Prediction of phase composition and anticorrosive properties of Zn-Ni-Co alloys

V V Schmidt, I G Zhikhareva and D V Denisenko*
Tyumen Industrial University, 38, Volodarskogo st., Tyumen, Russia, 625000

*ardiasardias@gmail.com

Abstract. The possibility of theoretical prediction of a given phase composition (intermetallide Ni5Zn21) of Zn-Ni-Co electrochemical alloys using four phase formation criteria: entropy (ns), dimensional (nd), energy (nε) and general (nο) is shown. A theoretical method is proposed, which allows to predict the ratio of metal ions in solution and the phase composition of ternary electrolytic alloys, using Zn-Ni-Co alloy containing intermetallides as an example. Formation conditions (chemical content of the components in the coating) and the length of concentration boundaries of the metal-solvent (Zn) for electronic compound Ni5Zn21 (γ phase) are calculated.

1. Relevance

Electrochemical alloys are widely used in various fields of technology as corrosion-protective coatings, structural materials with valuable physical properties. Binary zinc alloys, primarily Zn-Ni coatings, are often used as protective coatings in saline environments. They are economical, non-toxic, but have low selectivity. Zinc-based alloys, according to the state diagram [1], can contain 7 phases. Of these, only Ni5Zn21 intermetallide (γ-phase) has optimal anti-corrosion properties. The difficulty lies in the fact that it is formed in very narrow concentration limits; it is not yet possible to obtain a coating with a 100% γ-phase content in cast alloys. Triple alloys have an even more complex composition (an additional component is cobalt). Moreover, it is possible to form both a hexagonal close packed (hcp) phase, α-Co, and a face-centered cubic (fcc) phase, β-Co. Presence of β-Co phase in corrosion-protective coatings is undesirable, but presence of α-Co, on the contrary, increases the ductility and stability of the coating in an oil medium. Therefore, the use of triple alloys is more appropriate. As a rule, mixed crystals, especially solid solutions and intermetallic phases, have optimal properties. In Zn-Ni alloy, such a phase is Ni5Zn21 (γ-phase). The best anticorrosive properties have coatings with a content of 15-20 mass. % of Ni. Недостатком бинарных сплавов Zn-Ni является хрупкость и наличие микротрещин. The disadvantage of binary Zn-Ni alloys is fragility and presence of microcracks. To optimize the protective and corrosion properties of coatings, it is important to be able to predict the phase and chemical composition of the alloy, and this, in turn, requires reliable phase formation criteria. For binary galvanic Zn-Ni alloy, a forecasting effort has been carried out by the authors [2, 3]. They obtained coatings with Zn-Ni, Zn-Co electrolytic alloys containing homogeneous intermetallic phases. It follows from these studies that predicting a given phase composition is an urgent task, both in terms of saving scarce metals and improving the quality of the coating and its operational properties. For triple alloys, this task is even more important.
2. Overview
The aim of this work is to predict a given chemical and phase composition and to obtain coatings with Zn-Ni-Co alloy with optimum protective corrosion properties and microhardness.

The objective of the study was a theoretical prediction of the ratio of metal ions in the deposition electrolyte, the phase composition of Zn-Ni-Co alloy, and an optimization of concentration boundaries of the existence of Ni5Zn21 intermetallide (γ phase).

It was necessary to obtain a nanostructured coating (Zn-Ni-Co) with a predominant content of the γ phase and not containing nanopores and microcracks.

To develop a technology for producing a new protective and corrosive material that exceeds cadmium in terms of anticorrosion properties and the best coatings of world-class zinc alloys.

Methods for solving the stated problems were the development of a mathematical model for calculating the phase composition of Zn-Ni-Co alloy with intermediate phases based on four phase formation criteria: entropy (n_s), dimensional (n_d), energy (n_ε) and general (n_o) [2, 3].

The entropy factor characterizes the degree of difference in chemical bonds.

The dimensional factor (n_d), considering the molar fraction of mixing, characterizes the magnitude of the resulting distortion of the crystal lattice of the components.

The energy factor (n_ε) characterizes the possibility of redistribution of the electrons of the outer shells.

The total volume factor (n_o), considering the correction for molar fractions of the mixture n_o = n_d + n_ε, characterizes distortions of the electron shells due to the difference in the electron density of the substance.

The main task in the case of Zn-Ni-Co alloy was to obtain a coating with a maximum γ-phase content (Ni5Zn21). For this, the composition of an electrolyte (the ratio of metal ions) was first predicted at which the maximum extent of concentration boundaries of the intermetallide is expected. The widest region of existence of the γ phase is predicted with the ratio Zn2+:Ni2+:Co2+=0,6:0,3:0,1.

Presence of the intermetallide is evidenced by the constancy of n_s. The length of the concentration boundaries of the γ phase can be estimated from the length of the breaks in the dependences n_s = f(y_i); n_d = f(y_i) (Figure 1, 2) [2].

It should be noted that the boundaries of the region of homogeneity of the γ phase (Ni5Zn21) are very close to each other on the zinc side: in n_s Zn(0,79-0,82), and in n_d and in n_ε Zn(0,79-0,83), which is significantly lower than for the binary alloy Zn-Ni (Zn(0,74-0,86)) [2].

The energy factor n_ε enabled us to estimate only the lower boundary of the zinc content in Zn-Ni-Co alloy.

Thus, it can be said that a large role in the appearance of one or another phase is played by structural factors compared with the relative difference in the chemical bond (n_s).

![Figure 1. Estimated dependence of the entropy (n_s) factor.](image1)

![Figure 2. Estimated dependence of the dimensional (n_d) factor.](image2)
3. Experimental part

Structural characteristics. To verify reliability of the theoretical prediction results of the components’ chemical content and the phase composition of Zn-Ni-Co alloy, it was necessary to obtain a precipitate with a maximum length of the γ-phase boundaries (the formula composition of zinc in Ni₅Zn₂₁ is 81 atom%).

It should have a nanostructure, be crystalline, not contain nanopores, macro- and microcracks and have a minimum α-Co content in the alloy.

To obtain coatings with the required structural properties, we studied the chemical and phase composition, surface morphology, nanostructure, and grain size.

Precipitation was carried out from an electrolyte of the composition (mol./L): ZnSO₄ — 0.60; NiSO₄ - 0.30; CoSO₄ -0.10; (NH₄)₂SO₄ - 0.16; NH₄OH - 0.49; NH₄Cl - 0.35; p-ASA and o-ASA (amino sulfonic acid: p- and o- - para- and ortho-, respectively) - 0.01 - by the stationary method.

Electrolysis conditions: t = 20 ÷ 80 °C; i_k (cathodic current density) = 3 - 12 A/dm²; sedimentation time - 20 to 30 minutes.

Now, the best zinc-based protective corrosion-resistant alloys are produced by foreign firms (American and Japanese) [4]. Domestic coatings are inferior to them due to insufficient corrosion resistance; low microhardness, presence of cracks and pores, low efficiency, and uncontrolled quantitative composition of the phases [5,6,7].

It was necessary to optimize the content of intermetallide in the coating in accordance with predictive modeling, to remove cracks and pores by selecting special organic additives and introducing an additional component - cobalt - to give the sediment plasticity.

According to a previous calculation of the phase composition of Zn-Ni-Co alloy, one would expect the existence of a γ-phase with a zinc content in the sediment in the range of 79–83 mass. %

The existence of intermediates was judged by X-ray diffraction patterns obtained with a DRON-7 diffractometer (Co-κα radiation, Fe filter) and identified based on PCPDFWIN 2007 base maps (05-0727, 15-1806, 06-0653).

The experimentally determined phase composition is consistent with the calculated data (Figure 3, Table 1).

![Figure 3. X-ray diffraction pattern of Zn-Ni-Co alloy (o-ASA).](image)

A comparison of the experimentally determined phases in Zn-Ni-Co alloy with the calculated ones showed a high degree of reliability of the predicted phase composition (the relative error ranged from ±1.27% (p-ASA) to ± 7.72% (o-ASA)) (Table. 1).
Table 1. Comparative data on the phase composition of Zn-Ni-Co alloy.

| №  | Additive | Chemical alloy composition, mass. % | Phase composition | Deviation of phase formation exp. criteria from theor. boundaries of the γ-phase | Zinc content in the γ-phase/γt phase, % |
|----|----------|-------------------------------------|-------------------|---------------------------------------------------------------------------------|--------------------------------------|
| 1  | p-ASA    | 75 17 8                             | γ+α-Co            | γ>>α-Co ±5.06                                                                   | 98.193 81.5/81                       |
| 2  | p-ASA    | 78 18 4                             | γ+α-Co            | γ>>α-Co ±1.27                                                                   | 97.892 81.25/81                     |
| 3  | p-ASA    | 77 14 9                             | γ+α-Co            | γ>>α-Co ±2.53                                                                   | 97.468 84.62/81                     |
| 4  | α-ASA    | 74 21 5                             | γ+α-Co            | γ>>α-Co ±6.33                                                                   | 98.595 77.89/79                     |
| 5  | α-ASA    | 73.7 19.3 7                         | γ+α-Co +β-Co      | γ>>α-Co ±7.72                                                                   | 99.684 79.25/79                     |

As can be seen from Table 1, the optimum γ-phase content was obtained in the presence of p-ASA additive (No. 1 and No. 2) - the zinc content in the γ-phase almost coincides with the formula.

Ni₁₅Zn₂₁ phase, the structural type of CsCl (complex bcc), has an ordered structure of type I-43m and is a lattice with 52 atoms per unit cell [8].

The crystal lattice parameter for Zn-Ni-Co alloy (γ-phase) is very close to the crystal lattice parameter for Zn-Ni alloy (γ-phase).

Calculation of the crystal lattice parameters of Ni₁₅Zn₂₁ depending on the percentage of zinc in the Zn-Ni-Co alloy showed that this dependence is linear, i.e. obeys Vegard’s law.

The results of the experimental study indicate that the experimental phase composition practically coincides with the calculated one. The presence of an additional phase α-Co and/or β-Co is theoretically confirmed by the calculation of the work of two-dimensional nucleation [2]. With Aα << Aβ, only the hcp phase is in the coating.

According to published data, Zn-Ni alloys have numerous pores and cracks.

![Figure 4](image4.png) **Figure 4.** Topology. Ordered truncated triangles-crystals of the γ-phase 174 nm in size.

![Figure 5](image5.png) **Figure 5.** Ordered dark crystals of the γ-phase, white particles are nickel oxides on the γ-phase surface.

To avoid this drawback, we used two approaches: selection of special organic additives according to the Nechaev – Kuprin adsorption theory [9, 10] and introduction of cobalt into the alloy, which imparts more plastic properties to the coating. The effectiveness of these measures is confirmed by atomic force...
microscopy (Figure 4). The surface nanostructure of the alloy has a perfect texture along the axis [10\bar{1}0] (Figure 5).

The data of the electron microprobe method confirmed the presence of the intermetallide in the ternary alloy, showed the relative position of the phases and the distribution of the content of elements in different phases. Figure 6 shows the construction of the spectrum and distribution maps of elements in selected surface areas. In the case of Zn-Ni-Co alloy (p-ASA), the γ-phase and base metals are present. Fig. 7 shows images of crystals of the γ-phase and α-Co. Larger crystals belong to the α-Co phase; clusters of small particles characterize the γ-phase.

**Figure 6.** Elemental analysis data

**Figure 7.** Surface microstructure

An X-ray diffraction analysis of Zn-Ni-Co (o-ASA) alloy at low and medium cathodic current densities revealed an additional β-Co phase (solid solution of zinc in cobalt) (Fig. 2), which is possibly due to hydrogenation of the coating. The presence of the β-Co phase in Zn-Ni-Co alloy leads to a marked decrease in the anticorrosion properties.

A decrease in the β-Co content in the Zn-Ni-Co coating was achieved by us due to the introduction of the p-ASA additive into the electrolyte deposition.

Anticorrosion properties. The main purpose of galvanic coatings with Zn-Ni-Co alloy is to protect steel structures from corrosion in sea water and salt medium. An aggressive medium was a 3% solution of NaCl in water (pH 7.2) simulating sea water. As characteristics of the corrosion of coatings, weight (V1) and depth (V2) values were chosen (Table 2).

| №  | Coating          | V1, g/m²h, in 750 h | V2, μm, in 750 h | Microhardness, Nμ, MPa | l, %, in 750 hours | Phase               |
|----|------------------|---------------------|-----------------|------------------------|------------------|---------------------|
| 1  | Zn [11]          | 0.036               | 5               | 85 – 120               | -                | η-Zn                |
| 2  | Cd [11]          | 0.0014              | 2.1             | 250 – 590             | -                | -                   |
| 3  | Zn-Ni (p-ASA) [12] | 0.0015              | 2.4             | 401 – 482.4           | 80-83.5          | γ-phase             |
| 4  | Zn-Ni-Co (p-ASA) | 0.0010              | 1.65            | 697                    | 95               | γ-phase >> α-Co     |

The lowest depth index for the coating with Zn-Ni-Co alloy with a maximum Ni₅Zn₂₁ content (γ-phase) is 1.65 μm per 750 hours. The same precipitate has the lowest dissolution rate (0.0010 g/m²h). The phase composition has the greatest influence on the corrosion rate. Presence of a three-phase precipitate causes a significant increase in the corrosion rate (2.0 - 2.5 times).
Our result can be explained due to the high content of the $\gamma$-phase in the coating, high microhardness, and the presence of a nanostructure (Table 2).

The main reason is the optimum concentration of the $\gamma$-phase in the predicted alloy. It is known that currently it is not possible to obtain a homogeneous cast alloy with a $\gamma$-phase. An additional factor that increases the corrosion-protective properties is the nanostructure and the absence of impurities.

4. Conclusions
Using preliminary predictive modeling, it is possible to obtain a nanostructured coating with Zn-Ni-Co alloy with a given phase and chemical composition with high accuracy.

The presence of an additional component in the alloy - cobalt – enables us to expand the scope of use in automotive internal combustion engines. Thus, Zn$_{75}$Ni$_{17}$Co$_8$ alloy coating surpasses the world level of existing Zn-Ni coatings in terms of corrosion resistance, which enables us to recommend it for protection of oilfield equipment. In general, due to energy and material saving, as well as research time, it was possible to obtain a coating twice as economical as the current one.

References
[1] Hansen M. 1962 Structure of double alloys Moscow: Metallurgizdat. 2. pp. 1122-1124.
[2] Zhikhareva I.G. 2005 Modern aspects of electrocrystallization of metals. pp. 23-24.
[3] Shmidt V.V., Denisenko D.V., Zhikhareva I.G. 2020 J. Phys.: Conf. Ser. 1431, 012018.
[4] Ranganathan S. 2003 Allo yed pleasures: multimet alic cocktails Curr. Sci. 85, pp.1404–1406.
[5] Cantor B., Chang I.T.H., Knight P., Vincent A.J.B. 2004 Microstructural development in equiatomic multicomponent alloys, Mater. Sci. Eng. 375, pp. 213-218.
[6] Vitkova S. 1975 Electrodep. and Surface Treatment. 3(4) pp. 225–234
[7] Parfenov V.V., Orlovskaya L.V., Rachinskas V.S. 1990 Chemistry. 3(178), pp. 75-79
[8] Umansky Y.S. 1978 Physics of metals Atomizdat. 352 p.
[9] Nechaev V.A. 1978 Electrochemistry. 14(4) pp. 555-560.
[10] Loshkarev Y.M. 1972 Tez. Docl. III-Tartu. pp. 165-166.
[11] Melnikov P.S. 1991 Moscow: Mashinostroenie. 352 p.
[12] Zhikhareva, I.G. 2011 Chemistry and chemical technology. 54(4) pp. 76-78.