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Structure and magnetic properties of Fe-, Co-enriched composite titania coatings

M.V. Adigamova*, I.V. Lukiyanchuk, V.P. Morozova, I.A. Tkachenko
Institute of Chemistry, Far Eastern Branch, Russian Academy of Sciences, Vladivostok, Russia
*e-mail: adigamova@ich.dvo.ru

The "ferromagnetic oxide coating/metal" composites can find application in designs of absorbers of electromagnetic radiation, separators, catalysts, and microtransformers. Recently, a direction has been developed associated with the formation of such composites by the **plasma electrolytic oxidation** (PEO) technique, using electrolytes containing colloidal particles of iron, cobalt, or nickel hydroxides [1, 2]. During PEO treatment, electrolyte components are incorporated into the M_xO_y layer growing on the substrate metal. In this case, the metals from the electrolyte are distributed unevenly over the coating surface, concentrated in defective areas of the surface, including pores and cracks. In the pores, metals are concentrated in the composition of crystallites, which, apparently, are metal particles surrounded by oxide-hydroxide shell. The experimental data previously obtained for such systems suggest that it is the crystallites that make the main contribution to the magnetic characteristics of the formed composites. In this work, Fe+Co/TiO_2/Ti composites have been formed, and their magnetic characteristics have been studied in relation to their composition and structure, including those at the microlevel.

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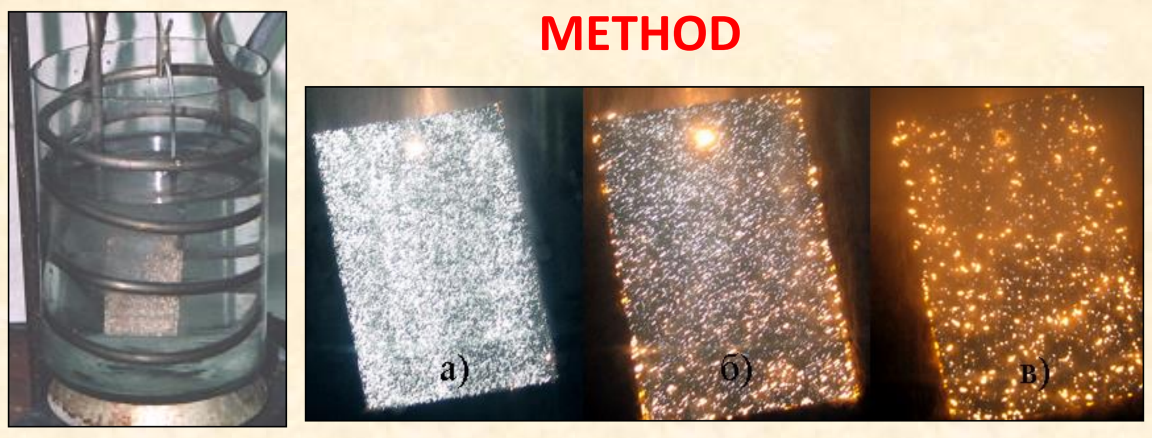
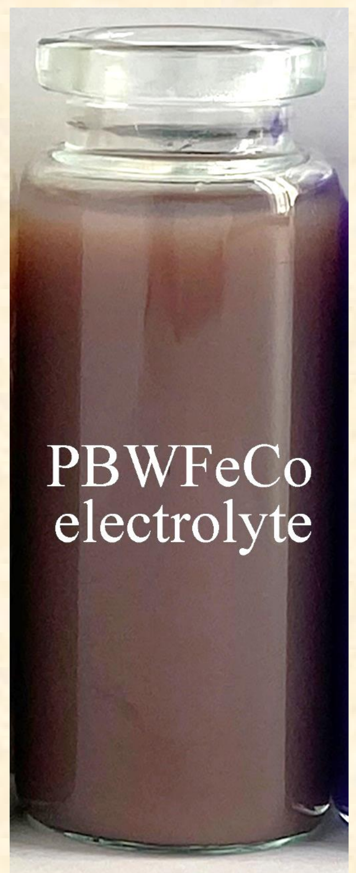
METHOD



Plasma electrolytic oxidation comprising anodic or alternating current anode–cathode electrochemical oxidation of metal and alloy surface by spark and arc electric discharges in the near–anode area allows obtaining porous oxide layers of a thickness from a few up to dozens of microns with inclusions of compounds originating from the electrolyte.

EXPERIMENT

Fe+Co-containing oxide PEO coatings with a thickness of 28 μm were formed at the constant effective current density i=0.1 A/cm^2 for 5 min on VT1-0 titanium sample (wt. %: 0.7 Al, 0.25 Fe, 0.10 Si, 0.07 C, 0.04 N, 0.2 O, 0.01 H; other impurity – 0.30 and Ti-balance)) in the aqueous alkaline PBWFeCo electrolyte containing (mol /L): 0.066 Na_3PO_4 + 0.034 $Na_2B_4O_7$ + 0.006 Na_2WO_4 + 0.015 $Fe_2(C_2O_4)_3$+0.04 $Co(CH_3COO)_2$.



COMPOSITES CHARACTERISATION

Surface images and data on the elemental composition, including individual surface components (crystallites in pores, pore bottoms and walls) were obtained using a Hitachi S5500 high-resolution scanning electron microscope (Japan) with a Thermo Scientific energy-dispersive analysis attachment (USA). Magnetic measurements were carried out on a SQUID MPMS 7 magnetometer (USA) at a temperature of 300 K. During the measurements, the samples were placed parallel to the direction of the magnetic field. When calculating the magnetization, the measured magnetic moment was normalized to the mass of the coated sample.

RESULTS

Fig. 1 presents electron microscopic images of the surface of the resulting coating on a titanium sample. The coating has developed heterogeneous surface with alternating elevations, depressions between the elevations, and numerous chaotically distributed pores (breakdown channels).

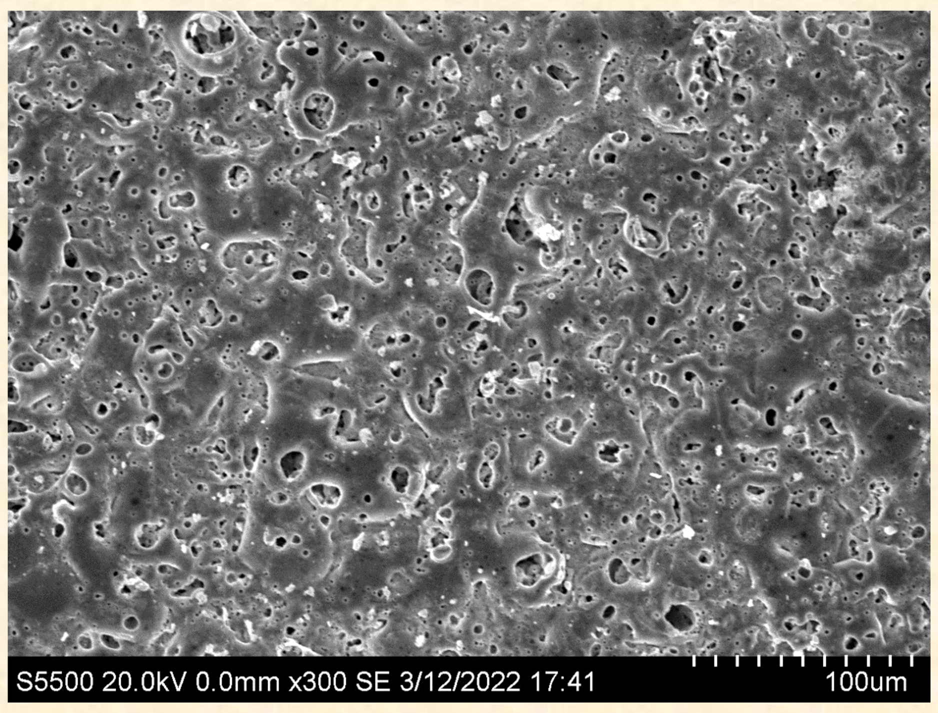


Fig. 1. SEM image of the surface of PEO coating on titanium.

During the PEO, iron and cobalt from the electrolyte are concentrated in pores in the composition of spherical formations with characteristic dimensions of ~70 nm, combined into agglomerates. Fig. 2 shows SEM image of crystallites in the pores PEO coating and elemental composition of dispersed particles.

The samples after PEO treatment have ferromagnetic properties with coercive force 179 Oe at 300 K.

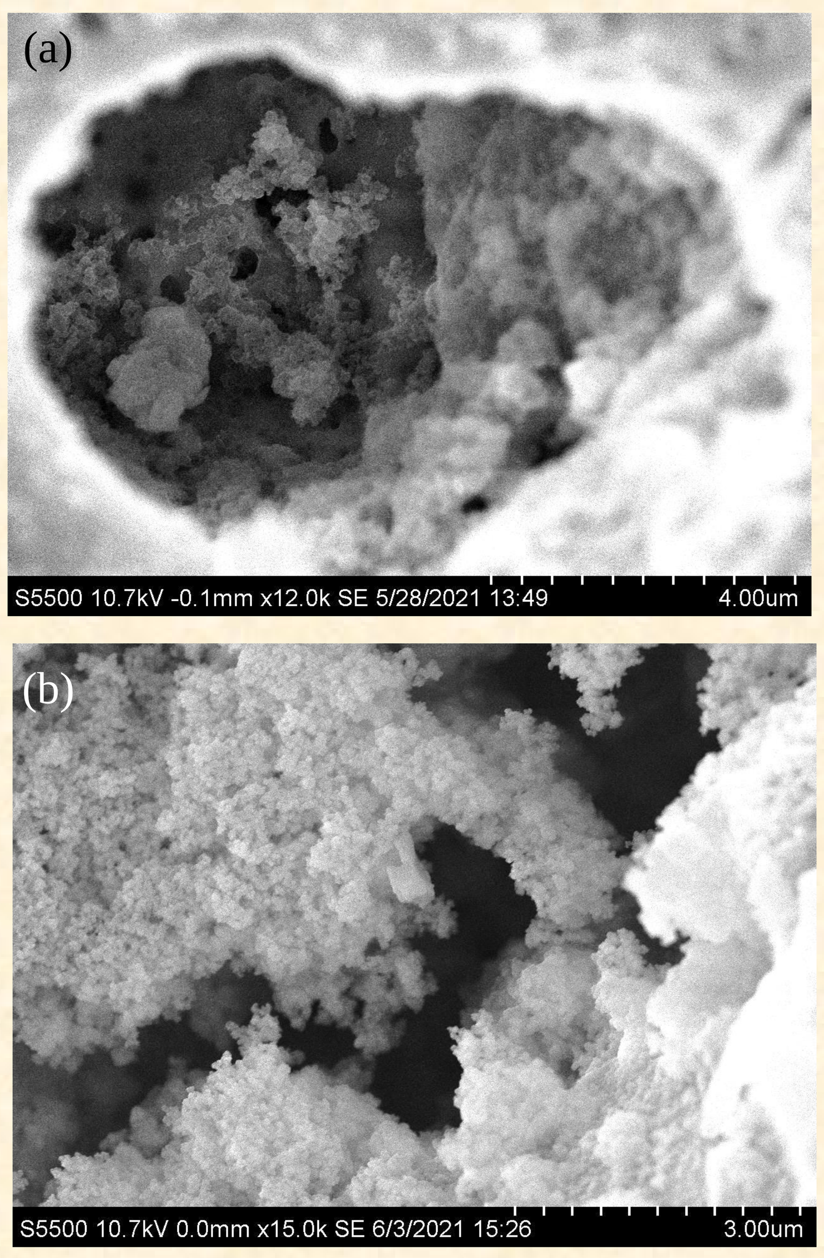


Fig. 2. SEM image of crystallites in the pore of the formed coating

The particles contain (at.%): 15.9 Fe, 25.7 Co, 37.1 Ti, 11.2 O, 7.8 P, 2.3 W, while the surface composition of the coatings is as follows (at.%): 22.9 C, 64.2 O, 4.6 Na, 4.4 P, 0.4 Fe, 2.3 Ti, and 1.2 Co. Elevated concentration of iron and cobalt and a lack of oxygen for the formation of their stoichiometric oxides may indicate the presence of reduced metals in the composition of crystallites localized at the bottom and walls of the pores. The crystallites apparently consist of a mixture of reduced Fe or Fe + Co metal cores, surrounded by oxide-hydroxide shell.

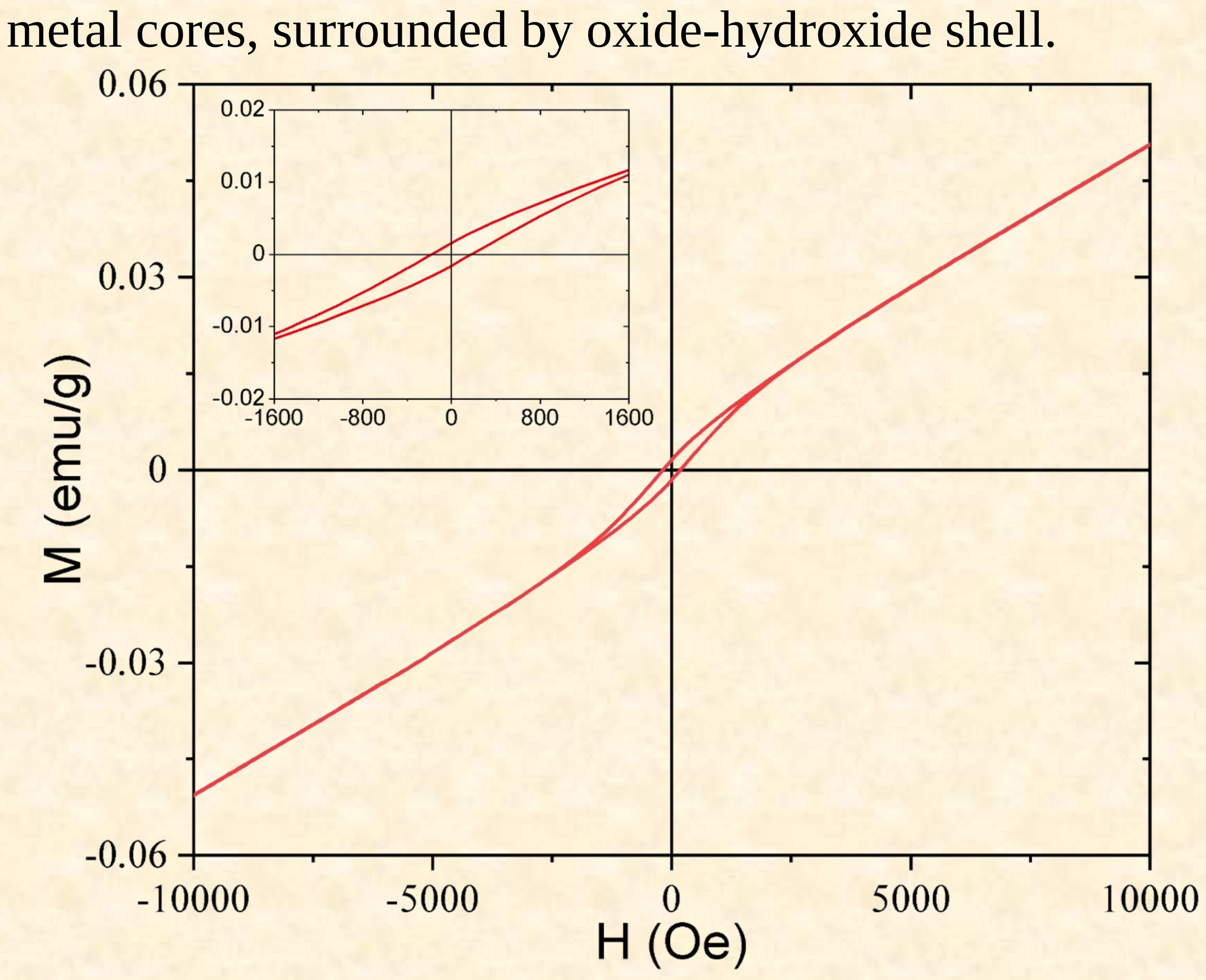


Fig. 3. The dependence of the magnetization on the strength of external magnetic field for PEO-coated sample.

CONCLUSIONS

Using plasma-electrolytic treatment of titanium in an electrolyte containing simultaneously colloidal particles of Fe(III) and Co(II) hydroxides makes it possible to form Fe+Co/TiO_2/Ti ferromagnetic composites.

The Co- and Fe-enriched crystallites in the pores of the coatings are apparently responsible for the ferromagnetism of the formed composites.

ACKNOWLEDGEMENTS

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