ANTI-CORROSION CERAMIC COATINGS ON THE SURFACE OF Nd-Fe-B REPELLING MAGNETS

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The results of vacuum-arc deposition of thin ZrO_2 coatings to protect the surface of Nd-Fe-B permanent magnets used as repelling devices in orthodontics are presented. The structure, phase composition and mechanical properties of zirconium dioxide films have been investigated by means of SEM, XRD, EDX, XRF, and nanoindentation method. It was revealed the formation of polycrystalline ZrO_2 films of monoclinic modification with average grain size 25 nm. The influence of the ZrO_2 coating in terms of its barrier properties for corrosion in quasi-physiological 0.9 NaCl solution has been studied. Electrochemical measurements indicated good barrier properties of the coating on specimens in the physiological solution environment.

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INTRODUCTION

Hard magnetic alloys (permanent magnets) are used as components in a wide range of industrial applications, in regulating and measuring controls and in medical equipment. Neodymium iron boron (Nd-Fe-B) or "neo" magnets offer the highest energy product of any material today and are available in a wide range of shapes, sizes and grades. However, the neo magnets have some limitations due to their corrosive behavior. Thus, for medical applications, a protective coating is highly recommended. In this case, zirconium dioxide in the form of thin buffer layer on magnet surface is a promising candidate, due to its biological inertness and corrosion resistance.

Nd-Fe-B magnets are frequently used as repelling devices for orthodontics and are advantageous over other materials used to move teeth, such as push-coil or elastic chain [1]. Nd-Fe-B magnetic devices are offered as optimum and biologically safe force-generating system. Neo magnets possess continuous force over extended periods of time for various kinds of tooth movement, and have no friction. Disadvantages of their application are corrosion products which are toxic.

Zirconium dioxide ZrO_2 ceramics possesses high resistance to crack propagation, high fracture toughness, high thermal expansion coefficient ($\alpha=11x10^{-6}$/K, similar to some types of steel) and due to these properties, it is very much suitable for joining ceramic and steel. It possesses also excellent thermal insulation/low thermal conductivity (2.5 to 3 W/mK) [2].

Various deposition methods, namely thermal oxidation of zirconium films, electron beam evaporation, pulsed laser deposition, DC/RF magnetron sputtering, sol-gel process and spray pyrolysis were employed for preparation of ZrO_2 thin films [3-8]. Physical vapor deposition (PVD) methods of coating application including vacuum arc evaporation in a reactive medium (oxygen, nitrogen) are widely used to obtain ceramic coatings with a high melting point [9-12].

In our experiments, thin ZrO_2 coatings were deposited using vacuum-arc evaporation with curvilinear filter for decreasing macroparticles (MPs) emitted from plasma flow in Bulat-type device. The structure, chemical and phase composition of the obtained ZrO_2 coatings have been investigated. Corrosion experiments were carried out in physiological 0.9 % NaCl solution.

1. EXPERIMENTAL SETUP

The ZrO_2 coatings on Nd-Fe-B magnets were obtained in "Bulat" type device by condensing vacuum-arc plasma purified from macro-particulates by means of the curvilinear filter [13]. The general view of the magnets is shown in Fig. 1.

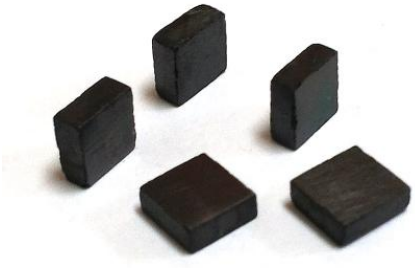


Fig.1. General view of the Nd-Fe-B magnets

The scheme of experimental equipment is shown in Fig. 2. The magnets 5×5×2 mm size were fixed in the holder that squeezed its opposite sides with a small effort. Chemically pure zirconium (99.999) was used as a cathode material. The chamber was preliminary pumped out to a pressure of 6×10^{-5} Torr. The pulsed negative bias of 1000 V with frequency 50 kHz was applied to the sample holder from the source PS-2. The rotation of the holder was turned on, vacuum arc was ignited (I_d = 115 A) and the four faces of the magnets were cleaned by zirconium ions in the pulsed mode: cleaning of 1.5 s and pause of 6 s; in total 15 cycles.

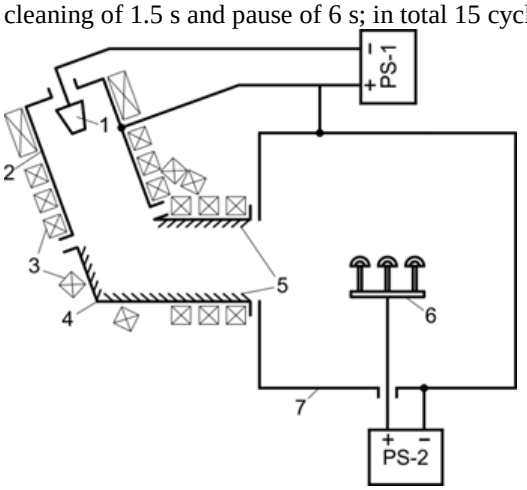


Fig. 2. Scheme of experimental equipment: 1 – cathode; 2 – anode; 3 – electromagnetic coils; 4 – duct; 5 – baffles; 6 – samples; 7 – vacuum chamber; PS-1 – arc discharge power supply unit; PS-2 – source of pulsed negative bias

Then the source PS-2 was turned off, the chamber was filled with oxygen to a pressure of about 4×10^{-3} Torr and zirconium dioxide was deposited during 12 min. Then the vacuum chamber was opened, the magnets were installed in the other position and ZrO_2 was deposited on uncoated faces for 7 min.

The surface topography of ZrO_2 was studied using JEOL JSM-6390LV scanning electron microscope (SEM) with an accelerating voltage of 20 kV, chemical composition was examined using energy-dispersive X-ray analysis (EDX).

Energy-dispersive spectrometer SPRUT-K (AO Ukrrentgen, Ukraine) was used for X-ray fluorescent analysis and was equipped with Si (Li) X-100 detector (Amptek, USA) in the arrangement with Si and KCl secondary target. Film thickness was determined by XRF examinations and comprised ~3 μm.

X-ray diffraction (XRD) analysis were performed using DRON-3M device, under Cu–Kα radiation, monohromated by (002) HOPG in diffracted beam. The XRD line scans were performed in θ…2θ scanning mode where the incident angle θ and diffracted angle 2θ are scanned simultaneously.

The nanohardness was measured by Nanoindenter G200 (USA). The loading and unloading rates of the nanoindentation were 10 mN/min. Samples were tested to a depth of 500 nm. 6 prints were made for each sample and the distance between prints were 15 μm.

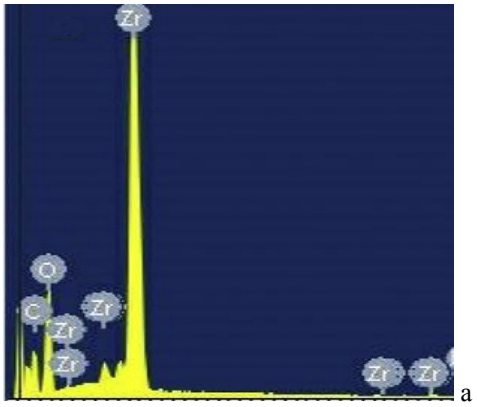
ZrO_2 films have also been analyzed for their corrosion properties in 0.9 % NaCl quasi-physiological solution.

2. RESULTS AND DISCUSSION

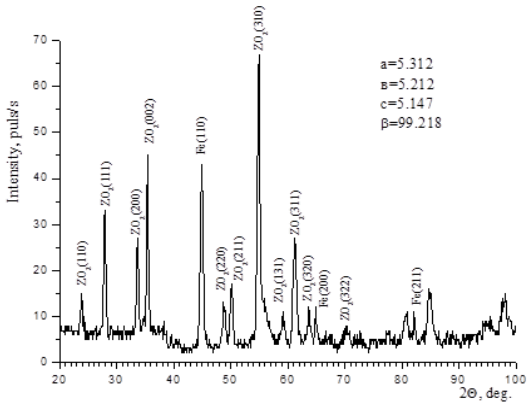
2.1. COMPOSITION AND STRUCTURE

Energy dispersive X-ray analysis (EDX) and X-ray diffraction analysis (XRD) were used to determine the chemical and phase composition of the deposited films. EDX spectrum of the as-deposited ZrO_2 films formed at oxygen partial pressure of 4.5×10^{-3} Torr is shown in Fig. 3,a.

The EDX spectrum consisted of the characteristic zirconium and oxygen peaks without presence of any other impurity peaks. The chemical content was Zr = 30.46 at. % and O = 69.54 at. % (Tabl. 1). It indicates that the deposited films were stoichiometric. There was no variation of the chemical composition in the films volume.



a



b

Fig. 3. EDX spectrum (a) and XRD pattern from Zr-O film (b)

Table 1

EDX chemical composition of Zr-O film

Element	Intensity	wt. %	at. %
O	0.6336	28.59	69.54
Zr	0.9100	71.41	30.46

The main diffraction peaks at 26.7°, 50°, 56.9°, and 61.5° related to the (111), (211), (310) and (311) reflects of monoclinic phase of ZrO_2 was monitored in XRD pattern (Fig. 3,b). The film is crystalline and exists in the single monoclinic ZrO_2 phase according to JCPDF (file 37-1484) with lattice parameters *a* = 5.312; *b* = 5.212; *c* = 5.147.

These results correlated well with the literature data which indicate that at low temperatures the most stable ZrO_2 phase is monoclinic form, which occurs naturally as the Baddeleyite mineral [14]. At the temperature 1478 K and ambient pressure the tetragonal structure becomes thermodynamically stable. At 2650 K the tetragonal structure changes into the cubic calcium fluoride structure.

The crystallite size of the deposited ZrO_2 coatings was calculated from the full width at half maximum intensity (β) (FWHM) of the X-ray diffraction angle (θ) of the (111) peak and the wavelength (λ) of copper X-ray radiation using Debye-Scherrer's relation [15], by taking into consideration that no strains were developed in the coatings:

$$D = K\lambda/\beta\cos\theta, \quad (1)$$

where K is a constant (K = 0.9 for copper X-ray radiation) and θ – the diffraction angle. Crystallite size of the zirconium oxide film was 25 nm.

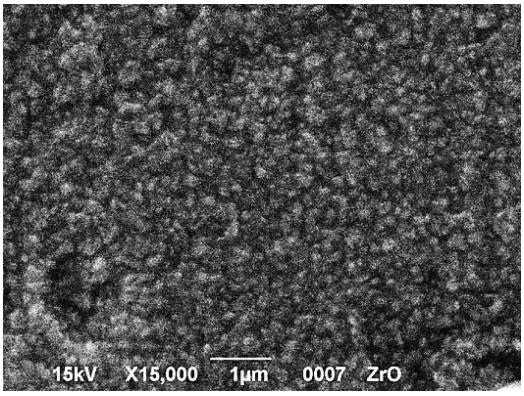


Fig. 4. SEM image of ZrO_2 coating

The surface morphology of deposited ZrO_2 thin film was investigated using scanning electron microscopy. Fig. 4 demonstrates homogeneous and crack free surface of ZrO_2 film.

2.2. MECHANICAL PROPERTIES

Plasticity index H/E and the ratio H^3/E^{*2} (where $E^* = E/(1 - \mu^2)$ – the effective elastic modulus; μ – Poisson's ratio) are qualitative comparative characteristics of material plastic deformation resistance. The shear modulus (G) and yield stress (σ_T) are defined as:
$G = E/2 \times (1 + \mu)$ and $\sigma_T = H\mu / 3$.

Table 2

Results of ZrO_2 coating mechanical tests

	E, GPa	H, GPa	H/E	H^3/E^{*2}	G, GPa	σ_T, GPa
1	210.32	13.488	0.064	0.049	131.45	4.49
2	204.754	13.785	0.067	0.055	127.97	4.59
3	208.546	12.979	0.062	0.044	130.34	4.32
4	202.983	12.816	0.063	0.045	126.86	4.27
5	213.961	13.56	0.063	0.048	133.73	4.52
6	197.203	12.573	0.064	0.045	123.25	4.19
	206.295	**13.2**	**0.064**	**0.048**	**128.93**	**4.40**

The results of H and E values for 6 prints, as well as G, σ_T, and H^3/E^{*2} parameters, are summarized in Tabl. 2.

According to nanohardness tests, the average value of nanohardness for ZrO_2 was 13.2 GPa, and the average value of elastic modulus was 206.295 GPa.

2.3. CORROSION PROPERTIES

Uncoated Nd-Fe-B magnet showed an electrode potential E of – 0.7 V. The coating of the zirconium dioxide leads to significant passivation of the magnet surface. The formed film possesses a high degree of continuity even on the edges. It also lacked pores, which could be easily detectable by electrochemical testing. Electrode potentials of Nd-Fe-B magnet in initial state and Nd-Fe-B magnet with ZrO_2 coating are presented in Fig. 5.

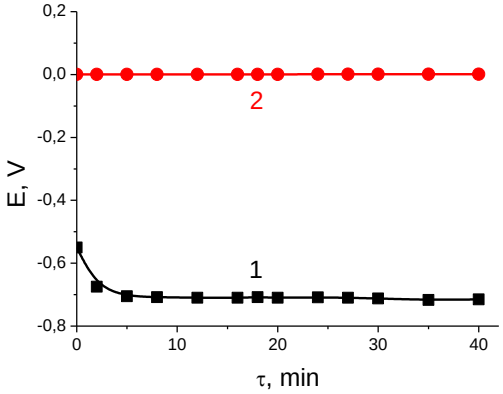


Fig. 5. Electrode potentials of Nd-Fe-B magnet in initial state (1) and Nd-Fe-B magnet with ZrO_2 coating (2)

CONCLUSIONS

Monoclinic m-ZrO_2 thin films have been synthesized on the surface of Nd-Fe-B magnets using vacuum-arc deposition with curvilinear filter in the presence of oxygen plasma in the "Bulat"-type device.

SEM investigations revealed the formation of uniform and crack-free structure of the film. XRD data revealed the formation of fine-crystalline structured films with average grain size of ~25 nm.

Corrosion experiments carried out in physiological 0.9 % NaCl solution showed significant passivation of the surface of the magnet with *E* turned into positive values. This indicates an increase of substrate resistance against electrochemical corrosion.

The proposed technology can be useful for applying buffer ZrO_2 coatings on Nd-Fe-B magnets used as repelling devices in orthodontics.

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АНТИКОРРОЗИОННЫЕ КЕРАМИЧЕСКИЕ ПОКРЫТИЯ НА ПОВЕРХНОСТИ СТЯГИВАЮЩИХ МАГНИТОВ Nd-Fe-B

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Представлены результаты вакуумно-дугового осаждения тонких покрытий ZrO_2 для защиты поверхности постоянных магнитов Nd-Fe-B, используемых в качестве стягивающих устройств в ортодонтии. Структура, фазовый состав и механические свойства пленок двуокиси циркония были исследованы методами SEM, XRD, EDX, XRF, наноиндентирования. Было обнаружено образование поликристаллических пленок ZrO_2 моноклинной модификации со средним размером зерна 25 нм. Изучено влияние покрытия ZrO_2 в качестве барьера для защиты магнитов от коррозии в квазифизиологическом растворе 0,9 NaCl. Электрохимические измерения показали хорошие барьерные свойства покрытия на образцах в среде физиологического раствора.

АНТИКОРОЗІЙНІ КЕРАМІЧНІ ПОКРИТТЯ НА ПОВЕРХНІ СТЯГУВАЛЬНИХ МАГНІТІВ Nd-Fe-B

А.В. Таран, І.Є. Гаркуша, В.С. Таран, О.І. Тимошенко, І.О. Місірук, Т.С. Скобло, С.П. Романюк, В.В. Стариков, О.А. Батурин, Г.П. Ніколайчук, М.В. Пивовар, Ю.П. Гніденко

Представлено результати вакуумно-дугового осадження тонких покриттів ZrO_2 для захисту поверхонь постійних магнітів Nd-Fe-B, що використовуються як стягувальні пристрої в ортодонтії. Структура, фазовий склад та механічні властивості плівки діоксиду цирконію були досліджені засобами SEM, XRD, EDX, XRF та наноіндентування. Було виявлено утворення полікристалічних плівок ZrO_2 моноклінної модифікації з середнім розміром зерна 25 нм. Вивчено вплив покриття ZrO_2 як бар'єру для захисту магнітів від корозії в квазіфізіологічному розчині 0,9 NaCl. Електрохімічні виміри встановили хороші бар'єрні властивості покриття на зразках у середовищі фізіологічного розчину.