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Influence of magnetostatic interactions on magnetization process of iron-containing coatings, produced using the plasma electrolytic oxidation method

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Abstract. In this paper we research the process of magnetization of iron-containing coatings obtained on aluminum and titanium plasma electrolytic oxidation. It is shown that the formation of a remnant magnetic moment mainly determined by the magnetostatic interaction particles (phases). This interaction leads to a decrease of the blocking volume of particles (phases). Thus, a large number of superparamagnetic particles (phases) obtain stable magnetic moments and are involved in creating of the remnant magnetization of the sample.

Introduction

The method of plasma electrolytic oxidation (PEO) is very perspective for single-stage production of magnetically samples of the "oxide coating / Al or Ti» [1, 2]. In the case of Fe-containing coatings formed in the electrolytes that produce hydroxide slurry, the iron is concentrated in the pores of the sructure of nano-sized crystallites, which determine the magnetic properties of the coatings. In crystallites presented both reduced iron and other metals of the electrolyte and substrate, also as oxidized. The crystallite sizes and their magnetic characteristics can be changed by adjusting the pore sizes. Chemical composition of the crystallites can be modified by changing the composition of the electrolyte.

According to the results of calculated modeling [3, 4], and the experimental data [5] crystallites most likely are the particles of recovered metals or their oxides, encapsulated in oxide or hydroxide coating.

In the experiments, showed in papers [1, 2, 5], the specific value of remnant magnetic moment of the observed samples at temperature T = 300 K, obtained in a field H = 1000 Oe, had the order $M_r \sim 0.1$ emu / g. The volume and mass of magnetized samples are - $V \sim (10 \div 20) \times 10^{-3}$ cm^3 and $\mu \sim (3 \div 5) \times 10^{-2}$ g, respectively.

The particles, which are responsible for the remnant magnetic moment of the sample and consisting of iron oxides, are located in the pores of coatings. Therefore, their concentration volume η in the sample, approximately equal to the multiplication of the iron concentration and of the relative amount of the coating of a sample. If the coating thickness is about 2×10^{-3} cm and the concentration of iron ~ 0.1, the volume concentration is $\lambda \sim 0.002$.

Let us estimate the remnant magnetic moment of the M_r sample assuming that it is formed by stable chemically homogeneous single-domain particles with typical dimensions of the order of 5×10^{-6} cm [5]. According to calculations [3, 4], the average saturation magnetization of the sample M_s

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~ 10 ÷ 20 G. Then the specific value of remnant magnetic moment is $M_r = (\lambda \times M_s) \times (V / \mu) =$ (0.004 ÷ 0.02) emu / g. This value is one to two orders less then obtained experimentally.

It is likely that, the magnetic moment of a sample is mainly due to the large number of small particles, which according to their size should be superparamagnetic at a given temperature. However, these particles may be combined in clusters with a sufficiently high concentration of strongly magnetic material, or be a two-phase (heterophasic) formations. In both cases, the magnetostatic interaction will stabilize the magnetic moments of the particles or phases against thermal fluctuations. Thus, the magnetic moment of a sample might increase a lot.

Supercomputer simulations of cluster atomic and subatomic films of magnetic material on the nonmagnetic surface conducted in the work [7] confirmed the existence of the so-called percolation threshold (critical concentration of magnetic material) at which the system of superparamagnetic particles becomes ferromagnetic, i.e. appears a spontaneous magnetization.

Results and discussions

Let's observe particles (crystallites) which have volumes in avarage smaller than the critical volume of supermagnitism:

$$v_b = \frac{2kT_b}{M_s(T_b)H_0(T_b)} \cdot \ln(tf_0),$$

where M_s (T_b) and H_0 (T_b) – saturation magnetization and critical field of single-domain particle at blocking temperature T_b, respectively; t – measurement time, f_0 – the frequency factor.

Let these particles merged in clusters with high enough concentration of strongly magnetic material. Then, the magnetostatic interaction, by stabilizing the magnetic moments of the particles in relation to temperature fluctuations leads to a decrease of a blocking volume [6]:

$$v_b(\mathbf{H}_i) = \begin{cases} v_b \Big/ \left(1 + \dfrac{|\mathbf{H} + \mathbf{H}_i|}{H_0}\right)^2 & , \quad |\mathbf{H} + \mathbf{H}_i| \le H_0 \quad , \\ v_b \Big/ \left(\dfrac{4|\mathbf{H} + \mathbf{H}_i|}{H_0}\right) & , \quad |\mathbf{H} + \mathbf{H}_i| > H_0 \quad . \end{cases}$$

Here $\mathbf{H}$ – external magnetic field, and the random field of magnetostatic interaction for a cluster or a field adjacent phase $\mathbf{H}_i$, collinear $\mathbf{H}$.

After switching off the external magnetic field for a time greater than the relaxation time, but shorter than the measurement time, the system will come to thermal equilibrium. In this case, the average magnetic moment is determined by the formulas:

$$\overline{m} = \begin{cases} m(T)\mathbf{tanh}\left[\dfrac{vM_s(T)|\mathbf{H} + \mathbf{H}_i|}{kT}\right] & , \quad v \le v_b(\mathbf{H}_i) \quad , \\ m(T)\mathbf{tanh}\left[\dfrac{v_b(\mathbf{H}_i)M_s(T_b)|\mathbf{H} + \mathbf{H}_i|}{kT_b}\right] & , \quad v > v_b(\mathbf{H}_i) \quad . \end{cases}$$

Thus, the magnetostatic interaction can significantly reduce the amount of blocking volume, especially in low coercitive particles and increase their average magnetic moment. Consequently, the magnetization of dispersed in the amorphous coating clusters, which are the systems of interacting particles, or hetero-structures will be determined by the grains, for which the $v > v_b(\mathbf{H}_i)$

Let's observe weakly magnetic particle (phase), that has a stable magnetic moment, for example, goethite $M_s \sim 5$ G or hydrogoethite $M_s \sim 0.5$ G. Let the external field equals zero. This particle creates a field in the nearby small in volume strongly magnetic particle (phase), which has a zero average magnetic moment and stabilizes that moment for example, magnetite (magnetite) $M_s \sim 480$ G. This way, an increasing number of small volume strongly magnetic particles (phase) contribute to the magnetic moment of the whole sample. When the external field is switched on, a sufficiently large in magnitude, the remnant magnetic moment is being formed.

Even if the average saturation magnetization of the Ms sample is small, but the volume concentration η of the magnetic material in clusters is sufficiently large, the characteristic field of the magnetostatic interaction in the cluster $\sigma = M\,[(H_i - < H_i >)^2] \approx 1.3\,\eta^{1/2}\,M_s$ can be sufficiently large [6]. Let $\eta \sim 0.25$ and $M_s \sim 100 \div 500$ G, then $\sigma \sim 100 \div 300$ Oe. At $H_0 \sim 100$ Oe in zero magnetic field, we get $v_b(H_i) = v_b / (4 \div 12)$, i.e. in the process of magnetization a contribution to the remnant magnetic moment also will be made by those strong magnetic particles which volumes are much smaller than blocking volume.

Conclusions

As shown previously by the authors in works [1, 2], the residual magnetization of the samples obtained on aluminum or titanium plasma electrolytic oxidation is related to the presence of pores of these coatings chemically heterogeneous ferromagnetic particles.

Evaluations of the effect of magnetostatic interaction on magnetization process of iron-containing coatings, carried out in this paper, help us to make following conclusions. Most of these encapsulated or heterophase particles can be superparamagnetic at this temperature. But the low-magnetic particles (phase), which have a stable magnetic moment, generate fields of dipole-dipole interactions, which in their turn begin to affect neighboring strong magnetic particles (phase). This leads to the time-averaged non-zero magnetic moment of the strongly magnetic particles (phases). Thus, the particles (phase) are also included in the formation of residual magnetization.

Another confirmation of the correctness of these conclusions is the behavior of the magnetic moment of the studied samples when heated. Hydroxides are very sensitive to temperature rise. The magnetic moment of these particles (phases) can become unstable or even be destroyed by heat. So, we can expect sharp decrease or even stop its influence on the magnetic properties of other particles (phases). In this case, magnetic moment of the whole sample will decrease sharply. Exactly this behavior is observed while heating the listed samples [4].

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