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AFM SURFACE ANALYSIS OF Fe-Co-Mo ELECTROLYTIC COATINGS

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The study aims at the investigation of the morphology and topography of the ternary Fe-Co-Mo electrolytic coatings. Compositions and morphology of the alloys are examined by scanning electron microscopy and X-ray analysis. Both topography and surface roughness are studied by an atomic force microscopy AFM using a NT–206 microscope. The Fe-Co-Mo coatings with an iron content of 47 at.%, cobalt 28 at.% and molybdenum 25 at.% are deposited on mild steel substrate by pulse electrolysis mode from citrate bath with the ratio of concentrations $c(Fe^{3+}):c(Co^{2+}):c(MoO_4^{2-})$ = 2.5:3:1. Atomic force microscope analysis topography of the coatings Fe-Co-Mo at the scanning area 39.9×39.9 μm show that their surface is more developed compared with the substrate material. Moreover the AFM analysis of the coatings morphology and surface topography indicates the parts with a globular structure with an average conglomerates size of 0.2–0.5 μm and singly located sharp grains. Within the same scan area, sites with a developed surface are detected the topography of which is identical to the crystal structure of cobalt with the crystallite size in the range of 0.2–1.75 μm. The parameters R_a and R_q for parts with different morphology as well as average characteristics of coatings demonstrated the low roughness of the surface. Electrolytic deposits Fe-Co-Mo can be attributed to 8–9-th class of roughness. The study tested the magnetic behavior of Fe-Co-Mo coatings. The coercive force of 7–10 Oe confirms the soft magnetic properties of materials which in combination with high microhardness open prospects for usage of Fe-Co-Mo systems in the production of magnetic head elements for recording and reproducing information.

Keywords: *AFM, pulse electrolysis, magnetic properties, morphology, ternary alloys, topography*

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, catalytic and magnetic properties combined with high microhardness makes such coatings universal and allows to significantly expanding their application area [4].

The functional properties of the coatings are structurally dependent so both their composition and surface morphology will determine the performance characteristics of materials. The roughness and surface friction are the main characteristics of the surface quality of the coatings. Previously, it was shown [5] that binary and ternary coatings obtained in a pulsed mode are characterized by higher microhardness and wear resistance due to their smooth surface. The roughness of electrolytic deposits can be significantly decreased using pulse mode [6]. Since the structure of the electrolytic alloys determine 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) [7–9], matters concerning the topography and morphology of ternary alloys as well as their influence on the properties of the coatings require a detailed study.

The aim of this work is to study the morphology and topography of the ternary alloy

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coatings Fe-Co-Mo using atomic force microscopy.

EXPERIMENT

The Fe-Co-Mo coatings were formed on a steel substrate of 08KP from electrolytic bath of composition, 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 [10]. Electrolysis was performed by unipolar pulse current with an amplitude of 3–4 A/dm^2 in the working range of the pulse t_i $1 \cdot 10^{-2}$–$2 \cdot 10^{-2}$ s and pause duration t_p $1 \cdot 10^{-2}$–$5 \cdot 10^{-2}$ s. The ratio of the cathode to the anode area was 1 : 5, volume current density was kept at the level 2 A/dm^3. Pretreatment of samples surface included mechanical polishing, degreasing, chemical etching in a mixture of the 50 % nitric and 50 % sulfuric acids, thorough washing with distilled water and drying.

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 verify the results, 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 an atomic force microscopy AFM using a 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]. The scan area 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 the 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. Including the root mean square (R_q), mean particle height and its distribution, surface skewness and particle diameter were obtained.

Magnetic properties of the coating of thickness 8 μm obtained on copper M1 substrate were determined by a vibrating sample magnetometer with fields up to 20 kOe at room temperature. Accuracy of measurement of the magnetic characteristics is ± 2 %. The coercive force and the saturation magnetization were determined based on the analysis of hysteresis loops obtained in parallel and perpendicular to the direction of magnetic field lines.

RESULTS AND DISCUSSION

Coatings Fe-Co-Mo with an iron content of 47 at.%, cobalt 28 at.% and molybdenum 25 at.% (in terms of metal) were obtained by pulse electrolysis mode from citrate electrolyte with the ratio of alloying metals salts concentration $c(Fe^{3+})$:$c(Co^{2+})$:$c(MoO_4^{2-})$ = 2.5:3:1. An uneven distribution of components in the coating is indicated by EDS data analysis (Fig. 1).

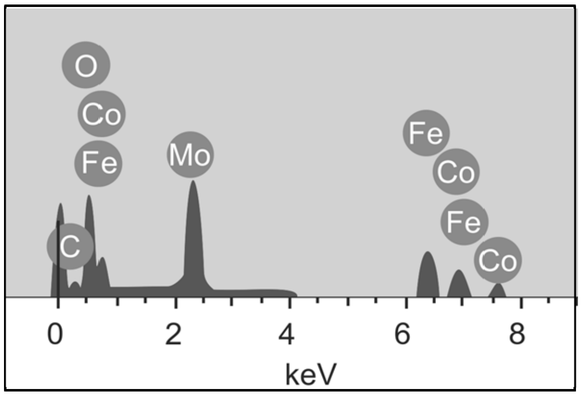


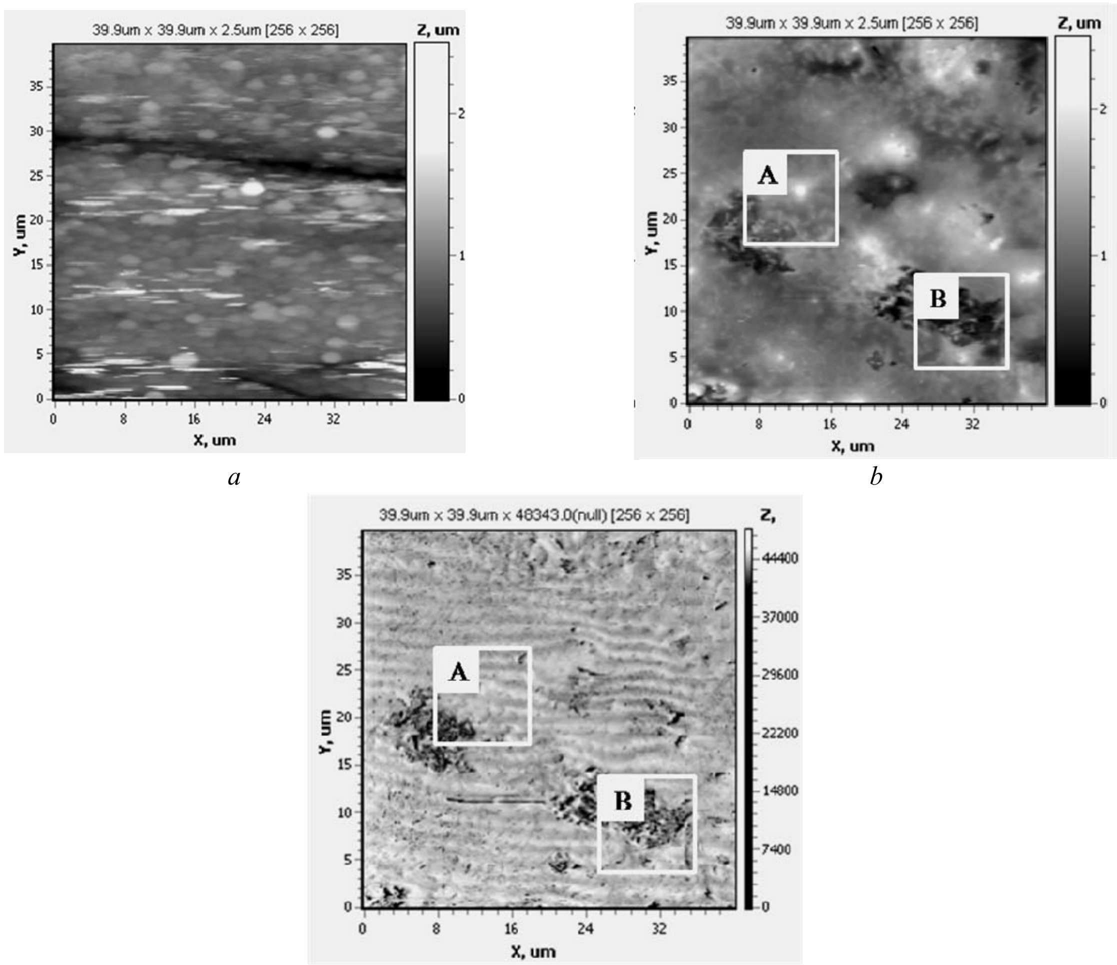
Fig. 1. EDS spectrum of the Fe-Co-Mo coating. Scan area SEM 100×100 μm

The substrate of steel 08KP is characterized by evenly surface (Fig. 2 *a*) with values of roughness R_a = 0.15 and R_q = 0.23. The surface of Fe-Co-Mo coatings (scanning area 39.9×39.9 μm) is more developed and globular comparing with the substrate as it follows from AFM 2D-maps analysis (Fig. 2 *b*, *c*). Moreover one can observe the parts of different morphology – site A and site B – at the surface of Fe-Co-Mo coating (Fig. 2 *b*).

The torsion of measuring console in one scan area substantially changes the skin friction at above mentioned parts indicating that the surface of the material is non-homogeneous [12, 13]. In this regard, the more detail study of the morphology of parts A and B is of great interest and importance.

The part A is characterized by a globular structure with an average size of conglomerates 0.2–0.5 μm and singly located cone-shaped hills with a base diameter of ~ 3 μm and a height of

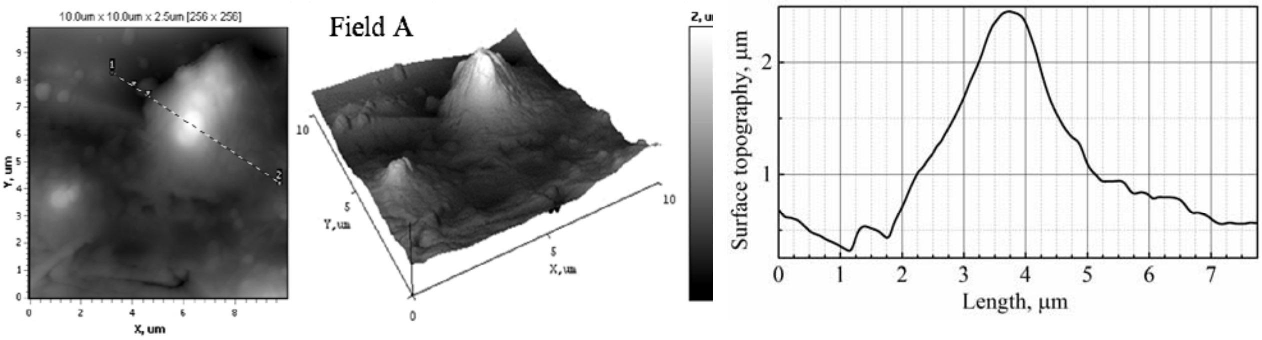
2.5 μm (Fig. 3). As appears from 2D- and 3D-maps topography of the surface (Fig. 3 *a, b*), the cone-shaped hills are consisted of the smaller spheroids.



a *b*

c

Fig. 2. 2D-topography (*a*) map of the surface for steel substrate of 08KP; 2D-topography (*b*) and 2D-torsion (*c*) maps of the surface for Fe-Co-Mo coating deposited in pulse mode. Scan area AFM 39.9×39.9 μm



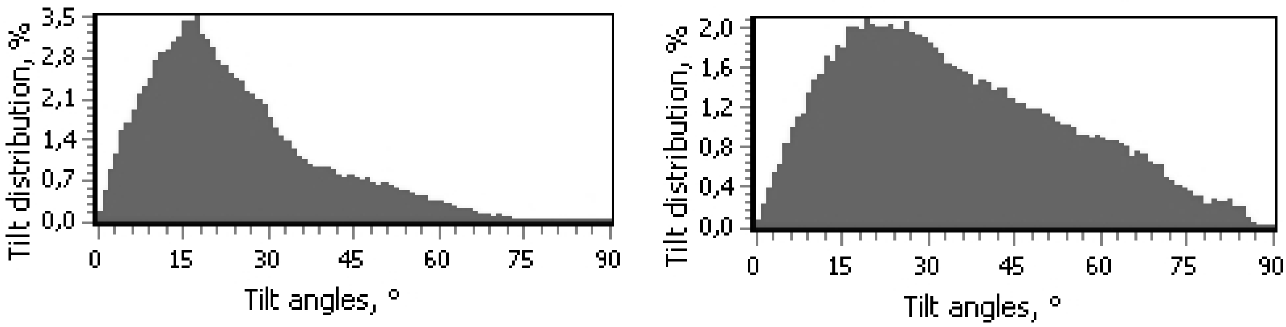
a *b*

Fig. 3. 3D- and 2D maps of the surface (*a*) and cross section profile between markers 1 and 2 (*b*) for part A of Fe-Co-Mo coating deposited in pulse mode. Scan area AFM 10.0×10.0 μm

The study of histogram of distribution the inclination angle to the surface normal indicates a predominance of spheroids (Fig. 4 *a*). It was found earlier [14] that globular structure of the surface is caused by the refractory metals presence in the alloy. Such composition and character of the surface are favorable for increasing microhardness, corrosion resistance, and catalytic activity of the material.

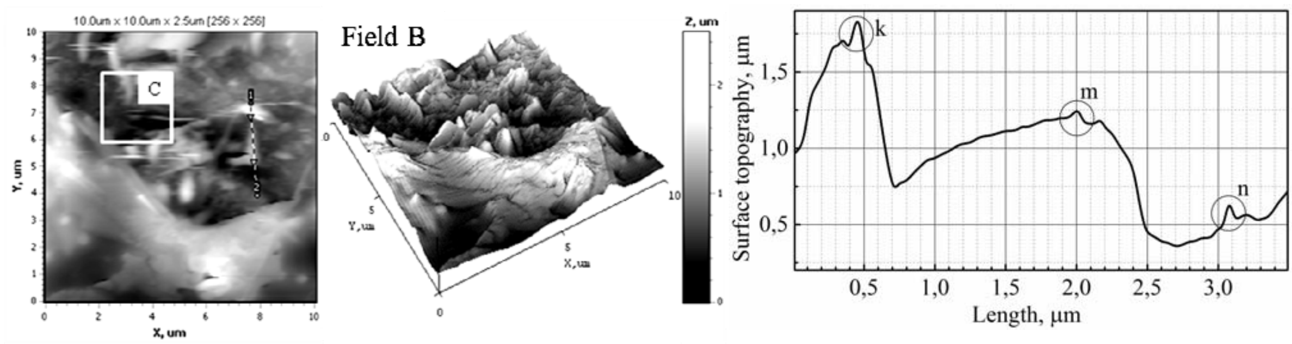
Site B is characterized by more developed surface compared with a site A. The hexagonal crystal lattice of cobalt with sufficiently sharp hills alternating by valleys is visualized at the 2D- and 3D- maps of the coatings surface (Fig. 5 *a*). The profile of cross section between markers 1 and 2 indicates that the crystalline sizes are in the range of 0.2–1.75 μm, wherein the surface of larger crystalline size of 0.5–1.75 μm is formed with a smaller grain size of 0.1–0.2 μm as one can see from Fig. 5 *b* for fields "k", "m", "n". Histogram of distribution of the inclination angle to the surface normal in this part demonstrates the uniform distribution of the sharp hills of different height (Fig. 4 *b*). Macropores (site C on Fig. 5 *a*) are visualized on photomicrographs of the coating surface in the zone adjacent to the site B.

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 availability of the high hills. However values R_q for parts of different morphology have no significant effect on the average roughness of the coatings R_a = 0.25. Accordingly to the R_a and R_q, the Fe-Co-Mo coating has a roughness class surface of 8–9.



a *b*

Fig. 4. Histogram of the angles to the surface normal distribution for the respective topography part A (*a*), part B (*b*)



a *b*

Fig. 5. 3D- and 2D maps of the surface (*a*) and cross section profile between markers 1 and 2 (*b*) for part B of Fe-Co-Mo coating deposited in pulse mode. Scan area AFM 10.0×10.0 μm

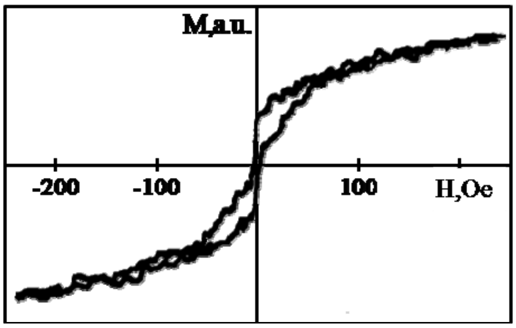


Fig. 6. Hysteresis loop for Fe-Co-Mo coating of composition, at.% : Fe – 47, Co – 28, Mo – 25. Substrate – copper M1

The observed both surface and volume heterogeneity of the coating causes their anisotropy which influences on magnetic properties. The study of the magnetic behavior of synthesized ternary electrolytic alloys confirmed the assumptions made. As one can see from Fig. 6, the shape of hysteresis loop in the saturation interval is smoothed that indicates the presence of parts with an amorphous structure in the coating. Concurrently, we observe the saturation of magnetization as well as demagnetization which is stepwise (Fig. 6) that confirms the presence of two magnetic phases in the coating. It was found the coercive force for synthesized coating of 7–10 Oe, so the material can be attributed to the soft magnetic.

CONCLUSION

Coatings Fe-Co-Mo with an iron content of 47 at.%, cobalt 28 at.% and molybdenum 25 at.% obtained by pulse electrolysis mode with an amplitude of 3–4 A/dm^2 are characterized by developed surface containing sites with globular structure and hexagonal crystal lattice of cobalt. Synthesized Fe-Co-Mo coatings with average roughness of 0.25 can be attributed to 8–9-th roughness class. The observed anisotropy of the coating caused by both surface and bulk heterogeneity is a prerequisite for the formation of magnetic properties. The coercive force of 7–10 Oe confirms the soft magnetic properties of materials which in combination with high microhardness open prospects for usage of Fe-Co-Mo systems in the production of magnetic head elements for recording and reproducing information.

Аналіз поверхні електролітичних Fe-Co-Mo покриттів методом атомно-силової мікроскопії

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Уніполярним імпульсним електролізом отримані Fe-Co-Mo покриття з вмістом заліза 47 ат. %, кобальту 28 ат. % і молібдену 25 ат. %. Методом АСМ досліджені морфологія і топографія поверхні. На поверхні покриття виявлено ділянку з глобулярною структурою і окремо розташованими конусоподібними виступами з розміром зерен 0.2–0.5 µm. Крім того, в межах однієї області сканування виявлені ділянки з більш розвиненою поверхнею, топографія яких ідентична кристалічній структурі кобальту, з розміром кристалітів в межах 0.5–1.75 µm. Визначено параметри R_a і R_q для областей з різною морфологією та досліджуваного покриття в цілому. Були вивчені магнітні властивості Fe-Co-Mo покриття. Коерцитивна сила складає 7–10 Е, що дозволяє віднести отримані покриття Fe-Co-Mo до магнітом'яких матеріалів.

Ключові слова: *АСМ, імпульсний електроліз, магнітні властивості, морфологія, тернарні сплави, топографія*

Анализ поверхности электролитических Fe-Co-Mo покрытий методом атомно-силовой микроскопии

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Униполярным импульсным электролизом получены Fe-Co-Mo покрытия с содержанием железа 47 ат. %, кобальта 28 ат. % и молибдена 25 ат. %. Методом АСМ изучены морфология и топография поверхности. На поверхности покрытия обнаружена область с глобулярной структурой и отдельно распложенными конусообразными выступами с размером зерен 0.2–0.5 μm. Кроме того, в пределах одной области сканирования обнаружены участки с более развитой поверхностью, топография которых идентична кристаллической структуре кобальта, с размером кристаллитов в пределах 0.5–1.75 μm. Определены параметры R_a и R_q для областей с различной морфологией и исследуемого покрытия в целом. Были изучены магнитные свойства Fe-Co-Mo покрытия. Коэрцитивная сила составила 7–10 Э, что позволяет отнести полученные покрытия Fe-Co-Mo к магнитомягким материалам.

Ключевые слова: *АСМ, импульсный электролиз, магнитные свойства, морфология, тернарные сплавы, топография*

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