

STRUCTURAL PROPERTIES OF Co, Ni AND Mo POWDERS OBTAINED BY ELECTROCHEMICAL DEPOSITION

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Abstract

Magnetic thin films based on iron group elements (Fe, Co, Ni) are currently used in computer's hard disk drives and in MEMS, whereas electrodeposition is a suitable method to obtain these materials. The powders of metals and alloys were obtained by electrochemical deposition at constant current density using alkaline ammonium electrolyte which consist one, two or three different elements Co, Ni and Mo. Ni and Co are deposited anomalously. The Mo element cannot be obtained electrochemically from the aqueous solutions. Electrochemical deposition of this metal is induced by codeposited iron-group metals, Ni and Co, for instance. This study investigates the influence of electrochemical parameters on composition and properties of obtained powders. Based on the obtained experimental results, it could be concluded that the particle size of deposited powders and chemical composition are influenced by the chemical composition of the electrolyte, with changing the concentration ratio of ions of metallic salts as well as current density imposed. As a consequence, the changes in magnetic properties are obvious. The structure and morphology of powders were investigated by Scanning Electron Microscopy (SEM). For demonstration of mechanism of powder deposition Image ProPlus software for SEM microphotograph analysis was used. The values of individual objects as well as formed clusters of powders were measured by this technique. The chemical composition of the powders was determinate using Energy Dispersive X-ray (EDX) analysis. XRD results suggested that obtained powders were of amorphous structure.

Key words: Co, Ni, Magnetic thin films, SEM, TM, Magnetic permeability

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Introduction

Electrochemically deposited alloys of iron group metals (Fe, Co, and Ni), in a form of powders or coatings, are important magnetic materials [1–11] as well as good catalysts for hydrogen evolution.[12–14] Certain elements, like Mo, W, and Ti, cannot be obtained electrochemically from the aqueous solutions.[15] Electrochemical deposition of these metals is induced by codeposited iron-group metals. This induced codeposition has some characteristics that make it distinguishable from the other deposition techniques, such as a limited amount of the element being deposited inductively.

Numerous different hypotheses focus on the mechanism of the induced deposition. One of the mechanisms is based on the hypothesized formation of a mixed complex ion that contains tungsten and iron-group metal in the electrolyte for deposition.[16] Depolarization may take place, because the reduction of these metals from their mixed complex ions is favored thermodynamically with respect to the reduction of each metal ion. Polarographic investigations suggest the presence of the Ni complex with tungstenites, from which tungsten is reduced completely to the pure metal or reduced partially to an oxide of tungsten with lower valence.

During the reduction of pure molybdates and tungstenites from the aqueous solutions, the products of mixed oxidation states between the hexavalent and pure metal are deposited on the cathode. Therefore, the hypothesis about the presence of oxide film on the cathode is based on the assumption that the oxide layer of partially reduced molybdenum and tungsten oxides is being reduced in reaction with hydrogen that is adsorbed on freshly deposited iron-group metals.[17,18] This catalytic reduction mechanism also assumes that the number of hydrogen atoms adsorbed on iron-group metals is equal to the number of unpaired electrons.

The studies of the mechanism of Mo deposition with the Ni from the citrate electrolytes have led to the hypothesis of adsorption and reduction of molybdate ion species.[19–21] According to this model, the reduction of bivalent Ni from the complex is controlled by the transport processes and the two-stage reduction that includes the presence of the adsorbed intermediate. In parallel, molybdate is catalytically reduced through an adsorbed Ni–Mo intermediate. In relation to this mechanism, Ni^{2+} (aq) ion species act as catalysts for molybdate reduction, which forms the adsorbed reaction intermediate $[\text{Ni}^{2+}(\text{aq})\text{MoO}_2]_{\text{ads}}$. Mo is deposited via a reduction of the reaction intermediate, and at the same time, the two Ni^{2+} are being regenerated. The reduction of Ni and Mo takes place through two parallel reactions. Different preparation conditions lead to considerable difference in structure, morphology, and composition of deposited powders, which can affect their magnetic and electrocatalytic properties. The aim of this study is to investigate how electrolyte composition and electrochemical parameters in the deposition process affect the composition and structure of prepared powders as well as to investigate how these features affect magnetic properties of this material.

Experimental

The powder samples were deposited from electrolytes with composition: CoSO_4 , NiSO_4 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, NH_4Cl and NH_4OH . The concentration of salts ratio of Co and Ni were varied from 1:1 (0,1 M Ni and 0,1 M Co) and 4:1 (0,16 M Ni i 0,04 M Co). Also, the concentration of salts of Mo were varied from 0,005 mol/dm³ to 0,06 mol/

dm³. The concentration of NH₄Cl was 74.13 g/ dm³ with addition of NH₄OH which has a role to make a constant pH of solution at 10,6.

The influence of changing of Co, Ni and Mo salts concentration in the electrolyte for deposition on electrochemical parameters of deposition was investigated. Also, the influence of changing of current density of deposition from 200 mA/cm² to 800 mA/cm² on the structure and weight composition of obtained powders was investigated.

The electrochemical deposition of powders were prepared in electrochemical cell (V= 5.5 dm³) equipped with special separated component with Lugin capillary. The saturated calomel capillary was used as a referent.

The Pb/PbO₂ anodes area was 100 cm² and Ti cathode was a plate with area 32 cm² and thickness of 0.5 cm.

The working temperature of electrochemical cell was maintained at 25 °C. The solution was prepared using the p.a. chemicals and distilled water. During the experiment standard current circuit was applied.

The powder of Co-Ni-Mo-O alloy was obtained by electrochemical deposition with constant current density. After electrolytic process decomposed powder was washed several times with distilled water.

Magnetic behavior was observed through the relative change of magnetic permeability. Measurements of the relative change of magnetic permeability were carried out by a modified Faraday method. Samples were pressed into pills of 8 mm diameter under pressure of 400 MPa. Pressed samples were placed in front of the solenoid where the gradient of the magnetic field was $\Delta H/\Delta z = 1.26$ mT/mm. The measurements were performed in argon atmosphere.

The morphology and dimensions of obtained powders were observed by JEOL JSM-6460 LV Scanning Electron Microscope (SEM).

The Image-Pro-Plus software for SEM micrographs analysis was used. The system for microphotograph analysis contains: microscope and digital camera. The microphotograph obtained by microscope can be transported to the camera. The microphotographs are transformed in picture format which can be recognized by PC where all visual information's have been collected. The image analysis was done by PC using corresponding software packages.

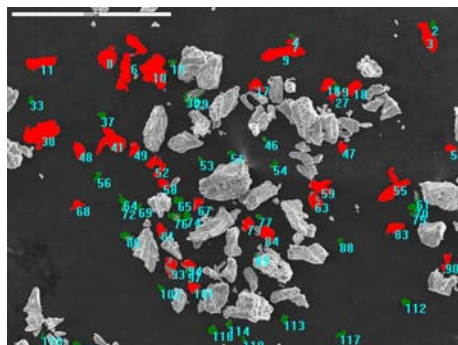
For microscope operators Image-Pro-Plus is leader in software package for image analysis, because the control and automatization tools for image creating is achieved.

Results and discussion

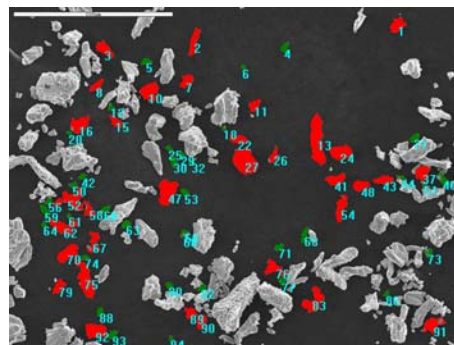
For electrochemically decomposed powders Ni and Co two SEM microphotographs were used for Image-Pro-Plus analysis. Figs1 – 4 shows analyzed images of Ni and Co electrodeposited at current density of 400 and 800 mA/cm².

The correlation between mean radius of grains and current density and chemical composition for each investigated element as well as correlation between mean radius of grains and only current density were determined using the least square method.

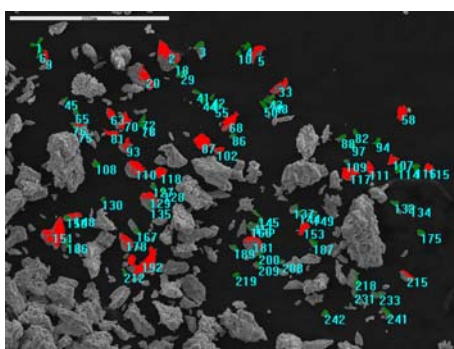
The high values of R square (0.97823) in first case when the radius is correlated with current density and chemical composition and in second case (R square is 0.749217) when radius is correlated only with current density shows correlation between current density and mean radius.



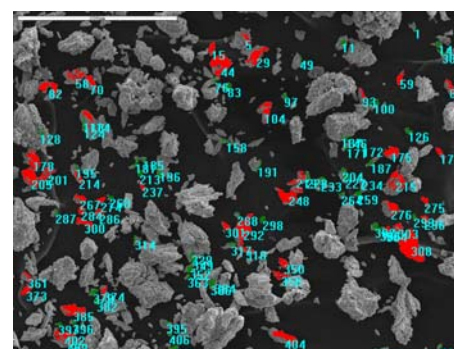
Ni 400-01



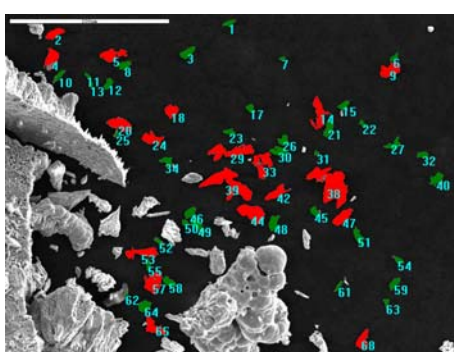
Ni 400-02

Fig 1. Analyzed images of Ni oxide powder at the current density of 400 mA /cm²

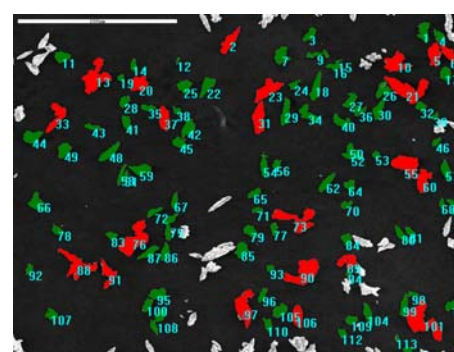
Ni 800-01



Ni 800-02

Fig 2. Analyzed images of Ni oxide powder at the current density of 800 mA /cm²

Co 400-01



Co 400-02

Fig 3. Analyzed images of Co oxide powder at the current density of 400 mA /cm²

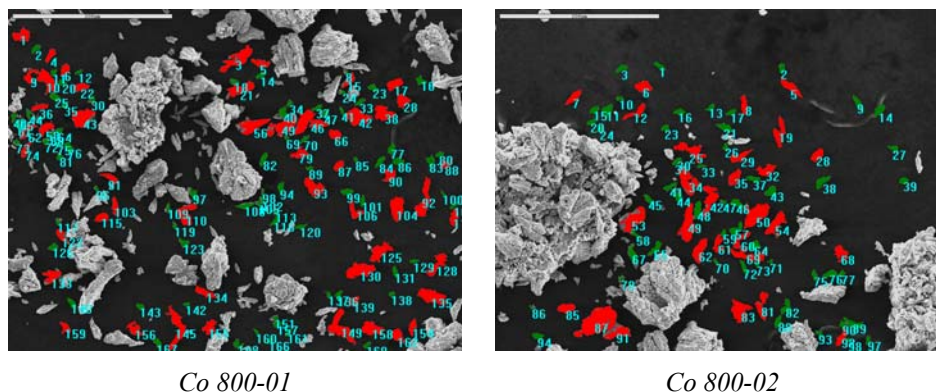


Fig 4. Analyzed images of Co oxide powder at the current density of 800 mA /cm²

Based on chemical composition of each metal in alloy composition, chemical formulas of metal oxides which are obtained by electrochemical deposition could be suggested (Table 1).

Table 1. The recommended chemical formulas of metal oxides

Name	CD, mA/cm ²	Ni	Co	Mo	O	O/Ni+Mo+ Co	Formulas
Ni400	400	63.86	0	0	36.14	0.565925	Ni ₂ O
Ni800	800	72.98	0	0	27.2	0.372705	Ni _{2.5} O
Co400	400	0	82.87	0	17.13	0.206709	Co ₅ O
Co800	800	0	77.53	0	22.47	0.289823	Co _{3.5} O
CoMo400	400	0	13.11	15.8	71.1	2.459357	Co ₂ Mo _{2.5} O ₁₁
CoMo800	800	0	14.2	14.3	71.3	2.501754	CoMoO ₅
CoNi400	400	35.42	33.25	0	31.34	0.456386	CoNiO
CoNi800	800	38.2	30.29	0	31.54	0.460505	Co ₂ Ni _{2.5} O ₂
CoNiMo400	400	0.57	13.66	9.51	76.26	3.2123	Co ₂₇ NiMo ₁₉ O _{152.5}
CoNiMo800	800	0.29	8.12	8.71	82.88	4.841121	Co ₂₈ NiMo ₃₀ O ₂₉₀
NiMo400	400	1.15	0	10.23	88.62	7.787346	NiMo ₉ O ₇₇
NiMo800	800	5.59	0	15.73	78.68	3.690432	NiMo ₃ O ₁₄
star 1	400	11.65	28.26	10.74	49.36	0.974531	Co ₅ Ni ₂ Mo ₂ O ₉
star 2	800	2.85	20.59	11.92	64.64	1.828054	Co ₇ NiMo ₄ O ₂
star 3	1600	10.78	18.06	7.76	63.39	1.731967	Co _{4.5} Ni _{2.5} Mo ₂ O _{16.5}

The powders Co-Ni, Mo-800 and Ni-Mo have not magnetic behavior at room temperature. The results of thermomagnetic characteristics of Co-400 and Ni-400 powders pressed into tablets are presented in Fig 5 a and b.

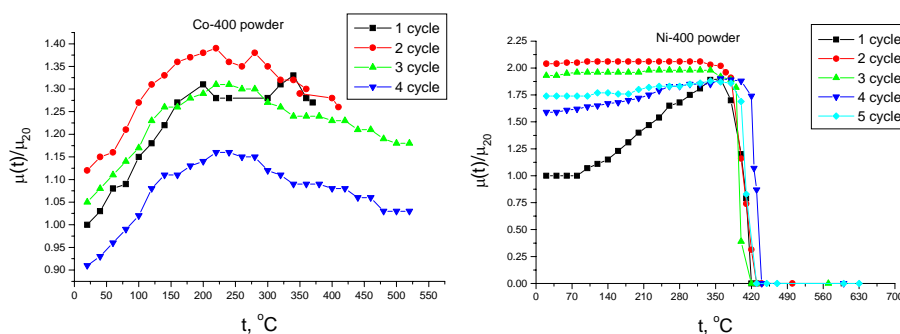


Fig. 5. The thermomagnetic behavior of a) Co-400 powder and b) Ni-400 powder

The Fig. 5a shows relative change of magnetic permeability in a function of temperature during the several heating cycles for the Co-400 sample. The magnetic permeability of cooled sample is increased for about 14% after first cycle of heating up to 370°C. This increasing of magnetic permeability is probably caused by structural relaxation of started nanostructural powder during the heating process. Also, this occurrence is followed by decreasing the both, internal stress and density of defects. As a consequence, the faster movement of magnetic domain walls and their easier aliening in magnetic field are achieved.

At the same time, the effect of high temperature energy and external magnetic field induce non oriented co-domain atoms to join with the domain with higher level energy, which has direct influence on aliening orientation of magnetic domains. Related to the first heating cycle, the magnetic permeability of cooled sample is for about 9% smaller after second heating cycle up to 410°C. This phenomenon is caused by appearing the crystallites which slow down the orientation of magnetic domains in applied magnetic field.

The magnetic permeability of cooled sample after third cycle of heating up to 500 °C is for about 23% smaller than magnetic permeability of the same sample after first cycle. This is very important result, because confirms that started powder consist higher amount of amorphous phase. Downswing of magnetic permeability after third cycle of heating up to 500 °C is caused by crystallization of amorphous phase (part) of powder and with growing the size the crystal grains. The magnetic permeability of cooled sample after first cycle up to 370 °C increased about 23% in relation to cooled sample after third cycle of heating up to 500 °C and confirms that the sample after first cycle of heating have nanocrystalline structure with significant presence of amorphous phase.

The thermomagnetic behavior of Ni-400 powder is presented in Fig 5b. Fig 5b shows that magnetic permeability of cooled sample increasing for about 104% after first cycle of heating up to 420 °C. The increasing of magnetic permeability is caused by process of structural relaxation with heating up to 420 °C. During the cycle, cooled sample have nanocrystalline structure with significant presence of amorphous phase. The downswing of magnetic permeability at 360 °C is ultimate by Curie temperature of

Ni. The lower values of magnetic permeability of cooled sample for about 11% after second cycle of heating up to 500 °C related to the values before heating are evident. During the second and third cycle of heating, magnetic permeability have constant value up to 360 °C. This result confirms good aliening of magnetic domains i.e. their independence at higher temperature which is typical for nanostructural and amorphous ferromagnetic. The decreasing of magnetic permeability of cooled sample for about 45% after third cycle of heating up to 570 °C is obvious. This effect is caused by growing the crystal grains and full crystallization of amorphous phase of powder.

Conclusion

Analyzing the results of observations as well as correlation of powders morphology with technology parameters of electrodeposition process, it could be concluded that with increasing current density the grain size of powders decreases. This is confirmed by empirical conclusion from electrochemical deposition of powders which suggest that current density has a highest influence on structure and morphology. The higher current density induces originate smaller crystal grains because the nucleation is faster. Also, this statement is confirmed by regression analysis. Using the least square method the main radius of grain and current density are correlated.

The results of thermomagnetic measurements confirm that magnetic permeability of cooled Co-400 powder after first cycle of heating has improved properties. Also, it is obvious that Co powder have nanocrystalline structure with significant amount of amorphous phase.

During the second and third cycle of heating, magnetic permeability have constant value up to 360 °C. This result of thermomagnetic measurements for Ni-400 powder show good aliening of magnetic domains at higher temperature which is typical for nanostructural and amorphous ferromagnetic. The decreasing of magnetic permeability of Ni-400 powder for about 45% after third cycle of heating up to 570 °C suggest that full crystallization and increasing size of the crystal grains of amorphous phase of powder is achieved.

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