

## FUNCTIONAL TERNARY Fe-Co-Mo(W) COATINGS

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Ternary Fe-Co-Mo and Fe-Co-W were deposited onto copper and mild steel substrates at galvanostatic mode from a complex citrate bath. The surface morphology of Fe-Co-Mo(W) thin films was studied by using an atomic force microscopy AFM. It was established that iron and tungsten undergo competitive cathodic co-deposition in the alloy. The tungsten content in the coating increases by reducing the iron content with rising current density. The elemental analysis of Fe-Co-Mo coatings obtained on a substrate of copper at various current densities demonstrates competitive iron and cobalt process of reduction. The data of the AFM analysis demonstrate the globular structure of the Fe-Co-W coatings, wherein the surface of a larger spheroid size of 2–5  $\mu\text{m}$  is formed with a smaller grain size of 0.2–0.5  $\mu\text{m}$ . The surface of Fe-Co-Mo deposits is more developed compared with Fe-Co-W films but the latter are characterized by smaller grain sizes. Moreover, 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. The grain size as well as the coating thickness resulting from the electrolysis mode are shown to be the main factors of the films magnetic properties. The presence of two magnetic phases in the Fe-Co-Mo coating is established. The coercive force for synthesized Fe-Co-W and Fe-Co-Mo coatings was found as 50–60 Oe and 7–10 Oe respectively, which allows us to classify the Fe-Co-Mo coatings as soft magnetic materials.

The researchers and technologists' increased interest to multicomponent galvanic alloys of iron triad metals with refractory elements (W, Mo etc.) [1, 2] is due to several reasons. The main one is creation of a new technology of coatings with a unique set of functional properties such as wear and corrosion resistance, increased catalytic activity and microhardness, magnetic properties, and others [3, 4]. This allows one to replace toxic chromium-plating, to create effective catalytic materials, more available compared to traditional platinum-based systems [5] and to obtain new soft magnetic films for the production of magnetic head elements for recording and reproducing information [6]. In

this connection, the electrochemical methods of deposition are considered to be a competitive alternative to the physical methods of production [7] due to the possibility of flexible process control and monitoring. This enables the formation of coatings of a varied composition and structure, which is a key factor for production of the materials with specified functional properties.

Many scientific papers delve into the electrodeposition of binary [8, 9] and ternary [10] iron and cobalt alloys with refractory components.

In [11], Fe-W and Fe-W-P coatings with high wear resistance and corrosion resistance were obtained from electrolytes of different composition. It is noted that friction coefficient of amorphous ternary Fe-W-P alloys is lower than that of binary Fe-W coatings.

The authors of [12] emphasize the increased wear resistance of Fe-W, Ni-W and Co-W coatings obtained from citrate and citrate-ammonia electrolytes at low bulk current densities.

The molybdenum incorporation into cobalt deposits leads to a significant decrease in the coercive force and an increase in the saturation magnetization of the materials [13]. It is shown [14] that the molybdenum content in the alloy increases as the potential shifts toward negative values. The structure of deposits varies from close-packed hexagonal to mixed crystalline and amorphous with increasing current density. It depends on coatings thickness: thin films have an amorphous structure.

The great practical interest for works [15, 16] are due to electrosynthesis of ternary Fe-Mo-W alloys with increased physical-mechanical and corrosion protective properties for hardening machine parts.

Obviously, in each individual case the formation of the coating depends on the qualitative and quantitative composition of the electrolyte and on the synthesis conditions. It should be noted the modes and parameters of the electrolysis predetermine in a particular way the concentration ratio of the alloy components and phase composition of the coatings [17]. Accordingly, the functional properties of coatings dependent on the composition and structure can be controlled by the deposition conditions.

It should be noted that most published results cover the binary alloys Fe (Ni, Co) -Mo (W). Thereby it is relevant to study the process of electrosynthesis of ternary alloys and to analyze their properties.

### **Research methodology**

The Fe-Co-W coatings were formed on a copper substrate M1 and on a mild steel substrate from electrolytic bath of composition, g/dm<sup>3</sup>: Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O – 95–100; Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O – 30–45; Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O – 15–25; CoSO<sub>4</sub>·7H<sub>2</sub>O – 30–45; Na<sub>2</sub>SO<sub>4</sub> – 15–45; H<sub>3</sub>BO<sub>3</sub> – 6; the pH value

was adjusted within the range 4.0–4.5 by adding sulfuric acid or sodium hydroxide.

The Fe-Co-Mo coatings were formed on a copper substrate M1 and on a mild steel substrate from the same electrolyte but containing the sodium molybdate 15–25 g/dm<sup>3</sup> instead of sodium tungstate. The pH value was adjusted within the range 4.0–4.8.

The electrolyte solutions were prepared using the certified reagents of chemically pure grade on the distilled water. The acidity of working solutions was controlled with a pH-meter pH-150M with the glass electrode ESL-6307.

Pretreatment of the 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 coatings were formed in galvanostatic mode with the current density  $i = 2\text{--}6 \text{ A}\cdot\text{dm}^{-2}$ . The ratio of the cathode to the anode area was 1:5, volume current density was kept at a level of 2 A/dm<sup>3</sup>.

The chemical composition of the coatings was determined by the X-ray fluorescence method using a portable spectrometer “SPRUT” with a relative standard deviation of  $10^{-3}\text{--}10^{-2}$ . The error at determining the content of the components is  $\pm 1 \text{ wt. } \%$ . 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(W) thin films was studied by the 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  $5.0 \times 5.0 \mu\text{m}$  and the height of the surface relief was recorded at a resolution of  $256 \times 256$  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 analyse the AFM images, all image data were converted into Surface Explorer software.

Magnetic characteristics were measured using a vibration magnetometer for the fields up to  $1600 \text{ kA}\cdot\text{m}^{-2}$ . 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.

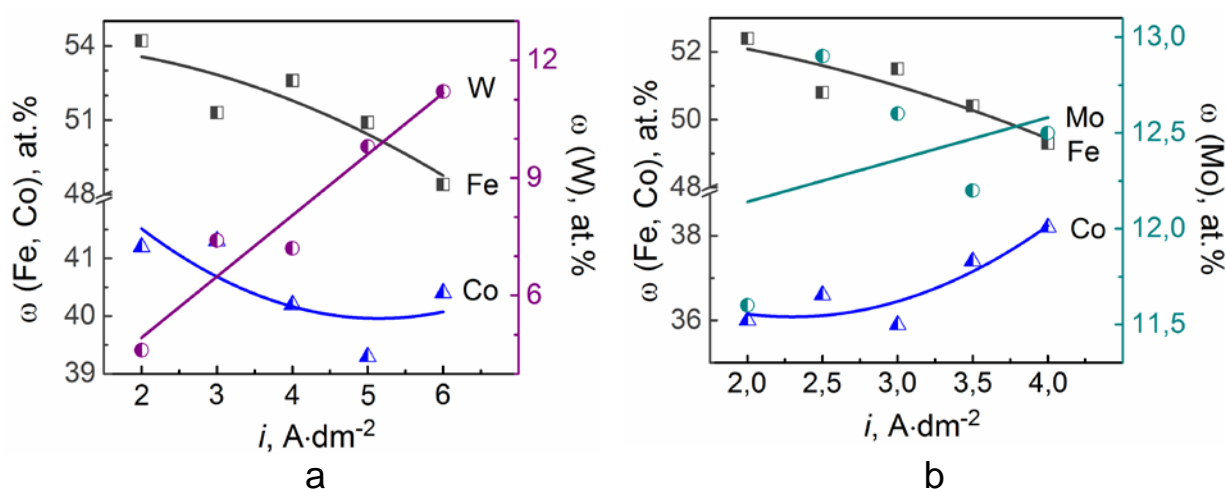
## Results and Discussion

### *Composition and morphology of Fe-Co-W(Mo) coatings*

The iron and tungsten competitive deposition in the Fe-Co-W alloy (Figure 1a) is observed in galvanostatic mode at varied current density of 2 to 6 A/dm<sup>2</sup>. The tungsten content in the coating increases from 4 to

11 at.% by reducing the iron content with increasing current density from 2 to 6 A/dm<sup>2</sup> as one can see from Fig. 1a. This is due to intensification of parallel reaction of hydrogen reduction forming ad-atoms H<sub>ad</sub>, which contributes to a more complete chemical reduction of intermediate tungsten oxides. The content of cobalt in this case varies within the range of 2 at.%.

The results of elemental analysis of the Fe-Co-Mo coatings obtained on a substrate of mild steel at various current densities demonstrates competition process of recovery between the iron and cobalt. Increasing current density increases the cobalt content of the alloy, the iron content thus decreases (Fig. 1b). The molybdenum content ranges from 2 at.%. The maximum molybdenum content of 13 at.% is reached at a current density of 3 A/dm<sup>2</sup> (Fig. 1b).



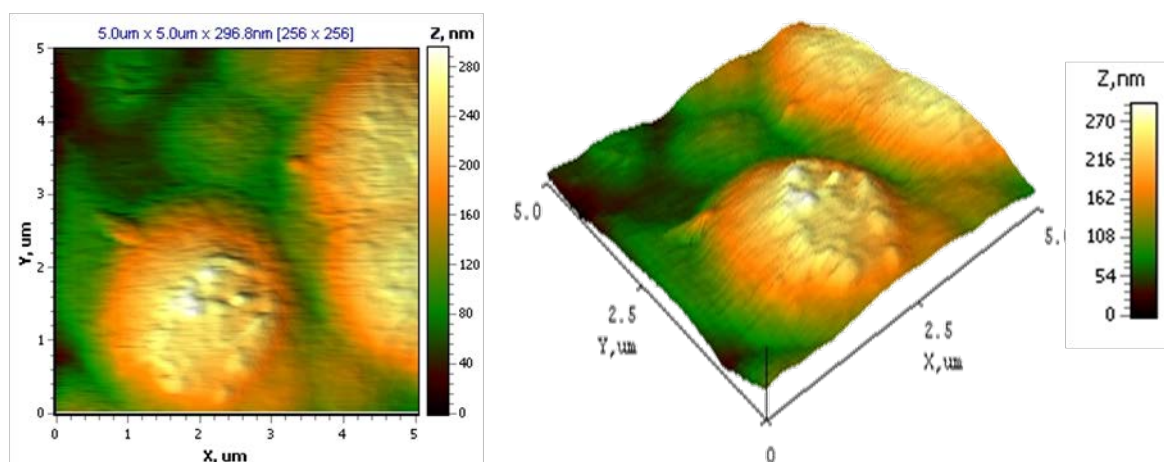
**Fig. 1.** The current density influence on composition of Fe-Co-W (a) and Fe-Co-Mo (b). Substrate copper M1

The data of the AFM analysis demonstrate the globular structure of the Fe-Co-W coatings. Wherein the surface of larger spheroid size of 2–5 μm is formed with a smaller grain size of 0.2-0.5 μm as one can see from Fig. 2. It was found earlier [18] 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.

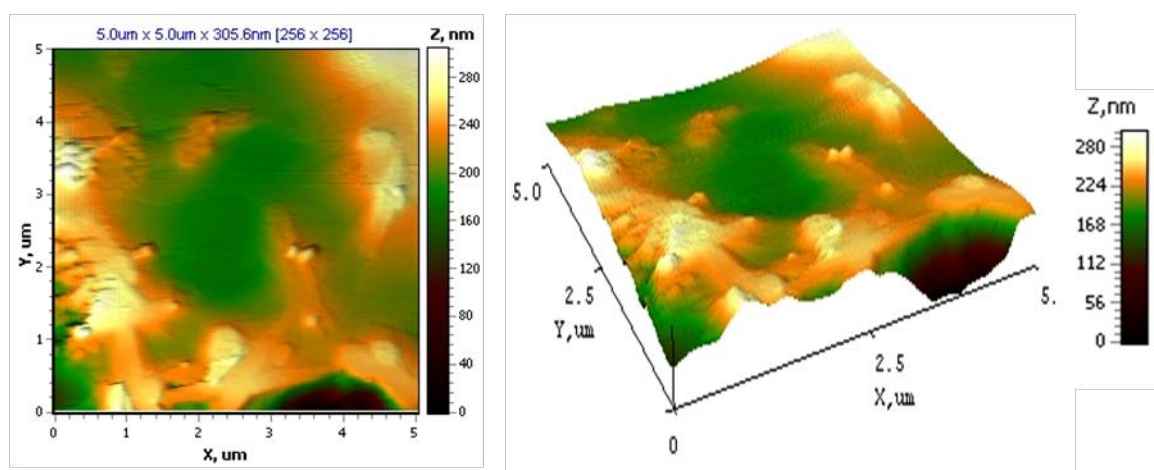
The Fe-Co-Mo coating is characterized by more developed surface compared with a Fe-Co-W coating. We observe smaller grain sizes for Fe-Co-W thin films. Moreover, the hexagonal crystal lattice of cobalt with sufficiently sharp hills alternating by valleys is visualized at the 2D- and 3D- maps of the coatings surface (Fig. 3).

Such a difference in the structure of alloys is associated with peculiarities of crystallization of alloy-forming metals.

The difference in the shape and parameters of the crystal lattices of iron, cobalt, tungsten and molybdenum (Table 1) will undoubtedly result in its distortion and deceleration of the linear growth of crystals and in this case we can expect the formation of somatoid structures.



**Fig. 2.** 2D- and 3D maps of the surface of Fe-Co-W coating deposited in galvanostatic mode. Scan area AFM 5.0x5.0  $\mu\text{m}$ . Substrate is mild steel



**Fig. 3.** 2D- and 3D maps of the surface of Fe-Co-Mo coating deposited in galvanostatic mode. Scan area AFM 5.0x5.0  $\mu\text{m}$ . Substrate is mild steel

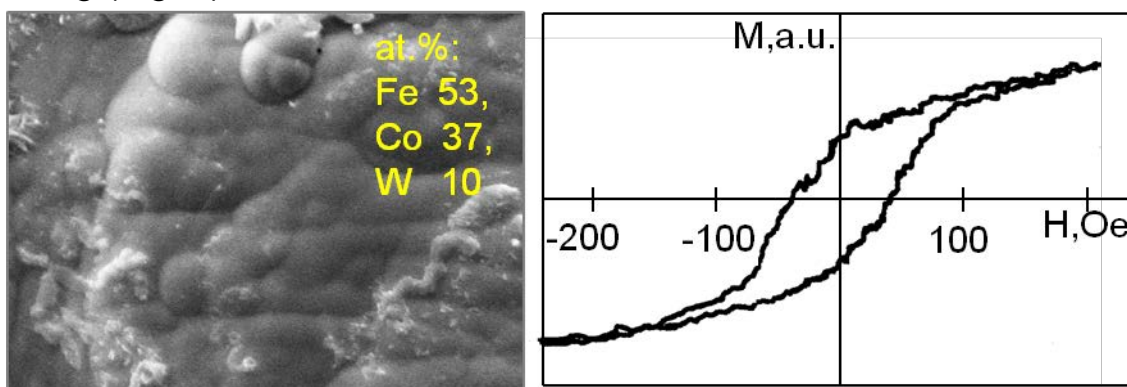
**Table 1.** Crystal-chemical parameters of alloying components

Parameters	Fe	Co	Mo	W
Atomic radius, nm	0.117	0.125	0.130	0.141
Lattice structure	volume-centered cubic	hexagonal	volume-centered cubic	volume-centered cubic
Lattice parameters, Å	2.866	a=2.505, c=4.089	3.147	3.160

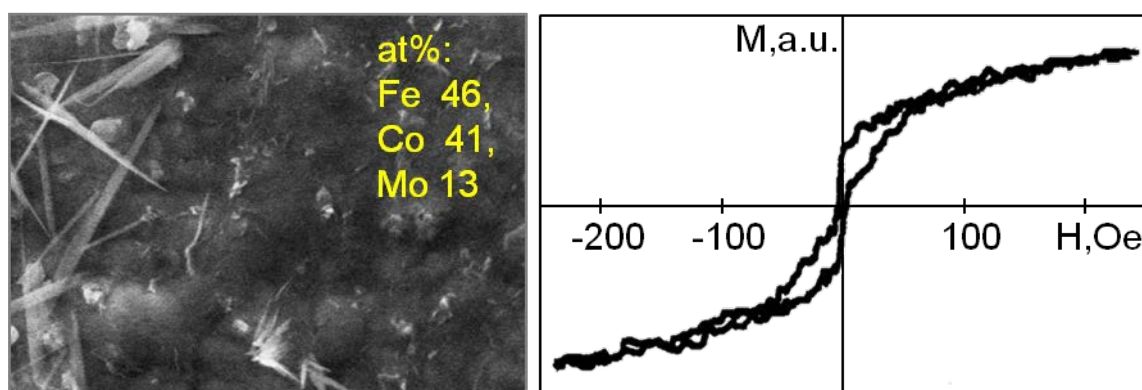
It should also be taken into account that the atomic radii of molybdenum and tungsten exceed the atomic radius of iron by 11 and 20 % accordingly (Table 1). Therefore during the formation of mono-atomic layer the attached atoms are forced to dislocate from equilibrium positions, increasing thus a probability of the realization of “polycrystalline to amorphous” transition with regard to the state of the films of deposited alloys [19]. Obviously, the distortion of the crystal lattice is the greater, the greater the difference in the values of the atomic radii of the alloying components.

#### *Magnetic properties of Fe-Co-W(Mo) coatings*

The magnetic behavior of Fe-Co-W and Fe-Co-Mo deposits obtained in the same conditions varies in some way. As one can see from Fig. 4 the shape of hysteresis loop for both alloys in the saturation interval is smoothed that indicates the presence of an amorphous structure in the electrolytic deposits. At the same time, the effect of smoothing the hysteresis loop for the Fe-Co-W film is stronger than for the Fe-Co-Mo ones (Fig. 4). Concurrently, we observe the saturation of magnetization as well as demagnetization for the Fe-Co-Mo film which is stepwise that confirms the presence of two magnetic phases in the coating (Fig. 5).



**Fig. 4.** Surface morphology and hysteresis loop for Fe-Co-W coating Substrate – copper M1



**Fig. 5.** Surface morphology and hysteresis loop for Fe-Co-Mo coating Substrate – copper M1

It was found the coercive force for synthesized Fe-Co-W and Fe-Co-Mo films as 50–60 Oe and 7–10 Oe respectively. Coercive force is a structure-sensitive material characteristic. Therefore, we can assume that the main reason for higher coercive force values for Fe-Co-W films are the larger size of grains compared to size of grains of Fe-Co-Mo films.

The obtained research results allow us to classify the Fe-Co-Mo coatings as soft magnetic materials and recommend for usage of such systems in the production of magnetic head elements for recording and reproducing information devices.

### **Conclusions**

1. The iron and tungsten competitive cathodic reduction is shown to be the most reliable mechanism for co-deposition in the Fe-Co-W alloy. The tungsten content in the coating increases by reducing the iron content with rising current density.

2. The elemental analysis of Fe-Co-Mo coatings obtained on a substrate of copper at various current densities demonstrates competitive iron and cobalt process of reduction.

3. The grain size as well as the coatings thickness resulting from the electrolysis mode are shown to be the main factors of the films magnetic properties.

4. The coercive force for the synthesized Fe-Co-W and Fe-Co-Mo coatings was found as 50-60 Oe and 7-10 Oe respectively, which allows us to classify the Fe-Co-Mo coatings as soft magnetic materials.

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