The role of nanostructure forming mechanism in the production of universal functional coatings with Fe-Ni, Co-Mn, Ni-Cr alloys

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

*ardiasardias@gmail.com

Abstract. Galvanic nanostructured coatings with Fe-Ni, Co-Mn, Ni-Cr alloys with enhanced operational properties are obtained. Three mechanisms of ultrafine particles formation are considered: usage of the high-voltage alternating current (HVAC) method (Fe-Ni, Co-Mn), presence of a new hexagonal phase ε-Fe, which has dimensional effects. 2) introduction of a special carbamide additive, N-acid (Ni-Cr). 3) due to multilayer films Cr(OH)₃₉(H₂O)₂H₂O in the absence of an inhibitor (Ni-Cr alloy), the relationship between the nanostructure forming mechanism and the spectrum of functional properties is shown.

1. Relevance
The modern development of technological processes requires new materials. Some of the most promising are nanomaterials with valuable performance characteristics. The latter largely depend on the ultrafine particles producing mechanism. The relevance of the study of nanostructured materials is associated with a direct dependence of the nanoclusters’ size with the most important functional properties. It is important to be able to classify basic nanostructure forming mechanisms and to predict the properties which will be affected by them.

Purpose of work. Establishing the relationship of various nanostructure forming mechanisms and size effects with the functional properties of coatings by Fe – Ni, Co – Mn, and Ni – Cr alloys.

Basic requirements for properties: 1) for Fe-Ni alloys - high microhardness, low cold brittleness threshold, high corrosion resistance in sea water and salt medium, presence of nanostructure and size effects. 2) for Co-Mn alloys - high content of α-Co phase, nanostructure, presence of a controlled concentration of the amorphous-metastable phase (AMP) Co(OH)₂. 3) for Ni-Cr alloys - high microhardness, nanostructure, predetermined phase and chemical composition.

Objectives. They were solved through 1) a new production method - high-frequency alternating current (AC) - Fe-Ni, Co-Mn alloys; 2) special additives (carbamide, N-acid) - Ni-Cr alloy; 3) a controlled amount of amorphized phase - Co-Mn alloy.

2. Literature review
One of the most important technologies for scientific and technological progress at the beginning of the 21st century is nanotechnology. The study of single crystal clusters is the subject of a large number of papers [1-3]. Promising nanomaterials in electroplating are amorphous [4], composite coatings [5], and
ultrafine particles [6] obtained in the presence of strong inhibitors. E. Epelboin and M. Froment observed [7] nanostructures upon electrocrystallization of nickel in the presence of a strong inhibitor.

Classical size effects are often observed in nanomaterials, when all mechanical and physical properties of a substance change with the change in its linear dimensions. These characteristics can be detected using magnetic properties and magnetic phase transitions [8].

3. Research method
HVAC - Fe-Ni and Co-Mn alloys and stationary (SM) - Co-Mn and Ni-Cr alloys. Coatings are obtained from simple aqueous electrolytes under stationary conditions. (P = 0.1 MPa., T = 298 K) [9]. The phase composition was determined using a D2 Phaser with Co-Kα radiation, an Fe-reflection filter, and Bragg-Brentano focusing was observed. Unit cell parameters of the phases were studied in the range of angles 2θ = 20-120 ° with an accuracy of 0.002 nm. The phase analysis results were compared with COD file cabinet. The surface structure of the coatings and the nanostructure was studied using an NTegra Aura probe atomic force microscope (AFM) (NT-MDT, Russia) using the semi-contact method with sample scanning. The lateral scanning resolution of the microscope is at least 1 nm, the height resolution is at least 0.5 nm. The study of microstructure, chemical composition of subsurface layers of JEOL-6510LVC with X-ray analyzers. Resolution up to 1.2 nm. The measurement error in determining the content of elements ± 0.2 wt.%. Microhardness was determined by durometric analysis method using a PMT-3M microhardness tester with an indenter load of 20-50 g. Measurement error - 5-7% according to GOST 9450-76.

4. Experimental part
Precipitation was carried out from simple sulfate and chloride-sulfate electrolytes. The chemical and phase composition, microstructure, nanostructure and some physical properties were studied (Table 1). The chemical content of the metal-solvent in all cases was extremely high (up to 99.1 wt.%). This largely determines the phase composition. An exception is the appearance of a new ε-phase for Fe-Ni alloy. Under stationary conditions, it does not form. A nanostructure was obtained for all studied alloys, but the size effects were found mainly for coatings with Fe-Ni alloy (Table 1, No. 1, 2) and Co-Mn alloy (Table 1, No. 3). The coating thickness (δ) is determined mainly by the production method. The widest range of δ was noted for coatings obtained by the HVAC method.

| No. | Alloy. Production method. Condition. | Chemical composition of elements,% | Phase composition | Size of crystals, microns | Size of nanoclusters, nm | Thickness δ, μm |
|-----|-------------------------------------|-----------------------------------|------------------|--------------------------|------------------------|-----------------|
| 1   | Fe-Ni HVAC f= 5 kHz                 | 87-13                             | α-Fe 77          | 2.5                      | -                      | 2-1500          |
| 2   | Fe-Ni HVAC f= 9 kHz                 | 84-16                             | α-Fe 68          | 1.9                      | -                      | 2-1500          |
| 3   | Co-Mn HVAC α-ASA                    | 97.5-2.5                          | α-Co 96.2        | 4.3                      | 25-30                  | 2-10            |
| 4   | Co-Mn CM α-ASA                      | 99.1-0.9                           | α-Co 74.5        | 7.1                      | 50-80                  | 2-6             |
| 5   | Ni-Cr CM (NH₂)₂CO                   | 75-25                             | β-Ni 89.1        | 6.8                      | 50-80                  | 20-40           |
| 6   | Ni-Cr CM N-acid                     | 38-62                             | α-Cr 67.8        | 5.6                      | 80-100                 | 20-50           |
The experimental data analysis shows that the nanostructure of Fe – Ni, Co – Mn, and Ni – Cr alloys was formed by different mechanisms:

1) A feature of the Fe-Ni electrolytic alloy forming mechanism is formation of a new hcp-phase of \( \varepsilon \)-Fe due to the phase transition (p.t.) of \( \alpha \)-Fe. Previously, this exotic phase was discovered in the inner core of the Earth, iron meteorites, and was obtained in laboratory conditions with \( p = 11-11.5 \) GPa, \( T = 750 \) K; but when pressure is removed, the inverse p.t. occurs \( \varepsilon \)-Fe\( \rightarrow \alpha \)-Fe \[9\]. In other words, not a single laboratory production method enables us to preserve the \( \varepsilon \)-Fe phase under normal conditions, with the exception of the above-described high-voltage alternating current method. The calculations carried out according to the oriented electrocrystallization theory (OET) for two-dimensional nucleation work showed that the \( \varepsilon \)-Fe phase cannot exist in spontaneous processes, because \( A_{\varepsilon \text{Fe}} << A_{\alpha \text{Fe}} \), but texture matching is possible:

\[
\frac{\alpha \text{-Fe}(011)}{(110)} \rightarrow \frac{\varepsilon \text{-Fe}(112)}{(0001)} \quad [10].
\]

In the case of the HVAC method, p.t. passes along the orientational mechanism due to the anode component of electromagnetic waves. Size effects are provided by controlling the pulse duration within predetermined limits. As a result, the Fe-Ni alloy contains 2 phases: \( \alpha \)-Fe (bcc) and \( \varepsilon \)-Fe (hcp). The atomic force microscopy showed that polycrystals (Fig. 1) consist of 10 nm nanoplates located at a distance of 8 nm. This allows predicting the presence of enhanced functional properties for the Fe – Ni alloy (Table 2).
Table 2. Nanostructure forming mechanism and coating properties.

| No. | Alloy          | Mechanism                        | Properties                        | Areas of use                                                                 |
|-----|----------------|----------------------------------|-----------------------------------|-----------------------------------------------------------------------------|
| 1   | Fe$_{84}$-Ni$_{16}$ | HVAC, p.t. $\alpha$-Fe$\rightarrow$$\epsilon$-Fe. | HV=1780 MPa, T$_{xp}$=-150°C, K$_n$=0.6 mm/microns/year, d=8-10 nm. | Coatings for the protection of oil and gas production equipment operating in the Arctic, Corrosion-resistant protective coatings in the petrochemical industry. Nanocatalyst for Fischer-Tropper synthesis. Modulation systems. |
| 2   | Co$_{97}$-Mn$_{3}$ | HVAC, addition of o-ASA, $\alpha$-Co$\gg$$\alpha$-Mn Co(OH)$_2$ | Hc=1050 A/m, d=15-20 nm, HV=555 MPa, | Nanocatalyst for Fischer-Tropper synthesis.                                  |
| 3   | Ni$_{75}$-Cr$_{25}$ | Carbamide, $\alpha$-Cr, NiO, AMP | HV=985 MPa, d=50-80 nm. | Corrosion-resistant protective coatings in the petrochemical industry.       |
| 4   | Ni$_{32}$-Cr$_{68}$ | H-acid $\alpha$-Cr, $\beta$-Ni, CrO$_3$ | HV=690 MPa, d=80-100 nm. | Resistive elements                                                          |

2) Co-Mn is the best coating obtained by the HVAC method. No new phases are formed, but it becomes possible to control the percentage of the $\alpha$-Co aid phase (surfactant - o-ASA). The role of the latter is to maintain the pH of the near-cathode layer at the required level for H$_2$ binding. The nanostructure forming mechanisms in this case are reduced to providing size effects - a film of the amorphous Co(OH)$_2$ phase around the Co-Mn alloy clusters (Figure 3). In the presence of thin films, the Co-Mn alloy must have excellent magnetic and catalytic properties.

3) Ni-Cr coatings with high mechanical properties can be predicted using the oriented electrolysis theory (OET) [10]. The value of microhardness clearly correlates with the energy characteristic – the effective surface energy $\sigma_{\text{eff}}$: the higher it is, the higher the microhardness [11]. Having calculated the optimum surface energy values for the Ni-Cr alloy, a coating with high microhardness is obtained. Thus, we can conclude that microhardness can be controlled by obtaining a coating with high surface energies with activating adsorption and the presence of nanostructured films.

5. Conclusion
1. The nanostructure forming mechanisms of galvanic coatings based on iron subgroup metals are proposed and justified: as a result of p.t. and the formation of a new hcp-phase (Fe-Ni, HVAC). Due to the controlled content of the amorphous phase Co(OH)$_2$ and the predicted phase and chemical composition (Co-Mn, OET). Due to predicting and calculating of a given $\sigma_{\text{eff}}$ by the OET and the obtained amorphous films Cr(OH)$_3$·(H$_2$O)$_2$·2H$_2$O, (Ni-Cr).

The chemical composition of Ni$_{75}$-Cr$_{25}$ and Ni$_{32}$-Cr$_{68}$ alloys was obtained from an electrolyte of the same composition, but with different additives: carbamide and H-acid, respectively.

2. It has been shown that the most effective way to ensure the presence of a nanostructure is the HVAC method. The size effects were observed only with this method. A variety of physical and mechanical properties enables us to recommend coatings in various industries.

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