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Electrochemical Deposition of Film Materials Based on Co and Ag

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The technology deposition of film materials with spin-dependent scattering of electrons based on Co and Ag by electrochemical method from sulfate and iodide electrolytes described. The kinetics of electroreduction of Co and Ag from this electrolytes. Determined phase composition of multilayer coatings based on Co and Ag before and after thermal annealing to temperatures T = 523-743 K.

Keywords: Kinetics of electroreduction, Electrolysis solutions, Multilayer coatings, Phase composition, Granulated solid solutions.

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1. INTRODUCTION

Galvanic coating based on alloys or multilayer structures with different metals have significant advantages in physical and chemical and magnetic properties in comparison with separate coatings. In the multilayer film structures consisting of alternating ferromagnetic and nonmagnetic layers and in granular alloys, the phenomenon of giant magnetoresistance (GMR) is observed.

Most investigates of GMR in multilayers and film granular alloys made of relatively thin film systems on the order of several nanometers, obtained by vacuum condensation [1-3]. In the review [4] presented in 2010 known results of magnetoresistive properties of granular thin film alloys based on Co and Ag, Au, Cu, Ni, Zn and others metals in which there is a spin-dependent scattering of electrons and phenomenon GMR is realized. A distinctive feature of [4] is that it analyzed only those works in which the alloys obtained by electrochemical deposition. For generalization of the results about phase formation an important aspect is research on thicker samples (from nano- to micron thickness) on the basis not alloys but metal layers, to get where we used the method of electrochemical deposition of the corresponding electrolytes. In addition, electrolytic deposited multilayer structure with effects GMR have already found application in micro-and nanotechnology, computer engineering, etc., but the structural and phase state and influence of heat treatment on the phase formation processes in these systems a little research. In this regard, the problem is actualy and requires study.

The aim of our work was to investigate the kinetic process of electroreduction Co and Ag, establishing the optimal parameters (electrolyte composition, current density, temperature etc.) processes of electrochemical deposition of separate layers Co and Ag, the study changes the phase composition of multilayer coatings during thermal treatment.

2. EXPERIMENTAL METHODIC

The futures of phase composition of multilayer system S/[Ag/Co]$_n$ (n = 2-6) in which a substrate (S) used plate steel or brass, was investigated. As the anode plate cobalt or silver according to the electrolyte were used. Before the process of cathodic reduction of metal substrates were preliminary mechanical (grinding and polishing) and chemical treatment, which consisted of degreasing, etching and ablution. Etching was carried out for 2-5 min. at room temperature in solutions of hydrochloric acid. For deposition of coating Co used normal sulphate electrolyte, which characterized a stability and uniformity of deposition. The coating Ag obtained from iodide electrolyte. Coatings Co obtained at current density electrolysis (1-5)·10^2 A/m^2 and T = 293±3 K, and coating Ag – (0,2-2)·10^2 A/m^2 and T = 293±3 K. Regimes of electrolysis picked experimentally based kinetic dependencies "thickness covering - current density," "thick coating - electrolysis time" with regard to visual quality coating. Kinetics of electroreduction of metals was investigated by gravimetric method. Time of electrolysis asked with the expectation receiving layer thickness (1-5) microns. For the electron microscopic studies multilayer coating on the substrate to make thinner mechanical and chemical means in the electrolyte on the basis of HCl, $CuCl_2$, H_2O and C_2H_5OH.

To study the evolution of phase composition of samples annealing at T = (523-743) K for 2-4 hours. X-ray diffraction analysis was carried out using the diffractometer DRON - 4.0 in K$_\alpha$Cu radiation and electron microscope TEM-125K.

3. ELECTRODEPOSITION OF COBAL AND SILVER

Experiments with electroreduction of Co carried out in the electrolyte [5] of the composition (g/l): $CoSO_4 \cdot 7H_2O$ (20); H_3BO_3 (50); NaCI (5). For select the parameters of electroreduction of Co (i.e. the optimal current density, temperature and time) the experiment was carried out under various conditions of electrolysis. For establish the optimum current density were obtained depending on the sample mass increment (coating thickness) with current density. This dependence has a parabolic character. In general, the process deposition of Co even at room temperature accompanied by

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a large cathode polarization. This can be explained in different ways: the tendency of Co ions to hydration, delayed discharge and transition of hydrated ions in the intermediate active complexes adsorbed at the cathode. For determine the velosity of the process electroreduction of Co received depending of changes thickness of coating versus time, which are parabolic character, which suggests diffusion control process electroreduction of Co, because a diffusion is the very slow stage delivery of electroactive particles to the surface of the cathode. Experiments with the electroreduction of Ag were conducted in this electrolyte composition (g/l): AgI (15-200; KI (250-300), pH = 8. Optimal current density electrolysis was equale $(0,2\text{-}1)\cdot 10^2$ A/m^2 at the T = 293±3 K.

4. INFLUENCE ANNEALING ON PHASE COMPOSITION OF COATING

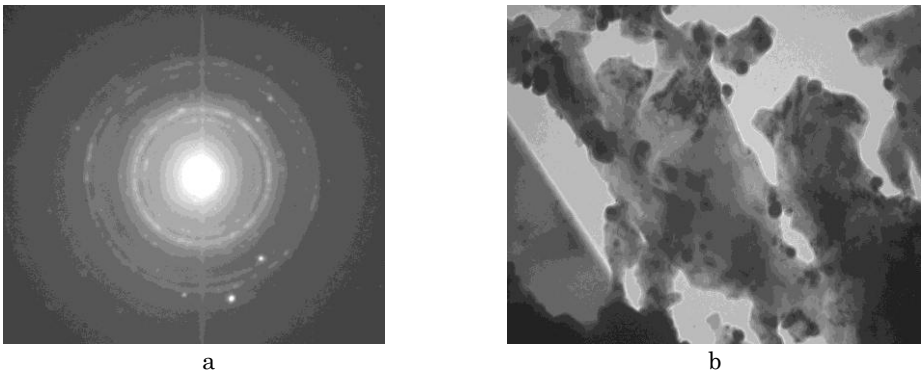
To establish the influence of annealing on phase composition of multilayer structures obtained X-ray patterns as a single-layer and multilayer samples before and after annealing. It was obtained that the phase composition of the single-layer coatings of Co and Ag before and after annealing the phase with hexagonal (HCP) lattice Co and cubic (FCC) lattice Ag.

At annealing samples S/Ag/Co phase composition of coatings does not change and corresponds to phases HCP Co + FCC Ag (perhaps this FCC phase corresponds to the solid solution (s.s.) as interplanar distance slightly less than with a massive Ag). However, in some cases, the deposited film X-ray patterns of the systems S/[Ag/Co]$_n$ (n = 2 - 6) recorded two or three lines of high-temperature phase of FCC Co (in bulk samples phase transition FCC Co → HCP Co is at 690 K). Stabilization FCC phase we associate with the action macrostress structural and thermal future, which cause the formation of defects packaging in the HCP Co phase, localization regions is FCC Co phase. At the annealing three-layer structures S/Ag/Co/Ag macrostress thermal future relax, area of packing defects healing and X-ray patterns are recorded only line from FCC s.s. atoms of Co in the lattice of Ag and HCP Co (Table 1).

Obviously, what s.s. stabilized based on FCC lattice of Ag, which leads to a decrease in interplane distances in comparison with the bulk Ag. Additional electron microscopic study (Fig. 1) of thinner samples indicates that s.s. are limited limited solubility and therefore the excess Co atoms form a granular with HCP lattice. On Fig.1 reflection of HCP Co is fixed in the form of extra reflexes below electron diffraction and on Fig. 1b - granular are fixed in the form of dark spots.

Table 1 – Interpretation of X-ray patterns from annealing at the T = 573 K coating S/Ag(12,8mkm)/Co(3,3mkm)/Ag(2,7mkm)

Experimental data					**Table data**					
S/Ag(12,8)/Co(3,3)/Ag(2,7)					Ag			HCP Co		
№	2θ, degree	d, Å	I, %	phase composition	hkl	d, Å	I, %	hkl	d, Å	I, %
1	42,0	2,152	23	HCP Co				100	2,150	25
2	45,0	2,015	100	Ag	200	2,040	53			
3	65,0	1,435	59	Ag	220	1,445	27			
4	76,7	1,243	23	HCP Co				111	1,250	70
5	78,0	1,225	65	Ag	311	1,232	53			
6	82,2	1,173	25	Ag	222	1,179	5			
7	93,2	1,061	16	HCP Co				222	1,064	60
8	98,2	1,020	12	Ag	201	1,022	1			
9	105,0	0,972	12	HCP Co				201	0,950	10
10	111,0	0,936	29	Ag		0,938	8			
11	114,9	0,915	12	Ag		0,915	5			



a b

Fig. 1 – Diffraction pattern (a) and corresponding microstructure (b) of annealing film system S/Ag(5,7mkm)/Co(2,4mkm)/Ag(3,5mkm)

5. CONCLUTION

The kinetics of electroreduction of Co and Ag and established the optimal conditions of electrolysis. The dependence of weight masse coating of current strength and time of electrolysis for the electroreduction of Co and Ag has a parabolic character, indicating diffusion control of these processes.

On X-ray patterns of the non-annealing multilyer film systems $S/[Ag/Co]_n$ ($n = 2 – 6$) are fixed, most likely the line s.s. Co atoms in Ag and the high temperature phase of FCC Co, stabilization of which we associate with the action macrostress that cause the formation of defects in the packing of HCP Co. With thermal annealing of these macrostress part (thermal component) relax, what leading to healing of defects in packing HCP Co and as a consequence - the disappearance of lines of FCC Co. On X-ray patterns of the annealed multilayer systems including fixed line Co atoms in the FCC lattice of Ag, which, by electron-diffraction and electron microscopy data is granular character, which may make the spin-dependent electron scattering in the study of magnetoresistive properties of film materials.

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