

Model forecasting of phase composition of electrolytic alloys Co-Ni-Mn (part 1)

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Abstract. With the help of four criteria for phase formation, a model forecasting of the phase composition of electrolytic alloy Co-Ni-Mn was carried out; the expected phases were calculated. The boundaries of the chemical content of the metal-solvent (Co) in these phases are determined, depending on the ratio of metal ions in the electrolyte of deposition. Model forecasting of the phase composition of Co-Ni-Mn alloys makes it possible to predict the type and number of Co phases (hexagonal close-packed - HCP- α -Co, face-centered cubic - FCC- β -Co) depending on the mole fraction of the solvent metal (Co). In the first approximation, the forecast allows one to determine the phase and chemical composition of the coating, which corresponds to the specified operational properties.

1. Introduction

Modern production places high demands on structural materials, such as hardness, cold resistance, catalytic and magnetic properties, etc. In turn, the latter directly depends on the structure of the material (phase and chemical composition, nanostructure, surface morphology).

An important role among the promising materials is played by galvanic coatings. Most often, binary alloys are used in practice, but selectivity and quality of high-alloy steels is higher.

Ternary alloys are preferable, but their introduction is inhibited due to the complex phase and chemical composition, the difficulties of experimental research, structural features and a number of other factors.

The solution of this most important task becomes possible with the help of preliminary theoretical modeling of the phase composition and the chemical content of the coating, taking into account the specified operational properties.

The aim of the work is to forecast the phase and chemical composition of ternary electrochemical alloys using the example of Co-Ni-Mn alloy with some given physicochemical properties.

Research objectives:

1. Forecasting the phase composition and chemical content of metals in the Co-Ni-Mn alloy using four phase-formation criteria, depending on the ratio of the component ions in the deposition solution.
2. Forecasting the ratio of the $\text{Co}^{+2}:\text{Ni}^{+2}:\text{Mn}^{+2}$ content in the electrolyte corresponding to the desired phase composition for the specified operational properties.

2. Materials and methods

Properties of electrochemical alloys of the same chemical composition often do not coincide with the properties of pyrolytic alloys. First of all, this is due to the phase composition of galvanic sediments,



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which are obtained in the nonequilibrium form of metastable phases.

To control the phase composition, it is necessary to have certain criteria.

For binary mixed crystals, Hume-Rosery [1] suggested that metals could form mixed crystals if their atomic radii differ by no more than 15%. When estimating the distortion of the structure of the components crystal lattice, it is necessary to take into account the differences in the dimensions of the atoms, so Hume-Rosery [1] introduced size factor $n_d = d_1/d_2$ (d_1, d_2 - the diameter of the first and second components) for solid solutions.

Mott [2], additionally introduced the volume ratio ($V_1:V_2$), characterizing the elastic lattice distortion, in n_d .

Later, Gordy [3] introduced energy factor n_e to take into account the electronic interaction.

The phase formation criteria for binary electrochemical alloys were proposed by A.I. Zhikharev and I.G. Zhikhareva [4], and for ternary ones, I.G. Zhikhareva and V.V. Schmidt [5-7] forecasted the phases of solid solutions using four criteria: n_s - entropic, n_d - dimensional, n_e - energy factor, $n_o = n_d + n_e$ - general factor.

Unlike the criteria proposed in [1-2] for cast alloys, the authors of [5] took into account the chemical content of the components in the electrolyte and alloy in calculating n_s and n_d , and in n_s , the correction for the mixing entropy was additionally introduced. Thus, the calculation of n_s in the research was carried out using formulas [8]:

$$n_s = \frac{\Delta S_{Me}^T}{\Delta S_{al}^T} \quad (1), \text{ where}$$

$$S_{al}^G = S_1^G x_1 + S_2^G x_2 + S_3^G x_3 - R[x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3];$$

$$S_{al}^C = S_1^C y_1 + S_2^C y_2 + S_3^C y_3 - R[y_1 \ln y_1 + y_2 \ln y_2 + y_3 \ln y_3], \text{ where}$$

S_i^G, S_i^C - entropy of the i -th metal in the gas and crystalline phase, respectively [8].

n_s characterizes the degree of difference in the chemical bond:

$$n_d = [(d_1/d_{al})^3 - 1 + y_1 \ln(y_1) + y_2 \ln(y_2) + y_3 \ln(y_3)] + [(V_1/V_{al}) - 1] \quad (2) [8],$$

where V_1 - volume of metal-solvent; V_{al} - the volume of a mixed crystal, calculated from the additivity condition; y_i - molar fractions of metals in the alloy.

n_d characterizes the magnitude of the resulting distortions of the crystal lattice.

$$n_e = 0,75(U_1 - U_{al}) \cdot (1 - n_d) \quad (3),$$

where U_1, U_{al} - the relative ionization potential of a metal and an alloy in relation to the ionization potential of hydrogen [8].

n_e characterizes the possibility of a redistribution of the electrons of the outer shells and a change in the configuration of the electron shells [8].

General factor $n_o = n_d + n_e$ (4), where n_o characterizes the difference in the geometric dimensions of atoms and the density of compound (n_d) and the distortion of the electron shells (n_e).

The main task in forecasting the Co-Ni-Mn phase composition was to obtain a coating with a maximum α -Co phase content and a minimum α -Mn phase content. For this, the ratio of the metal ions in the electrolyte was forecasted at first, at which the maximum extent of the α -Co phase boundaries is expected. The widest range of the existence of the HCP phase of Co is expected at a ratio of $\text{Co}^{+2}:\text{Ni}^{+2}:\text{Mn}^{+2} = 0.6:0.3:0.1$.

The phase composition of electrodeposited Co-Ni-Mn alloys was determined using equations (1) - (4). The calculation takes into account that alloys based on cobalt have a unique feature since Co is able to be in the alloy in the form of a hexagonal close-packed phase (hcp) α -Co, face-centered cubic (fcc) - β -Co) or a mixture of α -Co + β -Co [9-10], i.e. metal Co can be considered as a pseudoalloy. Theoretically, the type of phase can only be determined by comparing the work of nucleation (two-dimensional or three-dimensional) A_{Co}^α and A_{Co}^β . If $A_{Co}^\alpha < A_{Co}^\beta$, phase α -Co prevails. If $A_{Co}^\alpha \approx A_{Co}^\beta$, the presence of both phases is equally probable. If $A_{Co}^\alpha > A_{Co}^\beta$, then the alloy mainly contains a FCC-

phase. According to theoretical calculations, the α -Co phase is the main phase; the FCC-phase of Co is metastable.

The formation of solid solutions is indicated by values $n_s = 0.992 \div 1.001$; and the appearance of three-phase coatings is indicated by higher negative values of n_d and n_o (Table 1).

Comparison of the calculated dependences of the phase formation criteria on the molar fraction of Co in the Co-Ni-Mn alloy with a polynomial dependence (Fig. 1) showed their satisfactory agreement.

Table 1. Phase forecasting in the Co-Ni-Mn alloy according to the phase-formation criteria

№	Molar fraction of components in the alloy			Phase formation criteria				Forecasted phase
	Y ₁	Y ₂	Y ₃	n _s	n _d	n _e	n _o	
	Co	Ni	Mn					
1	0.769	0.218	0.013	0.992	-0.585	0.067	-0.518	α-Co
2	0.760	0.228	0.012	0.992	-0.593	0.069	-0.523	α-Co
3	0.704	0.274	0.022	0.997	-0.680	0.092	-0.588	α-Co >> α-Mn
4	0.686	0.287	0.027	0.998	-0.709	0.100	-0.609	(β-Co), α-Co >> α-Mn
5	0.682	0.297	0.021	0.998	-0.696	0.099	-0.597	(β-Co), α-Co >> α-Mn
6	0.660	0.312	0.028	1.000	-0.732	0.109	-0.623	(β-Co), α-Co >> α-Mn
7	0.654	0.333	0.013	0.997	-0.690	0.105	-0.586	α-Co
8	0.639	0.333	0.028	1.001	-0.746	0.117	-0.629	α-Co, α-Mn
9	0.607	0.385	0.008	0.998	-0.696	0.118	-0.578	α-Co
10	0.585	0.391	0.024	1.001	-0.761	0.133	-0.628	(β-Co), α-Co >> α-Mn
11	0.554	0.434	0.012	1.000	-0.728	0.137	-0.592	(β-Co), α-Co
Co ²⁺ :Ni ²⁺ :Mn ²⁺ =0.216: 0.28: 0.504								

The boundaries of the phase homogeneity of a solid solution can be judged from the kinks in the dependences $n_i - y$. Both the calculation data (Table 1) and the approximating curves indicate that in the Co-Ni-Mn alloys (when $y_{\text{Co}} = 0.654\text{--}0.704$), the formation of two phases α -Co, α -Mn is possible.

As is seen from Fig. 1, phase-formation criteria n_s , n_d and n_o give practically identical boundary conditions for the existence of α -Co and α -Mn phases. This indicates the prevailing influence of the chemical bond, geometric dimensions and density of matter on the limits of existence of these phases in comparison with redistribution of electronic shells and distortion of their configuration (n_e).

Thus, a model forecast of the Co-Ni-Mn ternary alloy was carried out at a certain ratio of metal ions in the electrolyte according to four phase-formation criteria. The boundaries of the homogeneity of the calculated phases were determined.

The second task of the theoretical research was to determine the phase and chemical composition of the Co-Ni-Mn alloy, which corresponds to specified operational properties.

It is known that Co-Ni-Mn alloy, on the one hand, has magnetic properties, and on the other hand, it is a heterogeneous catalyst for the Fischer-Tropsch reaction.

To ensure high magnetic properties, the alloy should possess a hexagonal close-packed lattice and contain a small amount of α -Mn ($2 \div 2.4$ mass %). The alloys (Table 1, №3 and №8) correspond to these conditions.

On the contrary, the main phases for the catalyst are β -Co >> α -Mn (Table 1, №4 – №6, №10).

3. Conclusion

The theoretical calculation of the phase composition of the Co-Ni-Mn alloy allows us to forecast not only the phase composition depending on the chemical content of metals in the alloy and the ratio of their ions in the electrolyte, but also forecasts, in the first approximation, the chemical and phase composition corresponding to the specified operational properties.

To estimate the accuracy of the forecasted modeling of the phase composition, it is required to

compare the calculated data with the experimental structural characteristics.

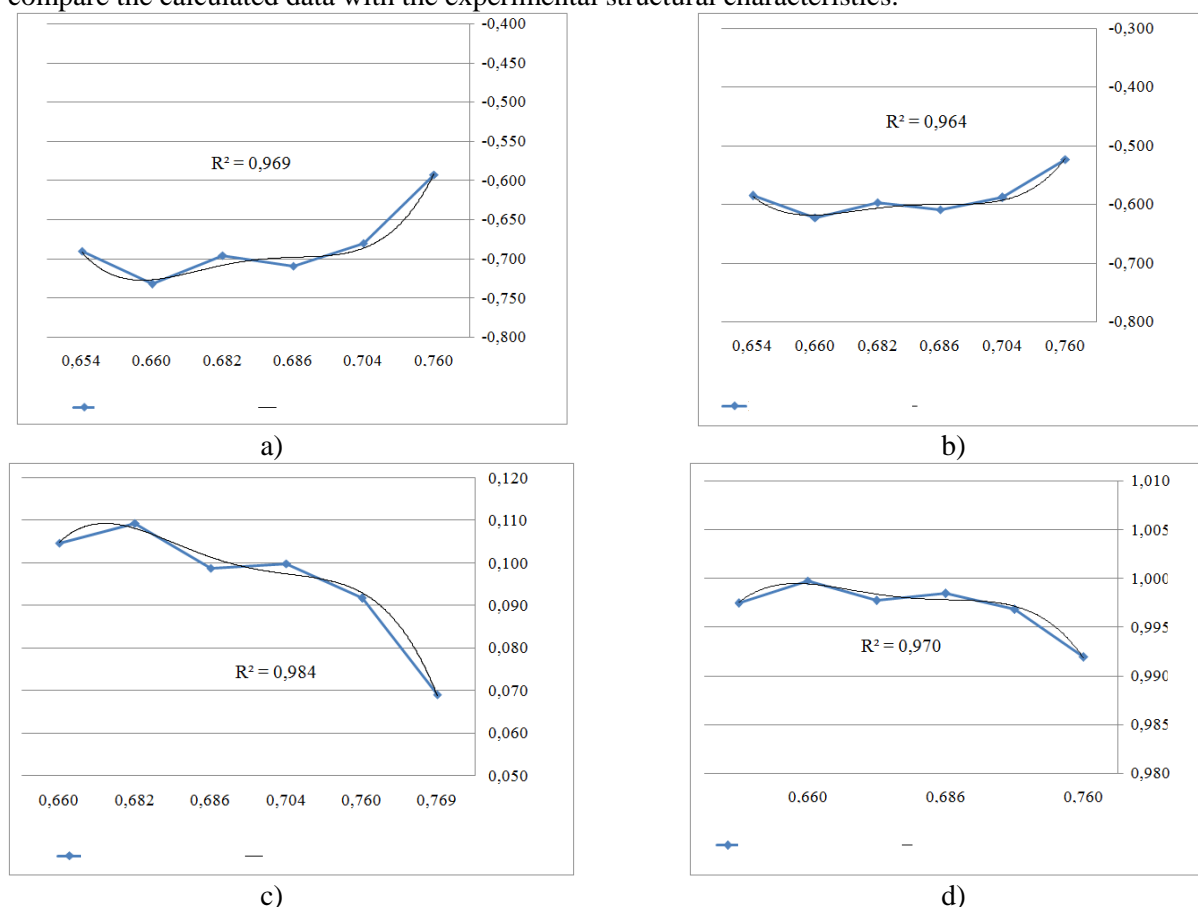


Figure 1. Dependence of the phase formation criteria on the molar fraction of Co in the Co-Ni-Mn alloy: a) dimensional; b) general; c) energy; d) entropic.

The relationship between the predicted structural characteristics and the given magnetic properties is described in the publication "Structure and magnetic properties of Co-Ni-Mn alloy coatings (part 2)" by Shmidt V.V., et al.

References

- [1] Hume-Rothery W 1966 *Success and physical sciences*. **88(1)** 125-128
- [2] Vozdvizhensky V M 1973 *In: General regularities in the structure of phase diagrams of metal systems (Moscow: Nauka)* p 103-109
- [3] Gordy W, Thomas W 1956 The Nature of Chemical Bond *J. Chem. Phys.* **124** 439-443
- [4] Zhikharev A I, Zhikhareva I G 1994 *Oriented electrocrystallization* (Tyumen: TGNGU)
- [5] Zhikhareva I G, Schmidt V V 2012 *Prediction of the structure and properties of ternary electrolytic alloys* (LAP LAMBERT Publishing)
- [6] Schmidt V V 2005 *Application of modeling in predicting the structure and physico-mechanical properties of triple electrodeposited Ni-Fe-Cr, Ni-Co-Cr and Fe-Ni-Co alloys* (Tyumen: TGNGU)
- [7] Zhikhareva I G, Schmidt V V 2003 Prediction of the macrostructure of the triple electrodeposited Ni-Fe-Cr alloy *Chemistry and chemical technology*. **46(3)** 100–103
- [8] Schmidt V V, Shchipanov V P, Smirnova N V, Zhikhareva I G, Shilov A A 2017 Directional structuring of ternary electrochemical Ni-Co-Cr and Cr-Ni-co alloys *J. of Applied Engineering Research*. **12(15)** 6127–6133
- [9] Armyanov S 1971. *Izv. Department. chem. Sciences Bolg. AN*. **4(2)** 203–210
- [10] Vitkova S 1975 *Electrodep. and Surface Treatment*. **3(4)** 225–234