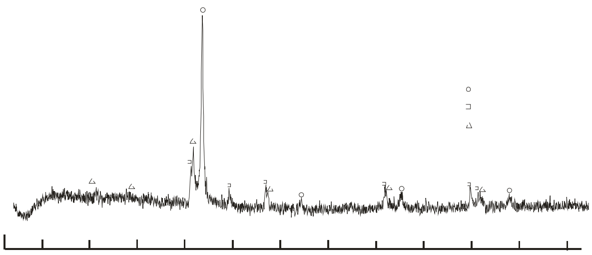

Fig. 8 X-ray diffraction patterns of $Nd_{4.5}Fe_{77}B_{18.5}$ sample, after plasma treatment

ACKNOWLEDGEMENT

This work has been supported by STCU project #881c.

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МОДИФИКАЦИЯ ПОВЕРХНОСТИ МАТЕРИАЛОВ НА ОСНОВЕ Nd-Fe-B ИМПУЛЬСНЫМИ ПОТОКАМИ ГЕЛИЕВОЙ ПЛАЗМЫ

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Рентгеноаморфная фаза $Nd_2Fe_{23}B_3$ синтезирована при взаимодействии импульсных потоков гелиевой плазмы со сплавами $Nd_8Fe_{87}B_5$ и $Nd_{4,5}Fe_{77}B_{18,5}$. Исследованы микроструктура и состав модифицированного слоя.

МОДИФІКАЦІЯ ПОВЕРХНІ МАТЕРІАЛІВ НА ОСНОВІ Nd-Fe-B ІМПУЛЬСНИМИ ПОТОКАМИ ГЕЛІЄВОЇ ПЛАЗМИ

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Рентгеноаморфна фаза $Nd_2Fe_{23}B_3$ синтезована при взаємодії імпульсних потоків гелієвої плазми зі сплавами $Nd_8Fe_{87}B_5$ і $Nd_{4,5}Fe_{77}B_{18,5}$. Досліджено мікроструктуру і склад модифікованого шару.