Surface analysis of Fe-Co-Mo electrolytic coatings

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Abstract. Coatings Fe-Co-Mo with a composition of 47 at.% iron, 28 at.% Cobalt and 25 at.% Molybdenum were deposited from citrate electrolyte using pulse electrolysis mode. Scanning electron and atomic force microscopy have established the surface morphology and topography. It was identified the parts with a globular structure which have an average size of 0.2-0.5μm and singly located sharp grains. Within the same scan area sites with developed surface were detected the topography of which is identical to the crystal structure of cobalt with the crystallites size of 0.2–1.75μm. The parameters Ra and Rq for parts with different morphology as well as average characteristics of coatings demonstrated the low roughness of the surface. It is found that the coercive force of Fe-Co-Mo films is 7-10 Oe, which allow us to classify the Fe-Co-Mo coatings as soft magnetic materials.

1. Introduction

Surface of machine and mechanism parts in the operation primarily exposed for external factors influence that cause wear of friction parts, the emergence of fatigue cracking, crushing and at the end - corrosion destruction. One of the common surface protection methods is electroplating wherein coatings by binary and ternary alloys of iron subgroup metals with refractory components are of great practical interest [1-2]. Such coatings are distinguished due to combination therein functional properties that exceed the corresponding parameters for alloying metals [3]. The complex implementation in thin layers of wear and corrosion resistance [4], catalytic [5] and magnetic properties [6] combined with high microhardness makes such coatings universal and allows to significantly expanding their application area. It was shown prospects for usage of Co-Mo systems in the production of magnetic head elements for recording and reproducing information [6].

The functional properties of the coatings are structurally dependent therefore composition and surface morphology will predetermine the performance behavior of materials. The roughness and surface friction are the main characteristics of the coatings quality. Previously, it was shown [7] that binary and ternary coatings obtained in a pulsed mode are characterized by high microhardness and wear resistance due to their smooth surface. The roughness of electrolytic deposits can be significantly decreased using pulse mode. Since the surface structure of the electrolytic alloys causes the properties and application of coatings, study of their morphology and topography remains relevant. In spite of a sufficient number of works devoted to the binary alloy Fe (Co, Ni)-W (Mo) [8–10] matters concerning the topography and morphology of ternary coatings as well as their influence on the properties requires detailed study.

The aim of this work is to study the surface morphology and magnetic properties of Fe-Co-Mo ternary coatings.

2. Experiment

The Fe-Co-Mo coatings were deposited onto a mild steel substrate from citrate electrolyte containing, g/dm^3: $Na_3C_6H_5O_7 \times 2H_2O$ – 95–100; $Fe_2(SO_4)_3 \times 9H_2O$ – 30–45; $Na_2MoO_4 \times 2H_2O$ – 15–25; $CoSO_4 \times 7H_2O$ – 30–45; Na_2SO_4 – 15–45; H_3BO_3 – 6. Pretreatment of samples includes mechanical polishing, polishing, degreasing, chemical etching in a mixture of the 50 % nitric and 50 % sulfuric acids, thorough washing with distilled water and drying. Electroplating was performed by unipolar pulse current with an amplitude of 3–4 A/dm^2 in the working range of the pulse t_{on} 10–20 ms and pause duration t_{off} 10–50 ms. The ratio of the cathode to the anode area was 1 : 5, volume current density was kept at the level 2 A/dm^3. The thickness of the coatings is controlled by the deposition time and is 8–10 μm.

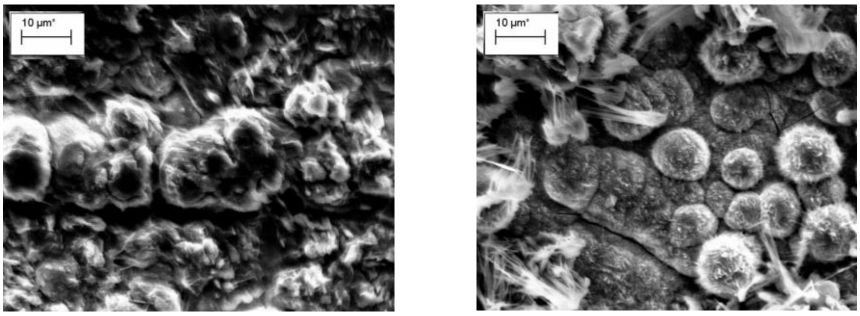
The chemical composition of the coatings was determined by X-ray fluorescence method using a portable spectrometer "SPRUT" with a relative standard deviation of 10^{-3}–10^{-2}. The error at determining the content of the components is ± 1 wt.%. To analyze the phase the energy-dispersive X-ray spectroscopy was performed using an electron probe micro analyzer Oxford INCA Energy 350 integrated into the SEM system.

The surface morphology of Fe-Co-Mo thin films was studied by an atomic force microscopy AFM using NT–206 microscope. The tapping mode was conducted to measure samples surface morphologies. Scanning was performed by using the contact probe CSC-37 with a cantilever lateral resolution of 3 nm [11]. And the scan sizes were fixed at 39.9×39.9 μm and 10.0×10.0 μm and the height of the surface relief was recorded at a resolution of 256×256 pixels. For each sample a variety of scans were obtained at random locations on the surface of Fe-Co-Mo thin films. In order to analysis the AFM images all image data were converted into Surface Explorer software. The root mean square (R_q), mean particle height and its distribution, surface skewness and particle diameter were determined [12].

Magnetic properties of Fe-Co-Mo coatings of thickness 8 μm were studied using a vibrating magnetometer with fields up to 20 kOe at room temperature. Accuracy of magnetic characteristics measurement is ± 2%. The coercive force H_c and the saturation field H_s were defined by hysteresis loops measured in the fields applied to the coating plane. The saturation magnetization I_s and the saturation induction B_s were estimated by hysteresis loops obtained for the magnetization of specimens by the film plane normal.

3. Results and discussion

The analysis of SEM images (Figure 1) shows the globular structure of Fe-Co-Mo coatings surface wherein agglomerates of larger size 2–5µm are formed from smaller spheroids of size 0.2-0.5µm. It was shown [1, 3, 7] that globular structure of the surface is caused by the refractory metals presence in the alloy. Such composition and character of the surface it was found to be favorable for increasing microhardness, corrosion resistance, and catalytic activity of the material [13-14].



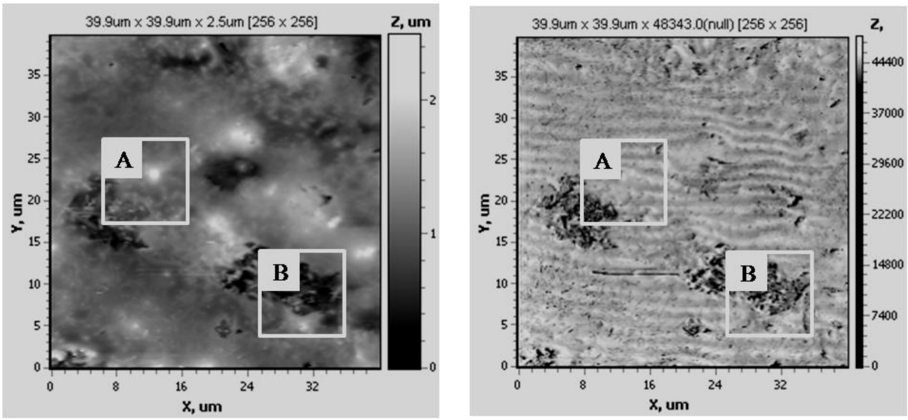
Coatings composition, at.%

Fe – 46.7; Co – 28.9; Mo – 24.4   Fe – 46.1; Co – 29.1; Mo – 24.8

a   *b*

Figure 1. SEM image and composition of Fe-Co-Mo coatings. Thickness 8 µm; pulse current density i, A/dm^2: a – 3; b – 4.

Topography maps of Fe-Co-Mo coatings reflect that their surface includes the parts A and B of different morphology as one can see from Figure 2. The torsion of measuring console and substantial changes in skin friction at these sites within the same scan area indicate non homogeneity of the material surface [12]. In this regard, the more detail study of the morphology of parts A and B is of great importance.

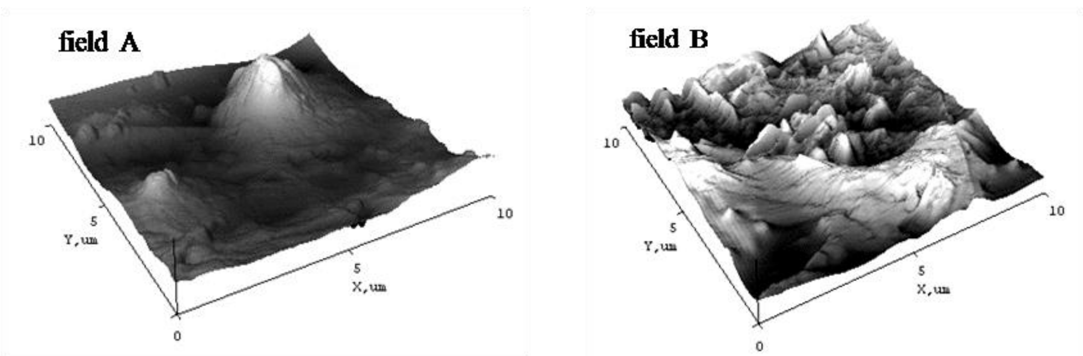


a b

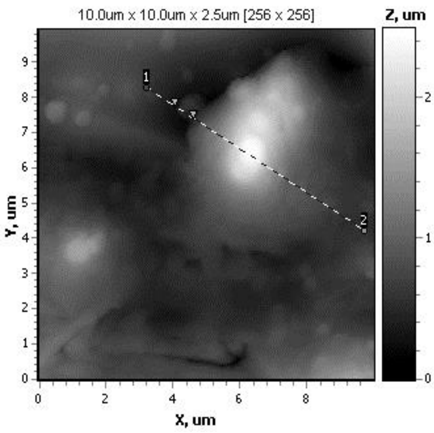
Figure 2. 2D-topography (a) and 2D-torsion (b) maps of the surface for Fe-Co-Mo coating deposited in pulse mode. Scan area AFM 39.9×39.9μm.

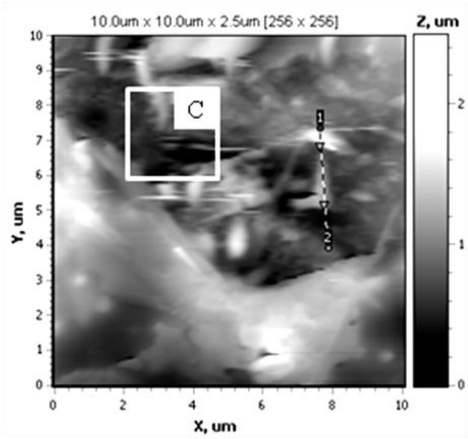
Figure 3 represents 3D- and 2D maps of the surface and cross section profile between markers 1 and 2 for different sites of coating Fe-Co-Mo. The part A differs by a surface consisting of spheroids (globules) 0.2–0.5 μm in size (Figure 3 *a*) and singly located cone-shaped hill with a base diameter of about 3 μm and height of 2.5 μm (Figure 3 *a*, *c*). As appears from 2D- and 3D- topography maps of the surface (Figure 3 *a, b*) the cone-shaped hills are formed of the smaller spheroids. The analysis of histogram of distribution the inclination angle to the surface normal of 17.5° indicates a predominance of spheroids on the surface (Figure 4*a*).

The part B is characterized by more developed surface compared with a part A (Figure 3 *d*). The morphology of the surface similar to pure cobalt [5] with sufficiently sharp hills alternating by valleys is visualized on the 2D- and 3D- maps of the site B (Figure 3 *d*, *f*). The cross section profile of coating between markers 1 and 2 allows determining the average size of agglomerates on the surface (Figure 3 c, g). This site B is characterized by a smaller difference in the size of the agglomerates of 0.5–1.75 μm and the heights of the hills and valleys of 0.5–0.7 μm. Histogram of distribution the inclination angle to the surface normal in this site demonstrates the uniform distribution of the sharp hills of different height (Figure 4*b*).

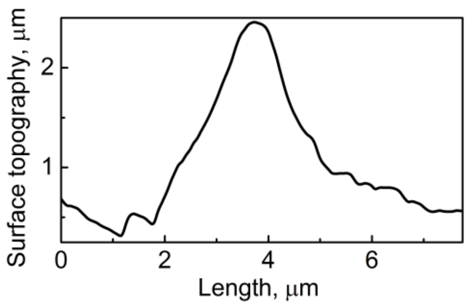


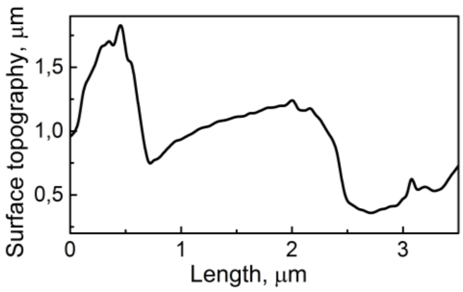
a d





b f

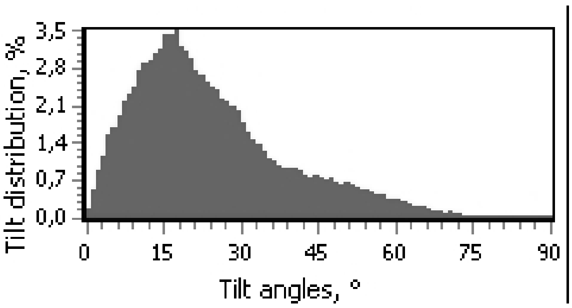


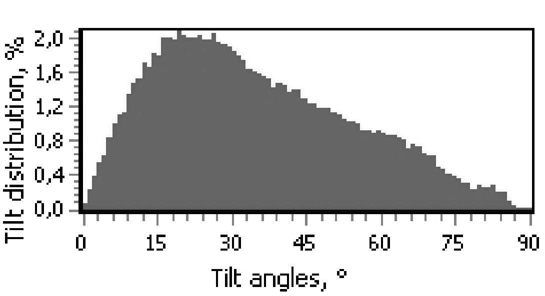


c g

Figure 4. 3D- and 2D maps of the surface and cross section profile between markers 1 and 2 for site A (a, b, c) and site B (d, f, g) of coating Fe-Co-Mo. Scan area AFM 10.0×10.0µm. Thickness is 8µm.

Micro pores (site C Figure 3*f*) are visualized at the coating surface in the area adjacent to the site B. Observed surface and volume heterogeneity causes anisotropy of the coating which is a prerequisite for the formation of different magnetic phases [6, 15]. The parameter R_q for part A and part B was defined as 0.35 and 0.30 respectively, reflecting the greater roughness of the part A caused by higher hills. However the distinction in the parameters R_q for parts with different morphology does not affect the average roughness of the coatings surface which is R_a=0.25. As follows from the values of R_a and R_q the surface has 8–9 grade of roughness.





a *b*

Figure 3. Histogram of the angles to the surface normal distribution for the respective topography sites A (*a*) and B (*b*).

As one can see from Figure 5 the shape of hysteresis loop in the saturation interval is smoothed that indicates the presence of an amorphous structure in the electrolytic deposits [10]. At the same time we observe the saturation of magnetization as well as demagnetization which is stepwise that confirms the presence of two magnetic phases in the coating (Figure 2).

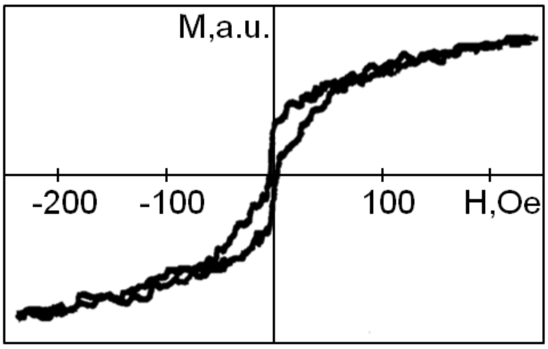


Figure 5. Hysteresis loop of Fe-Co-Mo coating.

It is found that the coercive force of Fe-Co-Mo films is 7-10 Oe, which allow us to classify the Fe-Co-Mo coatings as soft magnetic materials.

4. Conclusions

(i) Coatings Fe-Co-Mo containing 47 at.% iron, 28 at.% cobalt and 25 at.% molybdenum deposited by pulse current amplitude of 3–4 A/dm^2 are characterized by the surface containing different sites with globular structure alternating by sharp hills. The surface of Fe-Co-Mo coatings has 8–9 grade of roughness.

(ii) The observed anisotropy of the coating caused by both surface and volume heterogeneity is a prerequisite for the formation of different magnetic phases.

(iii) The coercive force of Fe-Co-Mo films is 7-10 Oe, which allow us to classify the coatings as soft magnetic materials.

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