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PVD Ti COATINGS ON Sm-Co MAGNETS

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The combination of conventional ion-plasma deposition (PVD) and pulsed plasma technologies (PPT) has been applied for rare-earth Sm-Co based magnets, to provide them with enhanced corrosion resistance. The influence of pulsed plasma treatment on Sm-Co magnets with deposited titanium PVD coatings has been investigated. It was revealed that thickness of modified layer significantly depends on the thickness of initial titanium film and plasma treatment regimes. As a result of plasma treatment with energy density of 30 J/cm^2 and pulse duration of ~ 5 μs fine-grained layer with the thickness of 70 microns has been formed on the Sm-Co magnet with pure titanium film of 50 micron. According to SEM analyses considerable diffusion of titanium to the bulk of the magnet, on the depth of 20 microns, took place. Such reaction enhances strong bonding between the coating and the magnet.

INTRODUCTION

Rare-earth magnets typically exhibit poor corrosion resistance to humid environments which severely limits their application. Unfortunately, until now, conventional coatings have been able to do very little to overcome the problem of poor corrosion resistance of rare-earth magnets, especially for long-term use [1]. Traditional metal or organic protective coatings, deposited by ion-plasma (PVD) or electrochemical methods on the surface of Nd-Fe-B and Sm-Co magnets, usually are in the highly stress state, which leads to the occurrence of cracks on the surface of the coatings and as a result insufficient corrosion resistance especially in the aggressive environments. The combination of conventional ion-plasma deposition and pulsed plasma technologies (PPT) can be a principally new way for obtaining wear and corrosion resistant modified surfaces [2-4]. Nd-Fe-B and Sm-Co magnets with previously deposited coatings can be reflown by powerful plasma streams up to 10…15 μm underneath the surface. Different pure metals as Ni, Ta, Ti and eutectic on their base can be used as initial pre-coatings [5]. At cooling rates of $10^6 \ldots 10^8$ K/s, the thin deposited films of eutectic compositions, with the thickness of 15 microns, will be in the amorphous state, which allow reaching a desirable corrosion tolerance and mechanical strength of coatings. Moreover, high-speed crystallization in the near-surface region, which cause the formation of finely dispersed structure, will define the high performance of near-surface layers [6].

EXPERIMENTAL SETUP

Experiments were carried out with pulsed plasma accelerator (PPA). The PPA device consists of coaxial set of electrodes with anode diameter 14 cm and cathode diameter 5 cm and vacuum chamber of 120 cm in length and 100 cm in diameter. The power supply system consists of condenser banks with stored energy of 60 kJ (for 35 kV). The amplitude of discharge current is < 400 kA, plasma stream duration is 3…6 μs. The pulsed plasma accelerator generates plasma streams with ion energy up to 2 keV, plasma density $2 \cdot 10^{14}$cm^{-3}, average specific power 10 MW/cm^2 and plasma energy density in the range of 5…40 J/cm^2. The nitrogen, helium, hydrogen and other gases can be used as working gases. The regime of plasma treatment was chosen with the variation of both accelerator discharge voltage and the distance of the surface from the PPA output [7].

PVD method (vacuum-arc ion-plasma deposition) was used for producing titanium coating. The regime of deposition includes the evacuation of vacuum chamber to the pressure not less than $3 \cdot 10^{-5}$ torr, ion-cleaning of the samples and finally deposition of the coatings. The thickness of the coatings was about 50 m.

The microstructure of treated surfaces and cross-sections of samples were examined by the optical microscope MMR-4 and scanning electron microscopy JEOL.

RESULTS AND DISCUSSION

One of the main requirements for the protective coatings, aimed to resist on corrosion, is the absence of pores. The pores can provide contact between aggressive environment and the surface of protected sample. Although the condensate which deposited from separated plasma stream under vacuum-arc ion-plasma deposition has low grain size (<1.5 μm), the number of open pores per unit area can reach critical level even for the coating with the thickness of 20 μm [8]. Moreover, such coatings have very non-equilibrium structure with the high tendency to aging. The brittleness of such coatings is increased during aging process which leads to the cracking of the coating and results in the deterioration of magnetic properties. All these drawbacks are expected to be overcome by the following treatment of the coatings with pulsed plasma streams. It should be noted that the thickness of preliminary coating and the regime of plasma treatment has to be accurately adjusted and controlled.

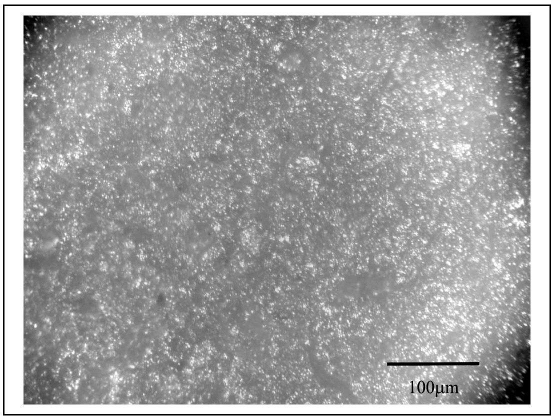

Fig .1 the surface of PVD Ti film on Sm-Co magnet

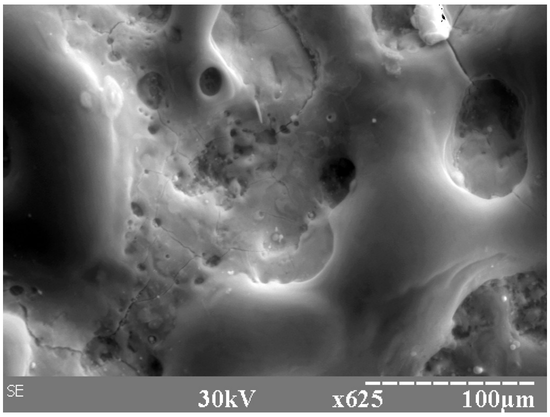

Fig. 2 SEM micrograph of Sm-Co magnet with titanium coating (50 microns) after helium plasma treatment at 28 J/cm^2 for 5 pulses

Fig. 3 The cross-section of Sm-Co manget with Ti coating (50 microns) after helium plasma treatment at 28 J/cm^2 for 5 pulses

Fig .1 shows the surface of PVD Ti film on Sm-Co magnet. Fig. 2 shows the surface of Sm-Co magnet with titanium coating (thickness of 50 microns) after helium plasma treatment. The melting of the titanium coating and the healing of open pores took place as a result of helium plasma treatment with energy density of 28 J/cm^2. Despite favorable healing of pores, the surface has a complex and non-homogeneous structure resembling streams of solidified metal. This shape of the surface can be evidence for the liquid state of the titanium coating under plasma treatment. Partial reflow of the Ti coating takes place on the flanks of the sample, but the area of thermal reflow is not uniform.

The cross-section of plasma treated Sm-Co magnet with the titanium coating is shown on Fig 3. It can be seen that as a result of the plasma treatment modified fine-grained layer with the thickness of 50…70 microns has been formed. The bulk part of the sample has typical structure of sintered Sm-Co magnet.

According to SEM analyses, the modified layer consists of pure titanium. It was observed that a considerable diffusion of titanium to the depth of 20 μm took place. Table shows the result of EDXF analysis of Sm-Co magnets with titanium coating after plasma treatment. The analysis was done on 20 μm beneath the Ti layer. A high concentration of titanium (33.1 at.%) has been observed in the transitional mixed layer. Whereas the content of samarium, copper and iron decreased (See Table), the concentration of cobalt increased significantly. This effect can be attributed to the high sputtering coefficients of Sm, Cu and Fe. Such a transition mixed layer can be formed as a result of two complex processes. Firstly, because of anomalous diffusion of Ti atoms stimulated by the ion bombardments of the sample surface before the deposition of the titanium film, for the surface cleaning. And secondly, due to complicated processes which take place during interaction between plasma and solid material. It seems that both process give contribution to the final composition shift.

Integral composition of Sm-Co magnet and magnet with the titanium coating (50 microns) after pulsed plasma treatment 28 J/cm^2 for 5 pulses

Element	Integral content of the bulk magnet (20 microns) under modified layer at. %	Bulk content of Sm-Co magnet, at. %
Sm	9.529	13.104
Co	37.955	56.081
Cu	2.948	6.690
Fe	16.437	22.021
Ti	33.130	-

The optimization of plasma treatment was carried out by adjusting both energy loads and the thickness of preliminary titanium film. It was revealed that the higher the energy loads of plasma treatment the higher the roughness of the modified surface. While the flanks of the sample underwent re-melting under high energy loads with energy density of 28 J/cm^2, the decrease of the energy density to 25 J/cm^2 was not favourable for the re-melting of the large area of the flanks. The surface of treated area became non-homogeneous.

The considerable decrease of energy loads to 20 J/cm^2 with simultaneous thinning of titanium film to 10 μm resulted in the delamination of the coating under the plasma treatment. Titanium layer became non-solid and partly covered the surface of the magnet. Besides, the grid of cracks appeared which can be result of non-equilibrium thermal process during high-speed cooling of the modified layer and due to the difference in thermal-expansion coefficient between treated layer and bulk.

CONCLUSIONS

Pulsed plasma treatment of Ti-coated Sm-Co magnets creates a porous and crack free protective coating on the surface. This Ti-rich layer can improve the bonding strength due to the penetration of the titanium into the porous Sm-Co magnet structure. According to SEM analysis considerable diffusion of titanium on the depth of 20 microns took place. However solidness of the protective titanium layer is significantly depends on the thickness of the initial Ti film and plasma loads.

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ІОННО-ПЛАЗМОВІ ЗАХИСНІ ТИТАНОВІ ПОКРИТТЯ НА МАГНІТАХ Sm-Co

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Традиційна технологія іонно-плазмового нанесення захисних покриттів та технологія імпульсної плазмової обробки було застосовано для покращення корозійної стійкості магнітів на базі сплаву Sm-Co. Досліджено вплив дії імпульсних плазмових потоків на магніти Sm-Co з попередньо нанесеною титановою плівкою. Встановлено, що товщина модифікованого шару значно залежить від товщини вихідної титанової плівки та режиму плазмової обробки. Після плазмової обробки магніту з попередньо нанесеною титановою плівкою (50 мкм) з густиною плазмового потоку 30 Дж/см^2 та довжиною імпульсу 5 мкс товщина модифікованого шару складала 70 мкм. За даними електронної мікроскопії було встановлено, що відбувалось суттєва дифузія титану у матеріал магніту на глибину до 20 мкм, що сприяло покращенню зчеплення між магнітом та покриттям.

ИОННО-ПЛАЗМЕННЫЕ ЗАЩИТНЫЕ ТИТАНОВЫЕ ПОКРЫТИЯ НА МАГНИТАХ Sm-Co

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Традиционная технология ионно-плазменного напыления защитных покрытий в сочетании с импульсной плазменной обработкой была использована для улучшения стойкости магнитов на базе сплава Sm-Co. Исследовано влияние импульсных плазменных потоков на магниты Sm-Co с предварительно нанесенным титановым покрытием. Установлено, что толщина модифицированного слоя значительно зависит от толщины исходного титанового покрытия и режима плазменной обработки. После обработки магнита с предварительно нанесенным титановым покрытием 50 мкм, высокоэнергетическими плазменными потоками с плотностью плазменного потока 30 Дж/см^2 и длительностью импульса 5 мкс толщина модифицированного слоя составляла 70 мкм. По данным электронной микроскопии было установлено, что происходила существенная диффузия титана в материал магнита на глубину до 20 мкм, что способствовало улучшению сцепления между магнитом и покрытием.