

Application of Plasma Electrolytic Oxidation for the Formation of Magnetoactive Oxide Laves

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Abstract

Using plasma electrolytic oxidation technique we obtained ferromagnetic coatings on titanium and alluminium. The measured coercive force, ~ 100 Oe at room temperature, is closer to the values corresponding to magnetically hard materials. The coatings are of interest as protective electromagnetic screens. The coatings were studied by XRD, XPS, XSA and SEM. There are crystallites of ~ 50 nm in size containing reduced and oxidized iron in the pores of the coatings. We consider that magnetic properties of the coatings are related with these crystallites.

Introduction

Anodic oxide films on aluminum formed by conventional techniques are used in the subsequent production of nanostructured magnetic materials [1]. For this purpose, first, an anodic film with preset pore sizes and wall thicknesses between them is obtained; then, a magnetoactive material, such as iron or nickel, is electrochemically deposited in pores. As Jin F.Y. with co-authors have recently shown, magnetoactive iron containing oxide coatings can be formed on an aluminum alloy by one stage Plasma Electrolytic Oxidation (PEO) in electrolyte with iron dispersed particles [2]. We investigated the formation of magnetoactive coatings on aluminum and titanium by PEO technique in colloidal electrolytes, containing oxycompounds of iron.

Experimental

The coatings were formed on planar specimens of technical VT1-0 titanium and aluminum AlMg5 alloy with a size of $2.2 \times 2.2 \times 0.1$ or $1.5 \times 0.5 \times 0.1$ cm. The compositions of both colloid electrolytes were based on phosphate-borate-tungstate solution and contained iron (III) oxalate: $\text{Na}_3\text{PO}_4 + \text{Na}_2\text{B}_4\text{O}_7 + \text{Na}_2\text{WO}_4 + \text{Fe}_2(\text{C}_2\text{O}_4)_3$. This electrolyte and the coatings formed in it are denoted as PBWFe. PBWFe-electrolyte was used for PEO treatment of titanium. Slurry electrolyte for PEO treatment of aluminum alloy additionally contained copper acetate $\text{Cu}(\text{CH}_3\text{COO})_2$. It was denoted as PBWFeCu. Each component was preliminarily dissolved in distilled water. Then, the solutions taken in the selected proportions were mixed and kept for no less than 1 h with stirring. As a result, precipitates of iron or iron and copper oxycompounds were formed in the PBWFe and PBWFeCu electrolytes.

Coatings on aluminum and titanium supports were formed at the anodic polarization at a mean current density of 10 A/dm^2 for 10 min. The current source was a computer-controlled unidirectional TER4-100/460N thyristor. The electrolyte solution was stirred with a magnetic agitator. The temperature of the solution did not exceed 30°C during the experiment. Specimens covered with PEO coatings were washed in tap and then distilled water and dried in air at 70°C .

The thickness of coatings was measured with a VT-201 vortex-current calibrator (Russia). The elemental composition and morphology of the surface were determined with a JXA 8100 X-ray spectral microanalyzer (Japan) supplemented with the INCA energy dispersive system (England) (method referred to below as XSA). The data obtained with the method were averaged over the surface analyzed, about $250 \mu\text{m}^2$. X-ray patterns of specimens covered with coatings were recorded with a D8 ADVANCE X-ray diffractometer (Germany) with $\text{CuK}\alpha$ radiation (XPA method). When carrying out X-ray phase analysis, the EVA search program with PDF-2 database was used.

The elemental composition of the produced coatings and the surface distribution of the elements were measured using energy-dispersive X-ray microanalysis (EDXA) with a Zeiss EVO50 raster electron microscope.

The magnetization of specimens was measured with a SQUID MPMS 7 magnetometer at temperatures of 300–2 K. The specimens were magnetized tangentially to the magnetic field direction at intensity of 1000 Oe. The temperature dependence of the magnetic moment was recorded with a step of 5 K in a range of 300–100 K, with a step of 2 K in the range of 100–10 K and a step of 1 K in the range of 10–2 K. Hysteresis loops were obtained at temperatures of 300 and 10 K. Magnetic measurements were also carried out with an automated vibration magnetometer. In this case the specimens were magnetized tangentially and normally to the magnetic field direction at intensity of up to 900 Oe. The temperature dependence of the magnetic moment was recorded with a step of 20 K in a range of 20–500 K. Temperature was changed uniformly for 80 min. Hysteresis loops and temperature dependences of the magnetic moment and residual magnetic moment of specimens were obtained.

Results

Amorphous coatings of thickness $33 \pm 2 \mu\text{m}$ were obtained on aluminum alloy in PBWFeCu-electrolyte. According XSA thickness- and area-averaged coating composition is following (at.%): 58.0 O, 2.2 Na, 5.8 Al, 9.3 P, 21.0 Fe, 2.3 Cu, 1.2 W. The coatings display ferromagnetic properties (Fig. 1). The value of coercive force ~ 100 Oe is close to the values corresponding to the magnetically hard materials [3]. The temperature dependence of the remnant magnetic moment indicates a ferromagnetic order in the oxidized surface layer.

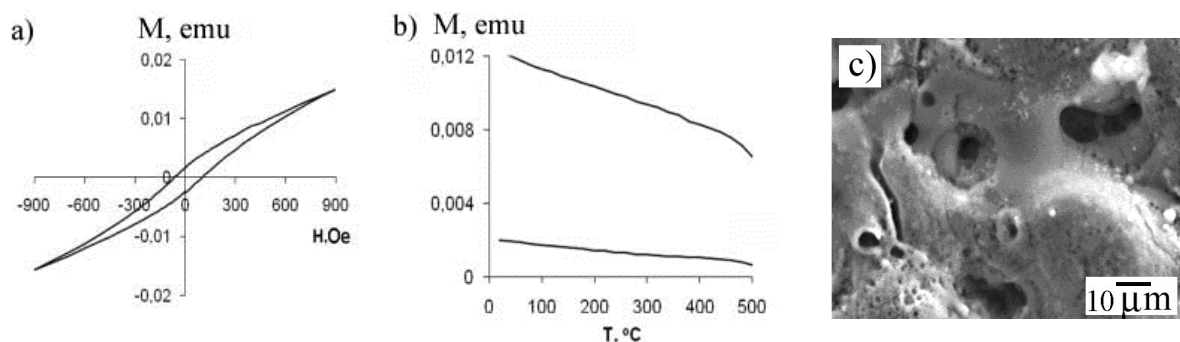


Fig. 1. a) Hysteresis loops at room temperature.
 b) Temperature dependencies of magnetic moments.
 c) SEM-images of PBWFeCu coating on aluminum alloy.

Magnetization curves recorded for titanium specimen obtained in PBWFe-electrolyte have a similar shape (Fig. 2) almost independent of the magnetic field orientation (normally or tangentially to specimen surfaces). The value of coercive force ~ 114 Oe is close to one determined for the Fe-containing coating on aluminum alloy.

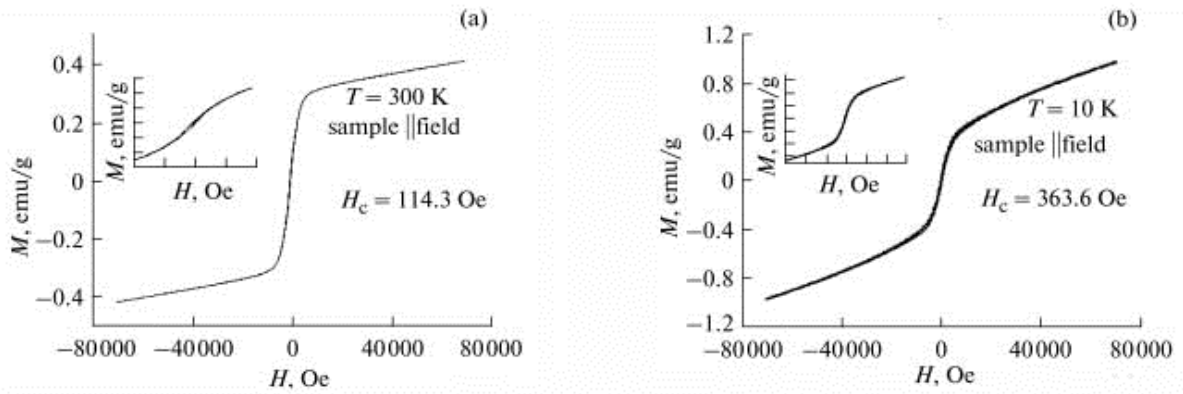


Fig. 2. Magnetic characteristics of PBWFe coated titanium specimen: (a, b) magnetization curves at (a) room temperature and (b) 10 K.

The thickness of the coatings formed on titanium is $17 \pm 1 \mu\text{m}$, elemental composition, at. %: 11.3 C, 67.2 O, 1.3 Na, 6.5 P, 5.4 Ti, 7.2 Fe, 1.0 W. The surfaces of coatings have complex heterogeneous structures (Fig. 3). There are structure elements typical for the layers formed by PEO method, i.e., pores surrounded with swells (black in the images), volcano-shaped protuberances around pores, structured valleys, dispersed particles (microgranules), cracks where the dispersed particles are concentrated, etc. As follows from the data of Fig. 4 iron is definitely concentrated in pores and structured valleys pierced with a large number of small pores. At the same time, the iron content at the slopes of volcano-shaped protuberances around pores is noticeably lower. Meanwhile, the inverse regularity is typical of the distribution of oxygen.

The elemental compositions of the bottom and walls of pores, as well as some sites at protuberances and at a midlevel between protuberances and hollows, were determined using a probing beam focused on a spot with a diameter of about $1 \mu\text{m}$ (Fig. 5).

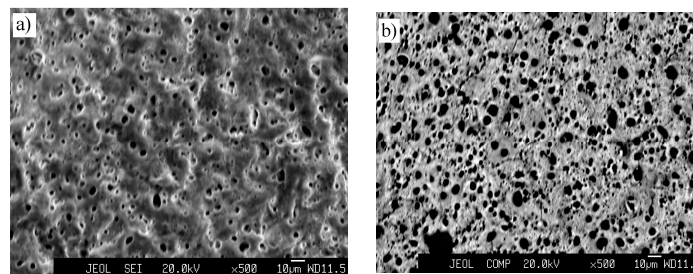


Fig. 3. SEM images of PBWFe surface: amplitude (a) and phase (b) representations.

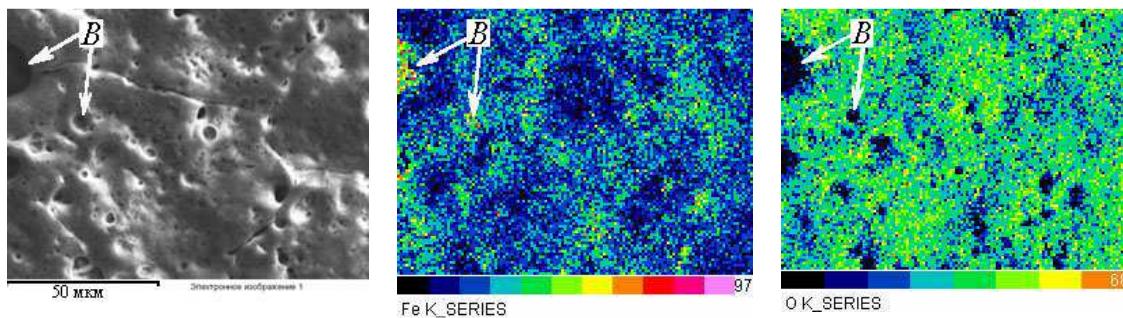


Fig. 4. Distribution maps of some elements over surfaces PBWFe-coatings on titanium. Arrows (B) show pores.

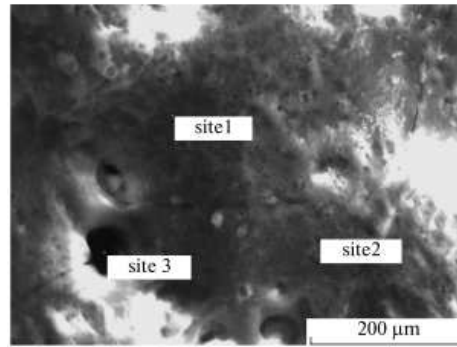


Fig. 5. Analysis of elemental composition of some surface sites of coatings at probing beam area of 1 μm : (1) mean surface level; (2) protuberance; and (3) pore.

As follows from the data of Table 1, the compositions of individual surface structures noticeably differ. Iron and titanium are concentrated in pores (at the bottom and walls). In the case of PBWFe coatings, oxygen is not found in pores; therefore, iron and titanium are probably present in reduced forms. It is possible that the reduced iron contained in pores determines the ferromagnetic properties of the coatings.

The resulting data (Fig. 4, Fig. 5 and Table 1) concerning increased concentration of iron in the pores are confirmed by specimens research with help of high-resolution electron microscopy and microprobe analysis. As shown in Fig. 6, conglomerates of crystallites, which consist of separated crystal-like formations of ~ 50 nm in size, are located in the pores.

Table 1. Elemental composition of three typical surface sites (Fig. 5): (1) mean surface level; (2) protuberance; and (3) pore.

Surface sites	Elemental composition [at. %]							
	O	Na	V	Ti	P	Fe	B	W
1	47.8	5.1	-	0.7	8.2	14.7	22.3	0.9
2	72.7	3.6	-	8.3	7.7	6.6	-	1.2
3	-	-	2.7	55.6	1.4	40.1	-	0.2

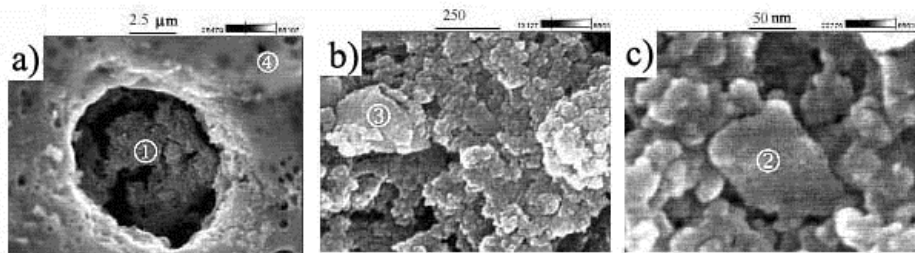


Fig. 6. Crystallite conglomerates in the pores.

The elemental composition of conglomerates and crystallites is following: 19.2 O, 7.2 C, 1.7 Na, 2.2 P, 13.5 Ti, 51.0 Fe, 5.2 W. Since oxygen content is not enough for oxide formation, so metals in the crystallites seem to be in reduced oxidation level primary or partially. As established in the paper, iron is in the crystallites of a typical size ~ 50 nm, which are associated into conglomerates. As to resulting data the crystallites have a multiphase composition. It seems that they contain both reduced metals and metal oxides.

Conclusions

Thus, the plasma electrolytic oxidation in colloid electrolytes allows one to obtain on aluminum and titanium Fe-containing coatings having ferromagnetic properties. In accordance with experimental results ferromagnetic properties of the coatings are determined by microcrystals of reduced iron, concentrated in pores of the coatings.

References

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