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DIAMOND-LIKE CARBON COATINGS ON NdFeB MAGNETS

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Abstract. Diamond-like carbon coatings on NdFeB magnets for wear and corrosion protection are described. The coatings, fabricated by arc plasma chemical vapour deposition and the pulsed laser deposition method, were found to be applicable to protect NdFeB from mechanical impact, but failed to protect against hydrogen chlorine and fluorine attack due to defects in the coatings.

Key words: NdFeB, diamond-like carbon, protective coating.

1. INTRODUCTION

Diamond-like carbon (DLC) is a versatile engineering material with increasing areas of application. DLC coatings and films are hard, chemically inert, optically transparent, and wear-resistant. They have low friction. Studies of DLC coating use in cutting instruments, turbine components, prostheses, and electronic circuits are conducted worldwide [1].

The aim of this study was to evaluate the DLC coatings on NdFeB magnets. NdFeB compounds are high-performance hard permanent magnet (PM) materials. There is evidence that they will replace other PM materials in most applications [2]. Unfortunately, the material consisting of reactive Fe and Nd, composed of several phases, is liable to corrosion [3,4].

The most common way to prevent or at least suppress corrosion is to treat or coat the magnet as a whole. The processes used for NdFeB magnets include:

– glazing by CO_2 [5], Nd:YAG [6], or excimer [7] laser light;

– phosphating, chromating, or fluorinating in H_3PO_4, H_2CrO_4, or HF [8–10];

– coating with metals (usually by galvanoplating): Zn, Ni, and Sn [5,8]; Au [11]; Al, Cu, and Cd [12]; ZnCo [3]; Nd [13]; Nd-Ti bilayer [14]; Nd-base film [15];

– coating by TiN [12] and epoxy resin [16].

In micromechanical devices, besides corrosion resistance, the wear resistance of magnets is important (e.g., [17] a linear motor with sliding or rotating magnet on silicon surface). In this case, DLC would be suitable for protective coatings on the magnet [18].

In this work, the corrosion resistance of DLC/NdFeB structure against hydrogen chlorine and fluorine attack was evaluated. Because these gases are highly reactive, it appears attractive to use NdFeB magnets in the couplings of gas circulation fans of excimer lasers, where these gases are present.

2. EXPERIMENT

As substrates, sintered NdFeB pellets (NEOREM 410a of Outokumpu Magnets Oy, Finland), were used, composed of Nd 31 p-%, Dy 1.5 p-%, B 1.15 p-%, Al 0.25 p-%, Fe-balance. Prior to coating, substrates were ground, polished, and cleaned in acetone in an ultrasonic bath for 10 min.

DLC coatings were manufactured by two methods:

1) pulsed arc discharge deposition from methane (for details, see [19]);

2) laser ablation deposition (LAD) from graphite target. Here, the light from an ArF excimer laser (wavelength 193 nm, pulse length 15 ns, and pulse frequency 10 Hz) was focused on the rotating pellet of pressure-compacted graphite powder. The energy density of laser light on the target was between 4–5 J/cm^2, the substrate was placed at the distance of 30 mm from the target perpendicular to the laser plume.

LAD film thickness was in the range of 100–300 nm and that of arc discharge deposited films was 500 nm, determined by Dektak^{3}ST Surface Profiler (force 0.1 mN). On some substrates, a Ti sublayer was formed by evaporation deposition prior to DLC coating. The films examined by optical microscopy were characterized by the Raman spectroscopy. Mechanical properties of the coatings were evaluated by indenter tests, using the Vickers hardness tester.

For corrosion tests, rectangular pieces with dimensions 5×5 mm were cut off from the coated pellets. The uncoated facets were protected from aggressive environment by fluorocarbon paint LF-32LN. Three corrosion tests were performed:

1) holding the samples in 5% F_2 in He at 2 bar for one week;

2) holding the samples in 3% wet HCl (in concentrated HCl vapours) for a week;

3) recording the potentiodynamic polarization curves in 0.1 M HCl (experiment described in [20]).

3. RESULTS

Figure 1 presents the micrograph of the surface of a DLC-coated NdFeB sample. The material contains many pores with dimensions up to 10 µm. After polishing and cleaning there remain particles on the surface, with dimensions of few micrometers, which are difficult to remove due to the magnetic attraction forces. The physical characterization was performed on the defectless areas.

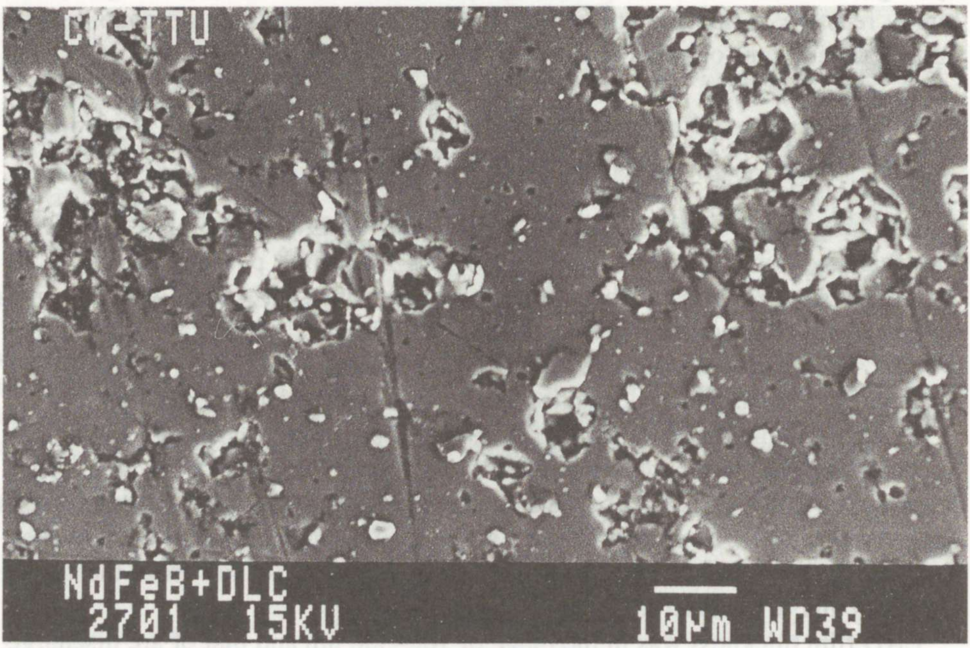

Fig. 1. Surface morphology of a diamond-like carbon-coated sintered NdFeB magnet.

In the Raman spectra (Fig. 2), both sp^3 band at 1300 cm^{-1} and sp^2 band at 1550 cm^{-1} can be distinguished. Considering that the Raman spectrometry is about 50 times more sensitive to sp^2 bonding [21], the DLC material, to a high degree, consists of sp^3 bonded carbon, which provides its high protective properties.

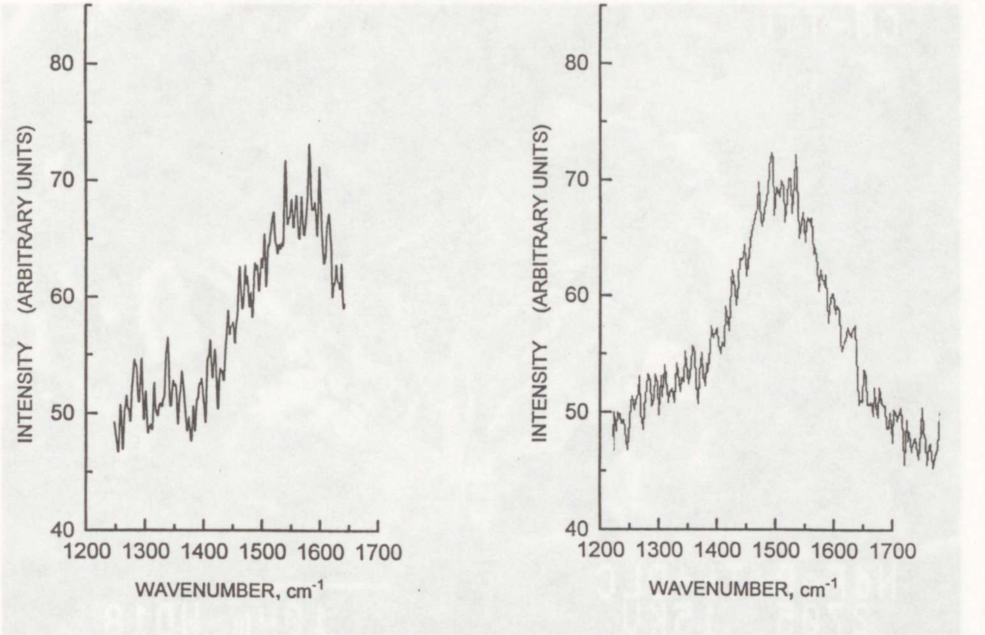

Fig. 2. Raman spectra of diamond-like carbon coatings, fabricated by arc discharge deposition; laser deposition; excitation 514 nm.

The adhesion and mechanical properties of the coatings were characterized by the indenter test. The coatings without buffer layer had poor adhesion and were delaminated from the surface at the lightest touch with the indenter tip. The presence of titan sublayer (about 0.1 μm) improved the adhesion significantly (Fig. 3). The fracture character is typical of hard and well-adherent coating on a softer substrate [22]. The coating breaks gradually in the course of indenter penetration, which results in many parallel cracks in the crater walls. The irregularities in the crack positions and spacing are due to the inhomogeneity of the substrate and pores in it.

In all corrosion tests, halogen penetration under coating was observed. In wet HCl, the coatings delaminated from the substrate totally in a few days. In the case of fluorine test, the structure remained unchanged, nevertheless, the coating delaminated from the surface after storage in the normal atmosphere for some months. Obviously, halogen reaches NdFeB through defects, pores, and cracks in the coating.

The delamination of the coating may be explained in the following way. The chemical reaction of halogen with neodymium and iron yields metal halogenides, which form complexes with water in the presence of water vapour. These complexes have larger volume than the starting metal compound, thus causing the delamination of the coating.

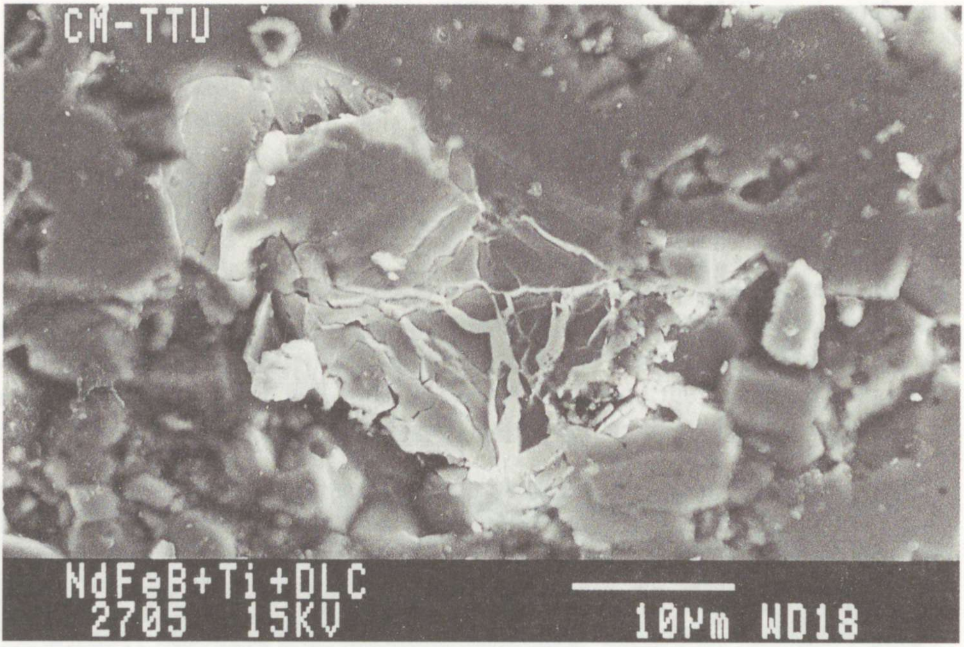

Fig. 3. Indentation crater on the surface of the diamond-like carbon-coated NdFeB magnet (with Ti sublayer); applied force – 2 N.

The presence of the reaction between halogen and NdFeB was confirmed also by potentiodynamic polarization measurements (Fig. 4). These curves indicate that the coating has little effect on the corrosion behaviour of NdFeB. The 50 mV shift of the corrosion potential may be attributed to the presence of Ti on the substrate. Since DLC is known to be inert to HCl, but reactive to NdFeB, corrosion is assumed to occur through defects in the coating.

The penetration of fluorine into DLC was examined by the Auger electron spectroscopy (Fig. 5). The profiles were taken from a smooth area without defects. According to the diagram, fluor does not penetrate deeper than 60 nm into the DLC (based on the fact that at the Auger profiling, the DLC layer of 500 nm thickness could not be milled through in 160 min), and certainly it cannot reach NdFeB in the case of continuous coating.

Reaction of fluorine with diamond was investigated in [23]. It was shown that fluor chemisorbs on diamond surface and forms a very stable and inert C–F surface layer. In DLC, which is a more disordered material, gas can penetrate deeper.

The slow rate of Ar ion milling (less than 3 nm/min) is another proof of high strength of the DLC coating, thus suggesting its usefulness in ion-plasma devices.

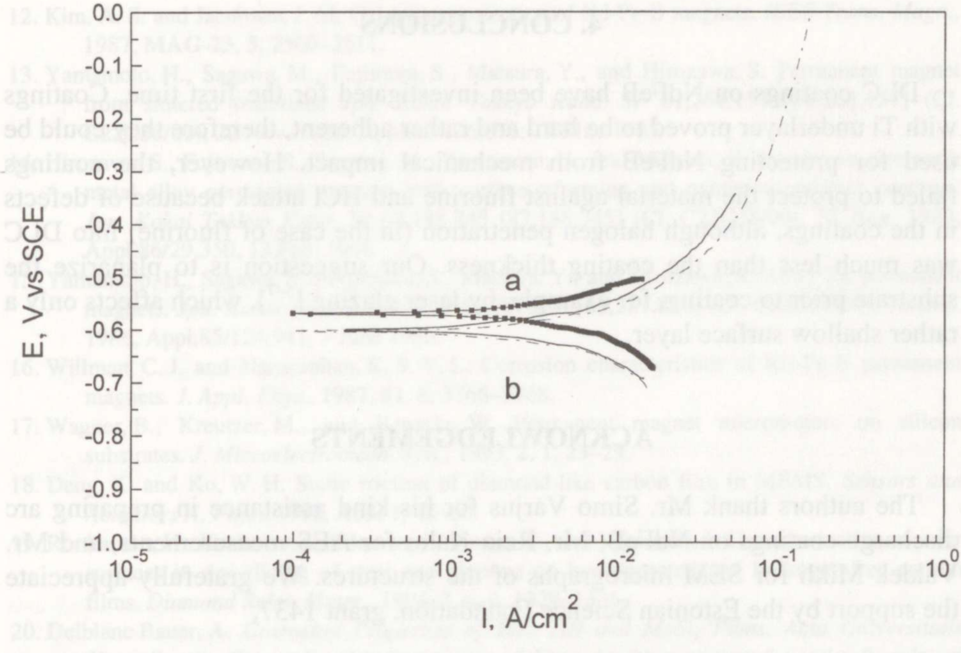

Fig. 4. Potentiodynamic polarization curves of bare NdFeB (a); diamond-like carbon-coated NdFeB (b). Electrolyte – 0.1 M HCl; scanning rate – 1 mV/s; reference electrode – saturated calomel electrode; counter electrode – platinum.

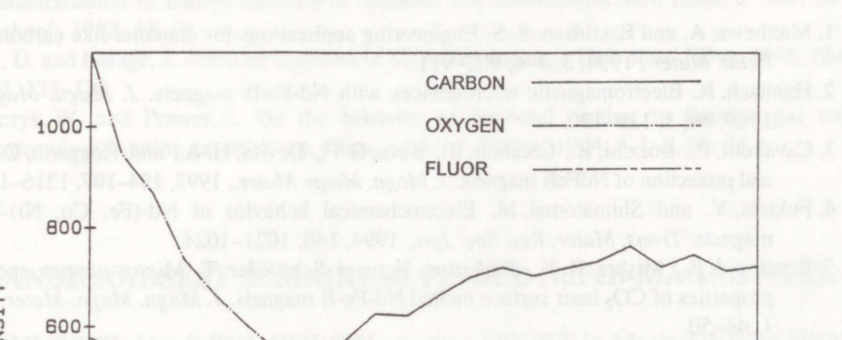

Fig. 5. Auger electron spectroscopy profiles of major elements in the diamond-like carbon coating, exposed to 5% fluorine for a week. Ar^+ ion energy – 3 kV, spot size – 10 μm, ion current – 0.4 mA.

4. CONCLUSIONS

DLC coatings on NdFeB have been investigated for the first time. Coatings with Ti underlayer proved to be hard and rather adherent, therefore they could be used for protecting NdFeB from mechanical impact. However, the coatings failed to protect the material against fluorine and HCl attack because of defects in the coatings, although halogen penetration (in the case of fluorine) into DLC was much less than the coating thickness. Our suggestion is to planarize the substrate prior to coating, for example, by laser glazing [5–7], which affects only a rather shallow surface layer.

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TEEMANDILAADSEST SÜSINIKUST PINDED NdFeB-MAGNETITEL

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On uuritud teemandilaadsest süsinikust pinnete suutlikkust kaitsta NdFeB magnetmaterjali korrosiooni ja mehaaniliste mõjutuste eest. Keemilise aursadestusega või lasersadestusega valmistatud pinnete kaitseomadusi HCl ja F_2 vastu on vaadeldud mikroskoopia, potentsiodünaamilise polaromeetria ja Auger' elektronide spektromeetria meetodil. Osutus, et pinded takistasid halogeeni sissetungi, kuid ei kaitsnud magnetit pinde defektide tõttu. Pinnete nake alusega oli titaanvahekihi kasutamise puhul hea.