

Directional Structuring of Ternary Electrochemical Ni-Co-Cr and Cr-Ni-Co Alloys

V.V. Schmidt, V.P. Shchipanov, N.V. Smirnova, I.G. Zhikhareva, A.A. Shilov

Industrial University of Tyumen, Russia.

Abstract

Theoretical prediction of the phase composition of ternary Ni-Co-Cr and Cr-Ni-Co alloys was carried out using four phase-formation criteria (n_i). The analysis of approximating dependences $n_i - y$ (y – the mole fraction of chromium in the alloy) shows a satisfactory coincidence of the calculated dependences with the polynomial. Refined dimensional (n_d) and general (n_o) criteria for phase formation are proposed, which made it possible to estimate the range of the extent of solid solutions in Cr-Ni-Co alloys. It has been found that, due to the use of various polyfunctional additives, both low-chromium ($Cr \leq 25$ mass %) with a nanostructure and high-chromium ($Cr \approx 60$ mass %) coatings can be obtained from the electrolyte with the same ratio of $Ni^{2+} : Co^{2+} : Cr^{3+}$ ions in solution. It is recommended to use coatings with a Ni-Co-Cr alloy as a structural material for critical parts in radio electronics, and a Cr-Ni-Co alloy in microelectronics for the production of resistor and strain-resisting elements.

RELEVANCE

Modern engineering places a high demand on new technologies and materials. An important place among promising materials is occupied by electrolytic coatings with alloys with increased strength, corrosion and special properties. For economy, selectivity and productivity, three-component alloys are preferred over binary alloys. But the task is complicated due to the complex composition of the electrolyte, the laboriousness of determining the phase structure, structural defectiveness and other criteria.

The solution of this topical problem becomes possible when combining mathematical modeling of the emerging structure, which allows describing its main regularities and predicting the expected operational properties, and experimental studies capable of characterizing the individual features of the coating structure and determining the optimum conditions for obtaining materials with the required physicochemical properties.

To solve the first problem - predictive modeling of the phase and chemical composition of the coating - reliable criteria for phase formation are required.

The second task - experimental research - is based on the correct choice of the research method and the electrolyte (additive) composition in accordance with the goal.

The goal of this paper is to predict the phase, chemical composition and production of electrodeposited coatings with Ni-Co-Cr and Cr-Ni-Co alloys with specified physical-mechanical properties.

RESEARCH OBJECTIVES:

1. Theoretical prediction of a given phase composition of Cr-Ni-Co alloys using four phase-formation criteria.
2. The choice of surface-active agents (surfactants) with various polyfunctional groups for deposition electrolyte, capable of providing a different composition of the alloy with the same initial composition of metal ions in solution.

Development of a Ni-Co-Cr and Cr-Ni-Co coating with increased microhardness due to the obtaining of a nanostructure.

INTRODUCTION

Properties of structural materials are primarily determined by their surface and internal structure. The latter is characterized by a number of parameters, which are difficult to determine in practice.

Properties of alloys of the same composition, obtained by casting and a galvanic method, do not usually coincide. First of all, this is due to the phase structure of electrolytic coatings, which are obtained in the nonequilibrium form of metastable phases.

To control the phase composition of ternary alloys, it is necessary to have reliable criteria.

It is known [1] that the possibility of forming binary mixed crystals can be judged on the basis of the Hume-Rothery dimensional correspondence theory, according to which metals are capable of forming a common crystal lattice if their radii differ by no more than 15%.

Hume-Rothery [2] introduced the dimensional criterion $n_d = d_1/d_2$ (d_i – the diameter of the component) for solid solutions. Mott [3] introduced the volume ratio ($V_1:V_2$) in n_d which characterizes the elastic distortion of the crystal lattice. Gordy [4] introduced the energy criterion n_e which takes into account electronic interaction. But all these works were of a qualitative nature and did not allow us to estimate the number and extent of the phases.

With few exceptions [5], the criteria for the phase formation of electrolytic alloys, which determine the appearance of a general crystal lattice (solid solutions and intermetallides), are absent.

A.I. Zhikharev and I.G. Zhikhareva proposed criteria for phase formation which allow one to view the possibility of forming a continuous series of solid solutions, a phase of a solid solution or a phase with limited solubility of the components in each other for binary alloys [5].

Predicting of the intermetallic phase in binary alloys was carried out in [6, 7].

I.G. Zhikhareva and V.V. Schmidt predicted the phases of solid solutions for ternary alloys [8, 9] using four phase-formation criteria: n_s – entropy, n_d – dimensional, n_e – energy and n_o – general.

In addition to similar criteria for binary alloys in [8]:

$$n_s = \Delta S_{Me} / \Delta S_{Al} \quad (1)$$

correction for entropy of mixing was introduced:

$$S_{al}^g = S_{x_1}^g + S_{x_2}^g + S_{x_3}^g - R[x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3] \quad (2)$$

$$S_{al}^c = S_{y_1}^c + S_{y_2}^c + S_{y_3}^c - R[y_1 \ln y_1 + y_2 \ln y_2 + y_3 \ln y_3], \quad (3)$$

where S^g, S^c – entropy in the gas and crystalline phase, respectively.

n_s characterizes the degree of difference in the chemical bond.

Instead of the volumetric (n_v) criterion for binary depositions, an improved dimensional criterion n_d for phase formation was proposed:

$$n_d = [(d_1/d_{cn})^3 - 1 + y_1 \ln(y_1) + y_2 \ln(y_2) + y_3 \ln(y_3)]$$

$$+ [(V_1/V_{al}) - 1] \quad (4)$$

where V_1 – the volume of solvent metal; V_{al} – the alloy volume calculated from the additivity condition; y_i – the mole fractions of alloy components; n_d – characterizes the magnitude of the resulting distortions of the crystal lattice of components.

n_e – the energy criterion [8] characterizes the possibility of redistribution of the electrons of the outer shells and a change in the configuration of the electron shells:

$$n_e = 0.75(U_1 - U_{cn}) \cdot (1 - n_d) \quad (5)$$

where U_1, U_{cn} – the relative ionization potential of a metal and an alloy with respect to the ionization potential of hydrogen.

n_o – general (full) criterion:

$$n_o = n_d + n_e, \quad (6)$$

consists of three components: two relate to the difference in the geometrical dimensions of the atoms (d_1/d_{cn}) and the density of the matter (both are taken into account in the dimensional criterion) and the third term (n_e) characterizes the distortions of the electron shells due to the difference in the electron density of the matter.

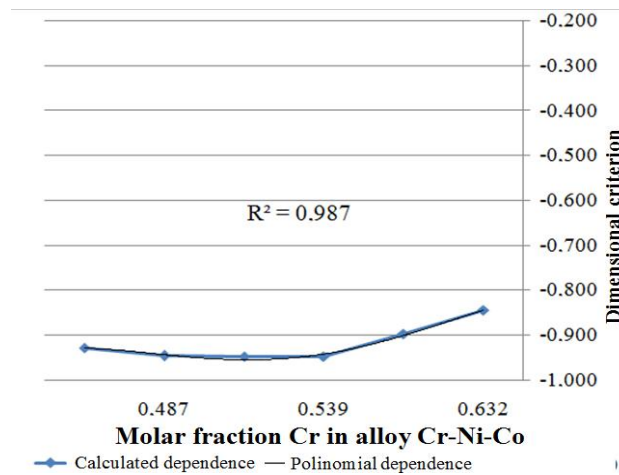
THEORETICAL PART

According to the phase diagram for the binary Ni-Cr alloy, the formation of continuous solid solutions of β -Ni and α -Cr is possible. For the Ni-Co alloy, respectively, β -Ni, α -Co and β -Co.

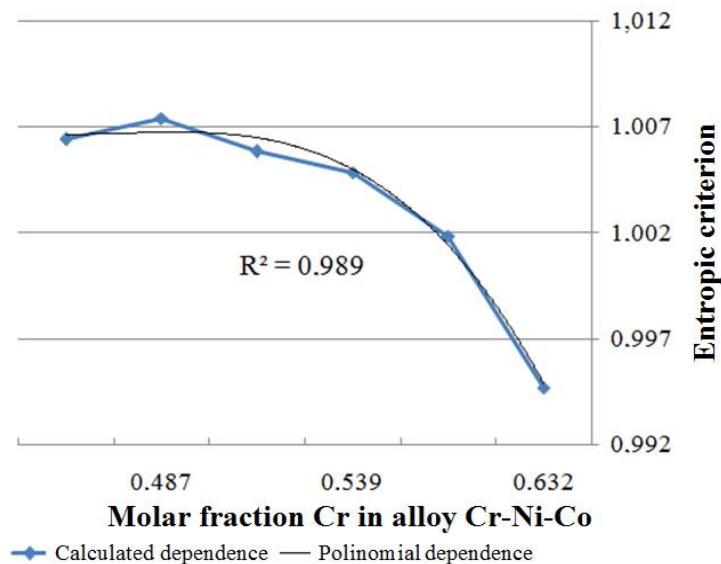
For the ternary Cr-Ni-Co alloy, a more complex phase composition should be expected. The theoretical calculation based on the phase-formation criteria confirmed this assumption (Fig. 1).

The dependence of the phase formation criteria on the mole fraction of chromium in the alloy made it possible to determine and refine the boundaries of the phase region of the solid solution and conclude that the magnitude of the distortions of the crystal lattice of the components has a smaller effect on the phase composition than the difference between the chemical bond.

The entropy criterion predicts four phases (the same result is given by the energy and general criteria), and the dimensional one predicts three phases.



(a)



(b)

Figure 1. Dependences of the phase-formation criteria on the mole fraction of Cr in the Cr-Ni-Co alloy:

a) entropy (n_s): $y = 0.00014x^3 - 0.002x^2 + 0.012x + 0.984$; (7)

b) dimensional (n_d): $y = -0.00071x^4 + 0.009x^3 - 0.030x^2 - 0.019x - 0.803$. (8)

(Entropy criterion; Mole fraction of Cr in Cr-Ni-Co alloy; Calculated dependence; Polynomial(Calculated) dependence; Dimensional criterion)

Theoretical calculations of the phase composition of Cr-Ni-Co alloys have been verified by experimental studies.

RESEARCH METHOD

The chemical content of the components in the alloy was carried out using a photoelectrocolorimetric method. The measurement error is 5 ÷ 10%.

The X-ray phase analysis was carried out on a DRON-6

diffractometer (Co $K\alpha$ -radiation, Ni-filter).

The parameters of the elementary cells of the cubic lattices were determined with an accuracy of $\pm (0.0001 \div 0.0002)$ nm, and for hexagonal syngonies with an accuracy of ± 0.002 nm using the PDW in 4.0 complex [10].

The nanostructure of the surface and the phase contrast were studied by the atomic force microscopy (AFM) using a probe nanometer laboratory "Ntegra", controlled by the Nova program. Scanning error was not more than 1 nm.

Chrome coatings have found wide application in a variety of industries due to their high heat resistance, hardness and strength.

EXPERIMENTAL PART

Cr-Co-Ni alloys, according to calculations, can be low-chromium (up to 25 mass% Cr) and high-chromium (≈ 60 mass% Cr).

We have shown that they can be obtained from electrolyte of the same composition, but with different additives (Table 1).

Sally [10] and Schluger [11] consider the presence of dispersed hydroxide or oxide inclusions of chromium as the main criteria determining the composition of chromium alloys. In this paper, in order to increase the amount of nanostructured crystals and to obtain a regulated amount of amorphous phase, ternary alloys and special additives were used.

Table 1: Phase composition of ternary electrodeposited Ni-Co-Cr and Cr-Ni-Co alloys

Alloy additives	Metal content in the alloy, mass. %			Calculated phase	Experimental phase	Relative error of exp. criteria to phase formation to calculated	Note: New exp. phases
	Ni	Co	Cr				
Ni-Co-Cr urea	50.0	37.5	12.5	β -Ni+ α -Co	β -Ni+ α -Co+ β -Co	$\pm 1.4 \div \pm 3.5$	
	37.5	43.5	19.0	β -Ni+ α -Co+ β -Co	β -Ni+ α -Co+ β -Co		
	32.0	48.5	19.5	β -Ni+ α -Co+ β -Co	β -Ni+ α -Co+ β -Co		
Ni-Co-Cr urea	42.1	40.9	17.0	β -Ni+ β -Co	β -Ni+ α -Co+ β -Co	$\pm 1.25 \div \pm 3.75$	AMC
	58.7	16.3	25.0	β -Ni+ β -Co	β -Ni+ α -Co+ β -Co + AMC		
Cr-Ni-Co p-ASA	17.7	19.1	63.2	β -Ni+ β -Co+ α -Cr	β -Ni+ α -Cr+ β -Co + CrO ₃	$\pm 1.5 \div \pm 4.5$	CrO ₃
Cr-Ni-Co H-acid	31.4	23.6	45.0	β -Ni+ α -Co+ α -Cr	β -Ni+ α -Cr+ α -Co + CrO ₃	$\pm 1.45 \div \pm 3.9$	CrO ₃
Cr-Ni-Co H-acid	32.4	15.4	52.2	β -Ni+ β -Co+ α -Cr	β -Ni+ α -Cr+ β -Co + CrO ₃	$\pm 1.33 \div \pm 4.73$	CrO ₃

Ratio of ions in electrolyte: Cr²⁺: Ni²⁺:Co²⁺=0.47:0.41:0.12

As a regulator of amorphous Cr inclusions in the Cr-Co-Ni alloy, such surfactants were used as: H-acid, urea, p-ASA.

Alloys in the presence of urea are low-chromium (up to 25 mass% Cr), and in the presence of p-ASA - high-chromium (up to 60 mass% Cr). Accordingly, the phase composition differs.

In the presence of urea, an alloy contains β -Ni, β -Co phases and a polymer film Cr(OH)₃(H₂O)·2H₂O (AMS-amorphous metastable system) (Table 1, No. 1, Fig. 2a), i.e., urea inhibits the discharge of Cr³⁺ ions.

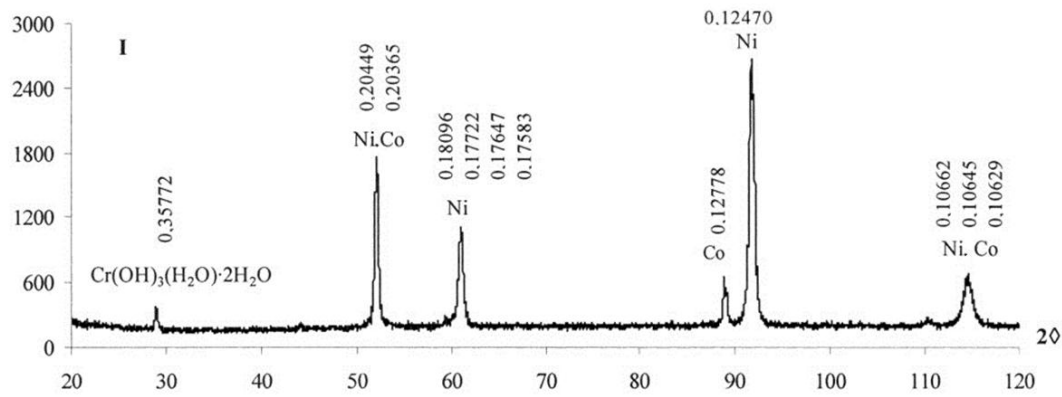
In the presence of p-ASA, an alloy contains three phases (α -Cr, β -Co, β -Ni) and an additional phase of CrO₃ (Fig. 2b), i.e., predominantly inhibits the discharge of Ni²⁺.

When comparing the depositions obtained in the presence of urea but with a different content of components, it follows that although the alloys are two-phase, the phases themselves are

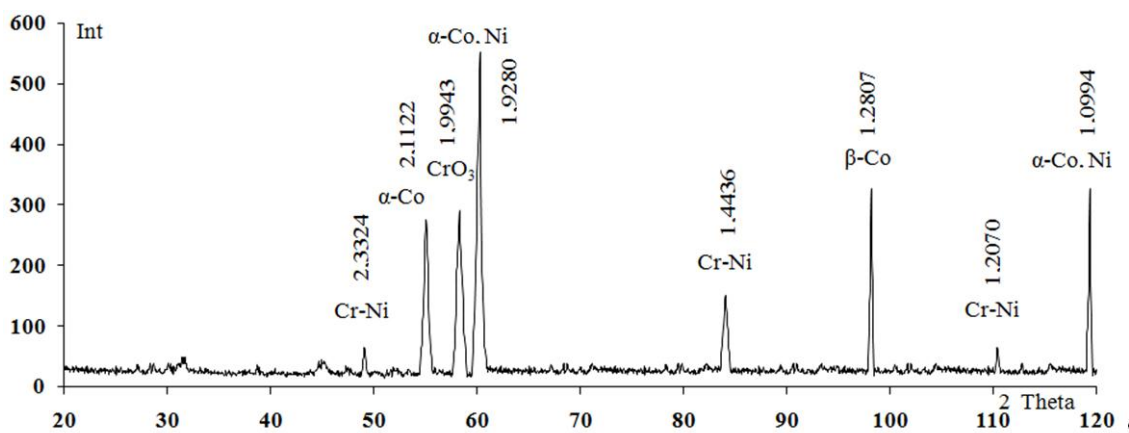
different.

Additives lead to a change in both chemical and phase composition. Comparison of the experimental phases with the calculated ones (by the phase-formation criteria) showed a good convergence of the results. An exception is the additional phase of CrO₃ and an amorphous-metastable system.

The Ni-Co-Cr alloy has a nanostructure. On the cross-sectional diagram of the section, an unusual regularity was observed: sections of the alloy whose boundaries are 0.7-1 μ m in width are enriched in chromium by 4-8% more than in their central regions. It is possible that the zones enriched with [Cr(OH)₃(H₂O)·2H₂O] serve as a matrix for nanoparticles of the Ni-Co-Cr alloy with dimensions of 50 nm. It was suggested that the formation of ultradisperse coating particles was facilitated by films of chromium hydroxides, which cause inhibition of electrocrystallization.



(a)



(b)

Figure 2: Diffractogram of the Ni-Co-Cr alloy:
 a) urea ($t = 60^\circ\text{C}$, $i_k = 5 \text{ A/dm}^2$); b) p-ASA ($t = 20^\circ\text{C}$, $i_k = 10 \text{ A/dm}^2$).

The experimental boundaries for the formation of phases coincided with the calculated ones with an error of $<5\%$ (Table 1).

The relative error Δl , % of the four phase-formation criteria to the calculated ones was determined by the formula:

$$\Delta l = \frac{n_i^T - n_i^E}{n_i^T} \cdot 100\% \quad (9)$$

where n_i^T, n_i^E – theoretical and experimental criterion of phase formation, respectively.

The ultimate goal of the study is to obtain Cr-Ni-Co coatings with a maximum H_μ .

Microhardness is a structure-sensitive property, therefore, it must be determined primarily by chemical and phase compositions.

Judging by the microhardness of pure metals [12] (Table 2), one would expect the highest values of microhardness for the alloy $\text{Cr}_{63,2}\text{Ni}_{22,0}\text{Co}_{14,8}$.

However, as can be seen from the results of the studies, two-phase depositions ($\beta\text{-Ni} + \alpha\text{-Cr}$) containing the amorphous phase $\text{Cr(OH)}_3(\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}$ and possessing the nanostructure with the lowest chromium content ($H_\mu = 985 \text{ MPa}$) have the highest microhardness (Table 3, No. 8).

Table 2: Microhardness of pure metal coatings

Metals	H_μ , MPa	Source
Ni	160-550	[12]
Co	200-450	[12]
Cr	550-750	[12]

Table 3: Effect of the content of components in Ni-Co-Cr and Cr-Ni-Co alloys on microhardness

Alloy additives	Cathodic current density i_k , A/dm ²	t, °C	Alloy composition, mass. %			Phase composition	H_{μ} , MPa
			Ni	Co	Cr		
Cr-Ni-Co p-ASA	6	20	30.8	32.3	36.9	α -Cr+ α -Co+ β -Ni	387
Cr-Ni-Co p-ASA	9	20	36.6	14.7	48.7	α -Cr + β -Ni	522
Cr-Ni-Co p-ASA	10	20	22.0	14.8	63.2	α -Cr+ α -Co+CrO ₃	590
Cr-Ni-Co p-ASA	11	20	44.1	30.0	25.9	α -Cr+ β -Ni+ β -Co	520
Cr-Ni-Co p-ASA	6	40	23.7	22.4	53.9	α -Cr+ β -Co+ β -Ni	480
Cr-Ni-Co p-ASA	6	80	55.3	18.8	25.9	α -Cr+ β -Ni+ β -Co	410
Cr-Ni-Co H-acid	6	20	22.5	18.9	58.6	α -Cr+ β -Ni+NiO	690
Ni-Co-Cr Urea	6	20	58.7	16.3	25.0	β -Ni+ α -Cr+CrO ₃	985

The highest microhardness among high-chromium alloys is shown by the Cr_{58,6}Ni_{22,5}Co_{18,9} alloy (Table 3, No. 7) corresponding to the α -Cr, β -Ni phases, the additional NiO phase.

Thus, microhardness is primarily affected by the phase composition and the presence of hydroxide and oxide phases: AMS in the case of the Ni-Co-Cr alloy and the CrO₃ phase for the Cr-Ni-Co alloys.

In the first case, the internal structure is characterized by small crystals (d = 50 nm) in the shell of Cr(OH)₃(H₂O)·2H₂O, and in the second case - a high content of chromium oxide CrO₃, giving additional hardness to the coating.

CONCLUSION

- Based on the study of structural properties and microhardness, it is possible to recommend a Ni-Co-Cr alloy for use in radio electronics and as a structural material, and a Cr-Ni-Co alloy for use in microelectronics for resistor and strain-resisting elements.
- Based on the four criteria for phase formation, including the refined dimensional and general criteria for ternary Ni-Co-Cr and Cr-Ni-Co alloys, the ratio of metal ions in solution, the phase composition and the boundaries of phases are predicted.

- It has been established that using the adsorption theory polyfunctional additives (urea, p-ASA, H-acid) are selected, allowing us to directly form the phase composition and nanostructure of the coatings.

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