Structure and magnetic properties of Co-Ni-Mn alloy coatings (part 2)

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Abstract. Using the method of high-frequency alternating current (HFAC), based on the preliminary model forecasting of the ratio of metal ions in the electrolyte and the phase composition of the coating, Co-Ni-Mn alloy precipitates with the specified magnetic properties are obtained. It is shown that precipitation with a hexagonal close-packed α-Co phase has the highest coercive force. The presence of a free phase in a small amount (2.1 - 2.6% of weight) of Mn increases the ferromagnetic properties of films due to the domain structures with a poorly defecting α-Mn crystal lattice. The adjustable amount of the amorphous $Co(OH)_2$ phase provides the nanostructure dimensions of the crystals.

1. Introduction

It is known that the magnetic properties of cobalt-based alloys are determined by the phase composition [1, 2], the surface structure [3], the presence of dispersed amorphous metal particles [4], the presence of structure and texture defects [5, 6], the thickness of the films [7].

A distinctive feature of Co and its alloys is the large difference in the values of the coercive force between crystals with a hexagonal close-packed (HCP) α-Co phase and a face-centered cubic phase (FCC) – β-Co [8, 9].

Earlier, the authors of [9] found out for the Co-Ni-Mn alloy that the coating contains two phases of a solid solution (α-Co, β-Co) and an amorphous phase. The value of coercive force H_c was increasing with a higher content of the α-Co hexagonal phase. But the influence of manganese, the composition of the amorphous phase, and the contribution of the Co-Ni-Mn alloy components to the ferromagnetic properties remained unclear.

Objective: to get the Co-Ni-Mn alloy coatings from an electrolyte with an optimum content of metal ions in a precipitation solution and a forecasted phase composition with the given magnetic properties.

Requirements for the obtained Co-Ni-Mn magnetic alloys are:
1) chemical content of Co > Ni >> Mn in the alloy;
2) the main phase of the solid solution is α-Co, the additional phase is α-Mn;
3) the presence of a nanostructure;
4) the texture along the axis $[11\bar{2}0]$;
5) the optimum value of the coercive force.

To solve the set tasks, the authors used:
1) preliminary forecast of the ratio of metal ions in the precipitation solution: $Co^{2+} : Ni^{2+} : Mn^{2+} = 0.6 :$

0.3 : 0.1;

2) the forecast of the chemical content of metals in the alloy: Co ≈ 70 – 75 % wt, Mn ≈ 2 – 2.5 % wt, the rest is nickel;

3) the nanostructure is formed in the presence of special organic additives. The ionization potential (IP) of the additive should be close to the IP of the alloy metals;

4) an additional factor for the formation of a nanocrystalline structure is the control of the pH of the solution due to amorphous compounds of metal-solvent - Co;

5) a new method of deposition – high-frequency alternating current (HFAC) [10, 11] is offered for the implementation of 1 – 4. A part of the coatings for comparison was obtained using a stationary method (SM).

2. Methods of research

I structural methods:

1) X-ray phase analysis (DRON-7). Co-K_α – radiation; Ni filter, the parameters of the unit cells were determined using the XFA PDWin 4.0 complex to determine the phase composition of the alloy;

2) probe atomic-force microscopy (AFM). The «Ntegra» probe laboratory, controlled by the Nova program. Accuracy of the scanner positioning ~ 1nm. It was used to study the nanostructure and phase contrast;

3) scanning electron microscopes Philips SEM 515; JEOL JSM – 6510 LV with X-ray spectral analyzers. The error in determining the content of elements is ± 0.2 % wt. They were used to construct the spectrum and maps of the distribution of elements, to study the microstructure and the elemental composition of the subsurface layers;

4) transmission electron microscopy (JEM 2000 FXII. Accelerating voltage is 80 – 100 kV). It was used to study the mutual position of the alloy phases.

II Magnetic properties:

1) vibration magnetometer – to determine the coercive force from the oscillogram of the hysteresis loop, the error is 3 – 5 %;

2) atomic force microscopy (AFM) to study the domain structure.

Precipitation was carried out from simple sulfate electrolytes in the presence of isomeric additives of ortho-aminosulphonic acid (o-ASA) (HFAC) and para-aminosulphonic acid (p-ASA) (SM). As required by the adsorption theory, the ionization potentials (IP) of ASA correspond to the IP of the deposited metals Co, Ni, Mn (7.43 – 7.86 eV). o-ASA is able to form chelate complexes predominantly with Ni^{2+} ions, which contributes to the enrichment of the alloy with cobalt. The obtained chemical composition of the alloy completely corresponds to the required ratio of components in the coating: $Co_{67}Ni_{31}Mn_2$.

Electrolytic alloys have a number of features:

1) the phase composition of electrolytic alloys often does not coincide with the phase diagrams;

2) the phase composition depends on the ratio of the concentrations of metal ions in the electrolyte [12];

3) emergence of new phases that are absent in the phase diagram is possible [11];

4) for galvanic precipitations, it is impossible to obtain all the phases represented in the phase diagram.

The HFAC method allows expanding the boundaries of existence of phases, and model forecasting [8, 12] makes it possible to predict the phase composition depending on the content of the components in the alloy.

3. Co-Ni-Mn coatings structure study

An analysis of the X-ray patterns of Co-Ni-Mn alloys showed (Figure 1) that coatings obtained by the HFAC method completely satisfy the specified phase composition: main phase α-Co, related to α-Mn (α-Co >> α-Mn), which agrees with the calculated phases (Table 1). The relative error of the experimental criteria for phase formation to the calculated ones is 2.03 ÷ 7.25% (HFAC) for Co-Ni-

Mn coatings, which is higher than for precipitation obtained by the stationary method. Perhaps this is due to the high intensity of electromagnetic oscillations and the periodic change in current.
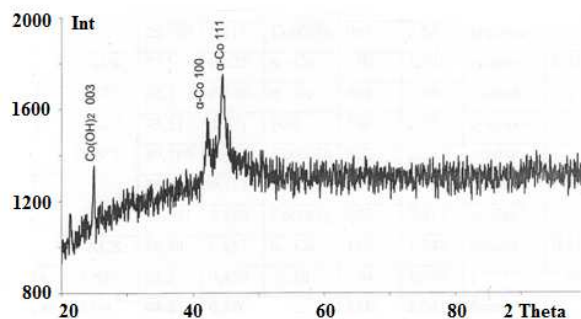

Figure 1. X-ray pattern of alloy Co-Ni-Mn (o-ACK, t=20^{0}C, g=1.5, f=8.3 kHz (HFAC))

Table 1. Experimental and calculated phase composition of Co-Ni-Mn alloys

№	Electrolysis conditions, additive	Chemical alloy content, %			Calculated phase	Experimental phase	The relative error of the experimental criteria for phase formation to the calculated, ±%	New experimental phases
		Co	Ni	Mn				
1	Stationary method	p-ASA, 80°C	61.6	37.7	0.7	β-Co α-Co	β-Co; α-Co; Co(OH)$_2$	±2.11 ÷ ±5.2	Co(OH)$_2$
2		p-ASA, 60°C	75.1	23.6	1.3	α-Co>> β-Co	α-Co>> β-Co Co(OH)$_2$	±1.75 ÷ ±2.86	Co(OH)$_2$
3	Non-stationary method	o-ASA, 20°C	67.1	30.8	2.1	α-Co>> α-Mn	α-Co>> α-Mn Co(OH)$_2$	±2.03 ÷ ±5.5	Co(OH)$_2$
4		o-ASA, 20°C	76.0	21.4	2.6	α-Co>> α-Mn	α-Co>> α-Mn Co(OH)$_2$	±6.41 ÷ ±7.25	Co(OH)$_2$

Under all the electrolysis conditions studied, Co-Ni-Mn alloy coatings based on cobalt were obtained. Manganese is a part of a solid solution of α-Co up to 1.3% wt (SM). At a higher content, the Mn crystals form the free α-Mn phase (HFAC). For comparison, Table 1 shows the data for the Co-Ni-Mn alloy at a steady-state current. As can be seen from Table 1, SM coatings lose to alloys obtained by the HFAC method, both by the chemical content (Mn does not form a separate phase) and by the phase composition. At steady-state current, precipitates are obtained containing additional phase β-Co.

The atomic-force microscopy method showed that Co-Ni-Mn crystals have a nanostructure. The nanoscale structure is provided by the dispersed Co(OH)$_2$ particles, which form rings (Figure 2a) and prevent the coarsening of nanocrystals.

This conclusion is confirmed by the data on the internal structure of the coatings (Fig. 2b). One of the most important characteristics of the structure is the chemical composition. The incorporation of isomeric additives contributes to the enrichment of Co-Ni-Mn alloys with cobalt.

It is known that the structural characteristics directly affect the operational properties.
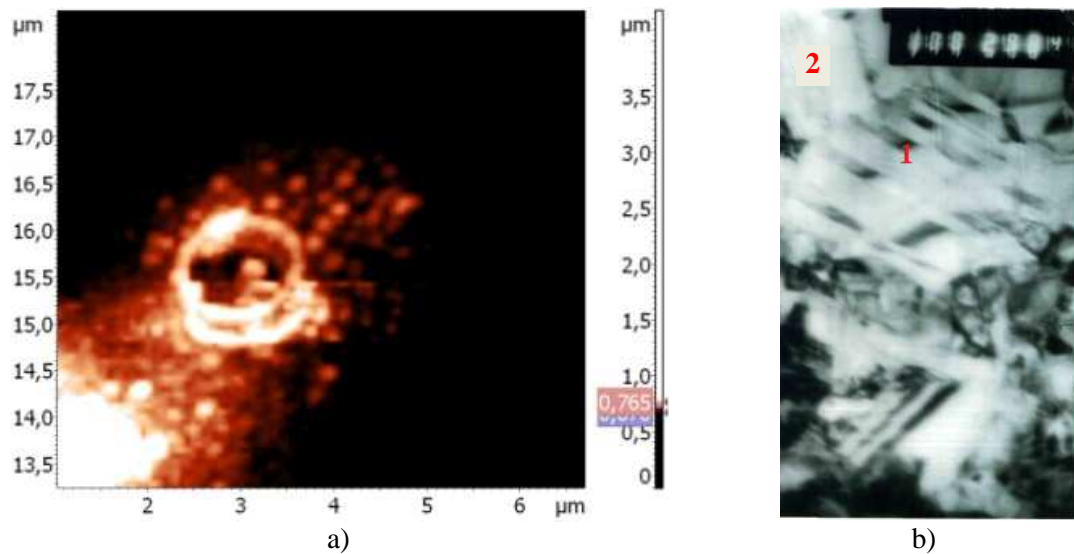
a)   b)

Figure 2. The nanostructure of the surface of the Co-Ni-Mn alloy:
a) phase contrast, rings (HFAC); b) internal structure (HFAC):
1 – α-Co phase (dark crystals), 2 – amorphous phase Co(OH)$_2$ (white formations).

4. Magnetic properties study

The magnetic properties of Co-Ni-Mn films were judged from the coercive force (Hc) (Table 2) and the domain structure (Fig. 3).

Table 2. Physico-mechanical properties of Co-Ni-Mn and Co-Mn alloys

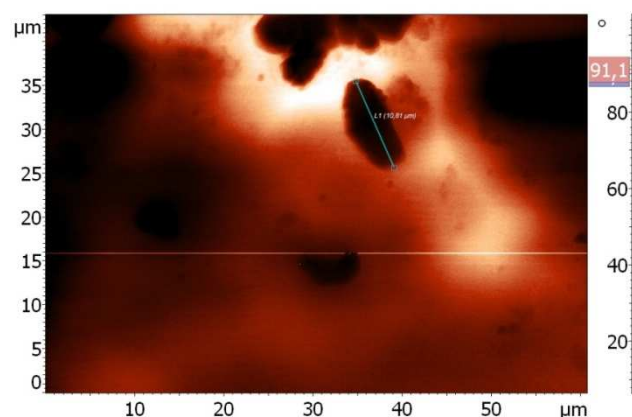| №	Alloy / Additive	H_μ, MPa	H_c, A/m	d_{Co}, nm	Phase
1	**Co-Ni-Mn o-ASA (HFAC)**	**555**	**1050.0**	**12**	**α-Co >> α-Mn, Co(OH)$_2$**
2	Co-Ni-Mn p-ASA (SM)	395	1930.8	27	α-Co, β-Co, Co(OH)$_2$ a lot
3	Co-Mn o-ASA (SM)	308	1810.4	30	α-Co, α-Mn, Co(OH)$_2$ a lot
4	Co–Mn o-ASA (HFAC)	447	1230.0	15	α-Co >> Co(OH)$_2$

Figure 3. Domain structure of the Co-Ni-Mn alloy (HFAC)

To evaluate the influence of the alloy components on the ferromagnetic properties, the distribution of magnetic field sources over the sample surface was studied (Fig. 3).

Polycrystals of the alloy consist of individual monocrystals having a high domain structure. The domain structure is typical for both α-Co crystals and smaller α-Mn particles.

The analysis of the physico-mechanical properties of the Co-Ni-Mn and Co-Mn alloys obtained using the HFAC and SM methods (Table 2) showed that an increase in the cobalt content in the alloy leads to an increase in the coercive force (Hc), but when a large amount of $Co(OH)_2$ appears, the amorphous phase leading to a 2-fold decrease in Hc begins to play the key role.

The magnetic films should have sufficient microhardness H_μ. This indicator, like H_c, indicates that the SM is losing to the HFAC method, and the ternary alloy is superior in all parameters to the binary one.

As one can see, the HFAC method has a clear advantage over the SM. Coatings with α-Co >> α-Mn phases are obtained. The content of manganese in the alloy is 2.1 – 2.6% wt. Due to the anode component, there is a minimum amount of the amorphous phase $Co(OH)_2$.

The surface structure of the Co-Ni-Mn precipitate looks like an ordered nanocrystalline structure. An explicit texture along the axis is seen (Fig. 2b). The best coating is obtained under the following conditions: porosity $g=I_a/I_k$ (I_a, I_k – the anode and cathode current rates, respectively) g = 1:5; frequency f = 8.3 kHz (Fig. 2, Table 2 №1).

Thus, it can be concluded that α-Co and α-Mn phases mainly affect the ferromagnetic properties, and the amorphous phase contributes to the reduction of the coercive force of the Co-Ni-Mn electrolytic coating. The optimum content of the $Co(OH)_2$ phase is maintained by the HFAC method and the addition of o-ASA to the precipitation electrolyte.

5. Conclusion

The study showed that the Co-Ni-Mn alloy coatings obtained with the given structure and magnetic properties is the most promising with the complex approach: theoretical forecasting of the phase composition and the ratio of the metal ions (Co^{2+} : Ni^{2+} : Mn^{2+}) in the electrolyte, the new deposition method – HFAC, selection of additives by the adsorption theory and modern physical methods for studying the phase composition, nanostructure and magnetic properties.

Based on the preliminary model forecasting of the metal ions ratio in the electrolyte and the phase composition of the coating, Co-Ni-Mn alloy precipitates having specified magnetic properties were obtained by a high-frequency alternating current (HFAC) method. It was established that the use of the adsorption theory based on the proximity of the ionization potentials (IP) of additives to the IP of the co-precipitated metals, the use of the bifunctional additive o-ASA allows the directional formation of the Co-Ni-Mn phase composition.

Using the HFAC method, Co-Ni-Mn galvanic precipitates with a given phase composition (α-Co >> α-Mn, $Co(OH)_2$), nanostructure, required dimensional effects (d, nm) can be obtained due to the controlled content of the amorphous phase $Co(OH)_2$.

Based on the obtained magnetic properties, the Co-Ni-Mn alloy can be recommended for the production of memory cards and spatially-modulated systems.

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