Hardening of coatings with Ni-Co-Cr alloy dye to nanostructure

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Abstract. The purpose – receiving a nanostructural electrochemical covering Ni-Co-Cr (Cr-Ni-Co) alloy with a high microhardness. The composition of electrolyte (a ratio of ions of metals in solution – Cr58.6Ni22.5Co18.9 (α-Cr + β-Ni + NiO); Ni58.7Cr25.0Co16.3(β-Ni + α-Cr)), optimum phase structure by means of 4 criteria of a phase formation. The nanostructure of d=50 of nanometer is received by means of special multifunctional additives. In the presence of H-acid a covering of Cr-Ni-Co HV = 690 MPa, and for (NH$_2$)$_2$CO additive – HV = 985 MPa possesses. Alloys are recommended for use in radioelectronics and microelectronics for resistor and the strain-resisting elements.

1. Relevance
Modern In technique much attention is paid to hardening of coverings. This problem can be solved due to grain refinement, change of phase, chemical composition. Existence of nanostructure has especially effective effect on a microhardness. As coverings on many responsible details Ni-Co-Cr alloys are used.

The purpose of this work is prediction of phase and chemical composition and receiving nanostructural, electrolytic Ni-Co-Cr alloy with anomalously high microhardness

Primal problems:
1. Prediction of phase structure taking into account a ratio of ions of metals in electrolyte;
2. Ensuring nanostructure of a covering due to selection of the corresponding multifunctional additives;
3. Receiving a covering from high HV due to existence of nanostructure.

2. Introduction
Chromiums found broad application in various industries owing to the high heat resistance, hardness and durability.

The modern technique imposes increased requirements to new technologies and materials. The important place among perspective materials is taken by the electrodeposited coatings alloys with the increased strength, corrosion and special behavior. On profitability, selectivity, efficiency preference is given to ternary alloys in comparison with binary. But the task becomes complicated at the expense of the complex structure of electrolyte, labor input of definition of the phase building, deficiency of structure and other factors.

The solution of this current problem becomes possible at a combination of the mathematical model operation of the formed structure allowing to describe its main regularities and to predict the expected operational properties, and the experimental studies capable to characterize specific features of structure.
of coverings and to define optimal conditions of receiving materials with the required physical-mechanical properties.

For the solution of the first task – expected model operation of phase and chemical composition of a covering – reliable criteria of a phase formation are required.

The second task – the experimental study – is based on the right choice of a research technique and composition of electrolyte (additive) according to a goal.

3. Literature review

Authors [1] on the basis of prediction of phase, chemical composition received the electrodeposition coverings Ni-Co-Cr alloys with the given physical-mechanical properties.

It is known [2] that it is possible to judge a possibility of formation of binary mix-crystals on the basis of the theory of dimensional compliance of Hume-Rothery according to which metals are capable to form the general crystal lattice if their radiuses differ no more, than for 15%.

Hume-Rothery [3] entered a dimensional factor of \( n_d = \frac{d_1}{d_2} \) (\( d_1 \) is diameter of a component) for solid solutions. By Mott [4] the relation of volumes (\( V_1:V_2 \)) characterizing elastic distortion of a crystal lattice was injected into \( n_d \). Gordy [5] entered the power factor of \( n_e \) considering electronic interaction. But all these works had qualitative character and didn't allow to judge quantity and extent of phases.

With rare exception [6] criteria of a phase formation of the electrolytic alloys defining emergence of the general crystal lattice (solid solutions and intermetallic) no.

A.I. Zhikharev and I.G. Zhikhareva offered the criteria of a phase formation allowing to judge a possibility of formation of the continuous number of solid solutions, phases of a solid solution or a phase with limited solubility of components in each other for binary alloys [6].

Prediction of an intermetallic phase in binary alloys was carried out in works [7, 8].

I.G Zhikhareva and V.V. Schmidt carried out prediction of phases of solid solutions for threefold alloys by means of four criteria of a phase formation: \( n_s \) – entropic, \( n_d \) – dimensional, \( n_p \) – power and \( n_o \) – common [1, 9].

In addition to similar criteria for binary alloys in [1]:

\[
\Delta S_M = \Delta S_M / \Delta S_A_i
\]

(1)

correction for entropy of mixing was introduced:

\[
\begin{align*}
S^d_{al} &= S^R x_1 + S^R x_2 + S^R x_3 - R[x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3] \\
S^d_{al} &= S^y y_1 + S^y y_2 + S^y y_3 - R[y_1 \ln y_1 + y_2 \ln y_2 + y_3 \ln y_3],
\end{align*}
\]

(2)

(3)

where \( S^d \), \( S^y \) – entropy in the gas and crystalline phase, respectively.

\( n_s \) characterizes the degree of difference in the chemical bond.

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

\[
n_d = [(d_1/d_2)^3 - 1 + y_1 \ln(y_1) + y_2 \ln(y_2) + y_3 \ln(y_3)] + [(V_1/V_2) - 1]
\]

(4)

where \( V_1 \) – the volume of solvent metal; \( V_2 \) – 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.

\( n_s \) – 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:

\[
n_s = 0.75(U_1 - U_2) (1 - n_al)
\]

(5)

where \( U_1, U_2 \) – the relative ionization potential of a metal and an alloy with respect to the ionization potential of hydrogen.

\( n_o \) – general (full) criterion:

\[
n_o = n_s + n_e
\]

(6)

consists of three components: two relate to the difference in the geometrical dimensions of the atoms \((d_1/d_2)\) and the density of the matter (both are taken into account in the dimentional 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.
4. Theoretical part
According to the phase diagram for the binary Ni-Cr alloy, the formation of continuous solid solutions of $\beta$-Ni and $\alpha$-Cr is possible. For the Ni-Co alloy, respectively, $\beta$-Ni, $\alpha$-Co and $\beta$-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) [10].

![Figure 1. Dependences of the phase-formation criteria on the mole fraction of Cr in the Cr-Ni-Co alloy:](image)

#### a) Entropy ($n_s$):

$$ y = 0.00014x^3 - 0.002x^2 + 0.012x + 0.984 $$

#### b) Dimensional ($n_d$):

$$ y = -0.00071x^4 + 0.009x^3 - 0.030x^2 - 0.019x - 0.803 $$

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.

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

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

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 $\pm 0.002$ nm using the PDW in 4.0 complex.

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.

6. 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).
Table 1. The calculated and experimental phase composition of Ni-Co-Cr 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 carbanide | 42.1 40.9 17.0 | β-Ni+β-Co | β-Ni+α-Co+β-Co | ±1.25 ± 3.75 | AMS |
| Cr-Ni-Co H-acid | 58.7 16.3 25.0 | β-Ni+β-Co | β-Ni+α-Co+β-Co + AMS | | |
| Cr-Ni-Co H-acid | 31.4 23.6 45.0 | β-Ni+α-Co+α-Cr | β-Ni+α-Cr+α-Co + CrO₃ | ±1.45 ± 3.9 | CrO₃ |
| Cr-Ni-Co H-acid | 32.4 15.4 52.2 | β-Ni+β-Co+α-Cr | β-Ni+α-Cr+β-Co + CrO₃ | ±1.33 ± 4.73 | CrO₃ |

Ratio of ions in electrolyte: Cr³⁺:Ni³⁺:Co²⁺ = 0.47:0.41:0.12

The main factors defining composition of chromic alloys, Sally [11], Shluger [12] consider existence dispersible the hydroxide or oxide inclusions of chrome. In this work to increase quantity of nanostructural crystals and to receive adjustable quantity of an amorphous phase ternary alloys and special additives were used.

As the regulator of amorphous inclusions Cr in Cr-Co-Ni alloy were used surfactant: N-acid and carbamide

Alloys in the presence of carbamide low-chromic (up to 25 masses. Cr %), and in the presence of N-acid high-chromium (up to 60 masses. Cr %). Respectively, also the phase structure differs.

In the presence of carbamide alloy contains the phases β-Ni, β-Co and a polymeric film of Cr(OH)₃(H₂O)·2H₂O (AMS – an amorphous and metastable system) (tab. 1, No. 1; fig. 2a), i.e. carbamide brakes the category of ions Cr³⁺.

![Figure 2. X-ray diffraction patterns of the Ni-Co-Cr alloy with various additives: a) carbamide (t = 60°C, iₖ = 5 A/dm²); b) H-acid (t = 20°C, iₖ = 10 A/dm²) [1].](image)

When comparing the precipitation obtained in the presence of carbamide but with different content of components, it follows that although the alloys are two-phase, but the phases themselves are different.
Additives lead to changes in both chemical and phase composition. Comparison of experimental and calculated phases (according to the criteria of phase formation) showed good convergence of the results. The exception is the additional phase of CrO$_3$ and the AMS.

Ni-Co-Cr alloy has nanostructure. On the chart of a cross cut of a microsection the unusual regularity was observed: sites of alloy, which borders 0.7 - 1 microns wide, are enriched with chrome 4 - 8% more in comparison with their central regions. The zones enriched are possible [Cr(OH)$_3$(H$_2$O)$_2$H$_2$O]$_2$, serve as a matrix for Ni-Co-Cr alloy nanoparticles with sizes of 50 nanometers. It is suggested that formation of ultradispersed particles of a covering was promoted by films of the hydroxide of chrome causing slowing down of process of an electrocrystallization.

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

The ultimate goal of the study is to obtain Cr-Ni-Co coatings with a maximum HV. Microhardness is a structure-sensitive property, therefore, it must be determined primarily by chemical and phase compositions.

Judging by the microhardness of pure metals [13] (Table 2), one would expect the highest values of microhardness for the alloy Cr$_{63.2}$Ni$_{22.0}$Co$_{14.8}$.

### Table 2. Microhardness of pure metal coatings

| Metals     | HV, MPa | Source |
|------------|---------|--------|
| Ni         | 160-550 | [13]   |
| Co         | 200-450 | [13]   |
| Cr         | 550-750 | [13]   |

However, apparently from results of the conducted researches, the two-phase settlings (β-Ni+α-Cr) containing the amorphous phase Cr(OH)$_3$(H$_2$O)$_2$H$_2$O and having nanostructure with the lowest content of chrome possess the maximum microhardness (HV = 985 MPa) (tab.3, No.2).

### Table 3. The influence of the content of the components in the Ni-Co-Cr alloy on the microhardness

| № | Alloy additives | Cathodic current density $i_k$, A/dm$^2$ | t, °C | Alloy composition, mass. % | Phase composition | HV, MPa |
|---|----------------|------------------------------------------|------|-----------------------------|-------------------|---------|
| 1 | Cr-Ni-Co H-acid| 6                                        | 20   | 22.5 18.9 58.6              | α-Cr+β-Ni+NiO     | 690     |
| 2 | Ni-Co-Cr carbamide| 6                                        | 20   | 58.7 16.3 25.0              | β-Ni+α-Cr+CrO$_3$ | 985     |

The highest microhardness among the high-chromium alloys provides alloy Cr$_{58.6}$Ni$_{22.5}$Co$_{18.9}$ (table. 3, No. 1), corresponding to the phases α-Cr, β-Ni, β-Co and having an additional phase NiO.

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 CrO$_3$ 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)$_3$(H$_2$O)$_2$H$_2$O, and in the second case - a high content of chromium oxide CrO$_3$, giving additional hardness to the coating.

### 7. Conclusion

On set of a research of structural properties and a microhardness it is possible to recommend Ni-Co-Cr alloy for use in a radioelectronics and as structural material, and Cr-Ni-Co alloy for use in microelectronics for resistor and the strain-resisting of elements.
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