

REGULARITIES OF INFLUENCE OF NICKEL AND CHROMIUM ON STRUCTURE FORMATION OF ELECTRODEPOSITED IRON

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Abstract: Structural investigations performed by the methods of X-ray diffractometry and scanning electron microscopy of electrodeposited iron-based coatings revealed common and specific features and regularities of influence of nickel and chromium on their structure formation. Significant changes in surface morphology, crystallographic texture and microhardness of the electrodeposited coatings caused by the insertion of nickel and chromium in the sulfate iron-plating electrolyte were found and compared.

KEYWORDS: ELECTRODEPOSITED IRON, NICKEL, CHROMIUM, ALLOY, COATING, CRYSTALLOGRAPHIC TEXTURE, SURFACE MORPHOLOGY

1. Introduction

Electrodeposited iron is used in industry particularly as coatings to restore worn steel machine parts of various type [1-2]. In comparison with materials obtained by metallurgical methods electrodeposited coatings usually possess increased hardness. Therefore, the use of electrodeposited iron coatings also provides surface hardening of steel items, which should be mentioned as their additional advantage.

To improve the performance of electrodeposited iron its alloying by various metal elements with the formation of electrodeposited alloys is utilized [2-3].

2. Preconditions and means for resolving the problem

Analysis of the literature showed that the majority of publications on electrodeposited iron-based alloys focus on electrochemical aspects of their production, while their structure formation is discussed insufficiently and the available data on the influence of alloying elements on the processes of structure formation is not systematized. Therefore, to find new possible ways of improvement of the complex of properties of iron coatings the investigations of influence of alloying elements on structure formation of electrodeposited iron is sufficiently urgent.

In previous research it was shown that the presence of nickel [3-5], chromium [6-7] or both alloying elements [8-11] in iron-plating electrolytes causes significant changes in structure formation of electrodeposited iron-based coatings. Thus, our recent investigations in this field [5, 7, 11-12] revealed drastic changes in surface morphology and crystallographic texture of such nickel- and chromium-alloyed iron coatings obtained from sulfate electrolyte. But it should be noted that the structure formation of electrodeposited metal coatings usually occurs in non-equilibrium conditions and depends on the process parameters and electrolyte composition significantly, which may lead to the formation of quiet unusual phase composition [13-14] and surface morphology [14] of coatings. Therefore, the prediction of structure of electrodeposited coatings is hindered and experimental investigations are still necessary in every case of usage of such coatings.

Thus, the aim of this work was further investigation, establishment and explanation of features and regularities of influence of nickel and chromium on structure formation of electrodeposited iron coatings obtained from sulfate electrolyte.

Iron-based coatings (1-150 μm thick) were electrodeposited at the temperature of 55-57°C and the current density of 10 A/dm² from sulfate electrolytes containing: Fe – 80 g/l, Ni – 0-40 g/l, Cr – 0-40 g/l (pH 2-3). The sources of Fe, Ni and Cr ions in the electrolyte were the sulfates FeSO₄·7H₂O, NiSO₄·7H₂O and Cr₂(SO₄)₃·6H₂O respectively. Also Al₂(SO₄)₃·18H₂O (100 g/l) was used as a buffering substance. Iron anodes were utilized during

deposition process. Industrial steel sheet 08kp without mechanical pretreatment was used as a substrate.

Surface morphology and element composition of the obtained coatings were investigated by scanning electron microscopy at the REM-106I microscope. Phase composition and crystallographic texture were determined by X-ray diffractometry at the DRON diffractometer in Cu-K α radiation.

3. Results and discussions

The surface structure of electrodeposited iron without alloying at the thickness of 15 μm is represented mainly by fine non-equiaxial crystals. With the increase of thickness to 50 μm and above tightly arranged equiaxial crystals with clear cut begin to dominate in the coatings (Fig. 1, a) and the surface relief becomes noticeably smoother.

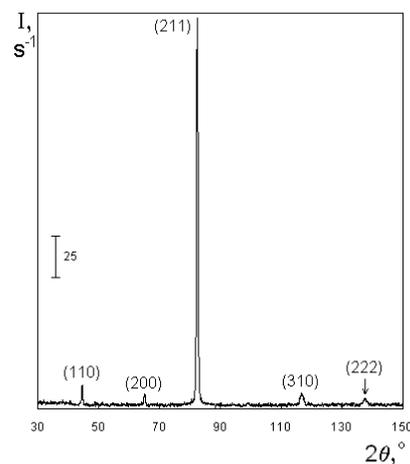
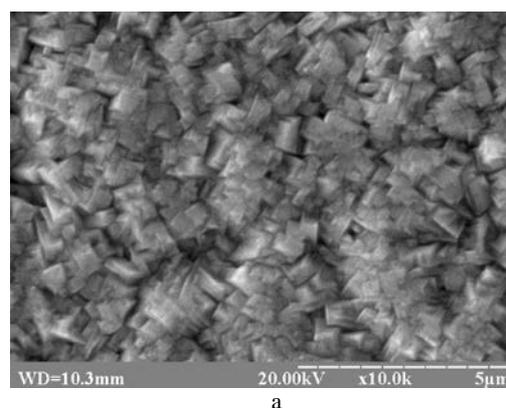


Fig. 1. Surface morphology (a) and X-ray diffractogram (b) of electrodeposited iron without alloying, coating thickness 50 μm

Crystallographic texture of electrodeposited iron (15-150 μm thick) is characterized by a strong axial $\langle 211 \rangle$ component (Fig. 1, b). Moreover, with the increase of thickness of the coatings in the investigated range the degree of perfection of texture increases.

Root-mean-square static displacements of atoms relative to their equilibrium positions in the crystal lattice equal 0.122 and 0,076 \AA for the 15 and 50 μm thick iron coatings respectively, indicating more non-equilibrium conditions at the initial stage of electrodeposition process, which leads to the formation of a more defective structure in thin coatings.

It is established that phase composition of all investigated coatings alloyed with nickel and chromium contains solid solutions based on the crystal lattice of α -Fe. Intermetallic compounds were not found in the coatings.

The content of chromium and nickel in the alloys increases with the increase of their concentration in the sulfate electrolyte throughout the whole investigated range (Fig. 2). However, for the Fe-Ni coatings such dependence is of an exponential type, while for the Fe-Cr alloys it is close to a logarithmic type, which is caused by a significant difference in the deposition rates of nickel and chromium at their different concentrations in the electrolyte.

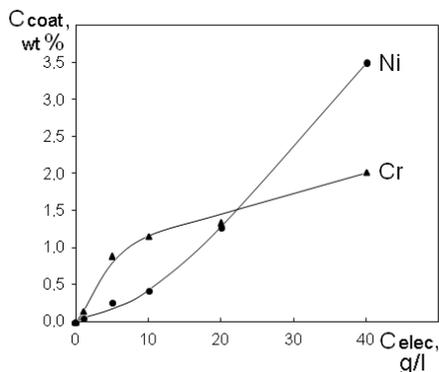


Fig. 2 Dependence of alloying element content in the coating on its concentration in the electrolyte

Analysis of cross-sections of the electrodeposited alloys Fe-Ni and Fe-Cr showed that the distribution of elements in both types of coatings is sufficiently uniform in thickness. Thus, after deposition of the initial layers the content of elements quickly stabilizes, which is observed at the thickness of about 8-10 and 10-12 μm for the Fe-Ni (Fig. 3, a) and Fe-Cr (Fig. 3, b) alloys respectively.

The surface structure of the Fe-Cr alloys electrodeposited from the sulfate electrolyte with 1 g/l Cr concentration is highly dispersed and consists mainly of small crystals (less than 1 μm) without clear cut forming a much smoother surface relief than the surface of electrodeposited iron without alloying. The increase of chromium concentration to 5 g/l is accompanied by a slight increase in the average crystal size and by the formation of relatively large crystal conglomerates. However, this structure, which looks coarser in comparison with the non-alloyed iron structure, actually consists of finer crystals forming such conglomerates. Further increase of the chromium concentration to 20 g/l leads to a gradual increase of the crystal size and at the concentration of 40 g/l some large crystals (more than 1 μm) appear in the surface structure of the alloy.

The insertion of nickel in the sulfate electrolyte and the increase of its concentration lead to significant changes in the type of crystal structure of the deposits. Thus, at the 5 g/l nickel concentration mainly fine needle-like crystals are present in the structure of the coatings, while the increase of its concentration to 10g/l leads to a significant increase of the share of spherulites, and further increase to 20 g/l is accompanied by the formation of a fully spherulite structure without any other forms of crystal growth.

Despite the relatively small amount of alloying elements in the obtained coatings (Fig. 2) the results of measurements indicate a significant influence of alloying on microhardness of the

electrodeposited iron-based alloys (Table 1). And the character of change of microhardness of the investigated coatings depending on the concentration of alloying elements is nonlinear and very similar for nickel and chromium (Table 1).

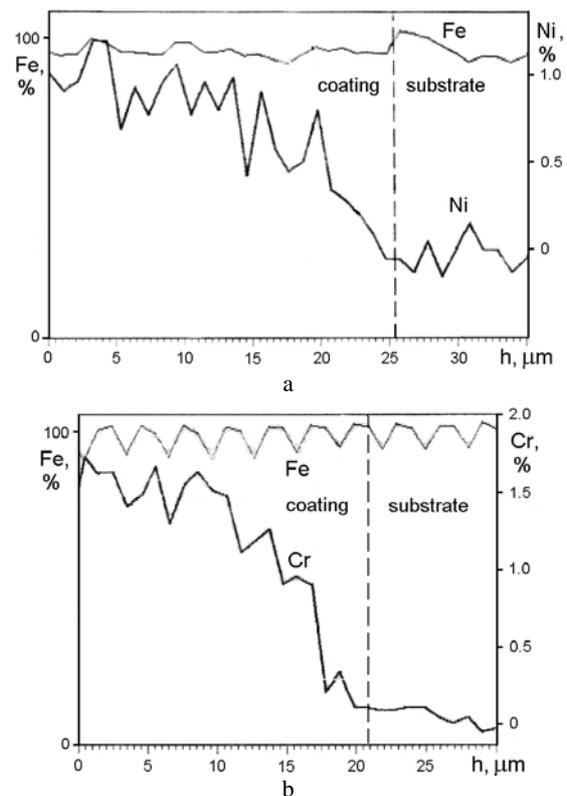


Fig. 3 Elements distribution in cross-section of iron-based coatings alloyed with nickel (a) and chromium (b)

Table 1. Microhardness of electrodeposited Fe-Cr and Fe-Ni alloys (50 μm)

| Alloying element concentration in the electrolyte, g/l | Microhardness HV 0,05, GPa | |
|--|----------------------------|-------|
| | Fe-Ni | Fe-Cr |
| 0 | 4.57 | 4.57 |
| 1 | 4.49 | 4.18 |
| 5 | 4.29 | 3.48 |
| 10 | 4.60 | 4.60 |
| 20 | 5.58 | 5.72 |
| 40 | 5.21 | 4.55 |

The cause of such nonlinear change of microhardness of the investigated electrodeposited coatings is the features of their structure formation. Thus, at the 5 g/l chromium or nickel concentration in the electrolyte mostly fine needle-like crystals dominate in the structure of the coatings in contrast to iron coatings without alloying. In the Fe-Ni alloys such crystals have a preferential $\langle 111 \rangle$ orientation and form a relatively smooth surface relief of the coatings. In the Fe-Cr alloys fine crystals form conglomerates of different sizes. In this case the preferential $\langle 211 \rangle$ crystal orientation typical for electrodeposited iron is preserved but the fraction of disordered crystals significantly increases. These structural changes lead to a reduction of microhardness of the coatings.

Further increase of the concentration of the alloying elements in the electrolyte to 20 g/l results in gradual growth of microhardness, which may be associated with the formation of specific structural components in the coatings. Thus, in the Fe-Ni alloys fine crystals form spherulites – the crystal units of radial-beam structure (Fig. 4, a). In the Fe-Cr alloys the formation of spherulites is not observed, however the formation of crystal

conglomerates occur (Fig. 5, a). Crystallographic texture of the coatings obtained at such concentration of the electrolytes is also represented by the axial $\langle 111 \rangle$ and $\langle 211 \rangle$ orientations for the Fe-Ni and Fe-Cr alloys respectively (Fig. 4, b and Fig. 5, b).

Further increase of the concentration of the alloying elements in the electrolyte to 40 g/l leads to structural heterogeneity of the electrodeposited coatings. Thus, in the surface structure of the Fe-Cr alloys some large crystals can be observed. And in the Fe-Ni alloys some areas of disordered needle-like crystals occur between spherulites with distinct radial-beam symmetry. At this concentration of nickel the fraction of crystals with axial $\langle 111 \rangle$ orientation typical for spherulite structure decreases. As it turns out in this case the structural heterogeneity is associated with a certain reduction of microhardness of the coatings.

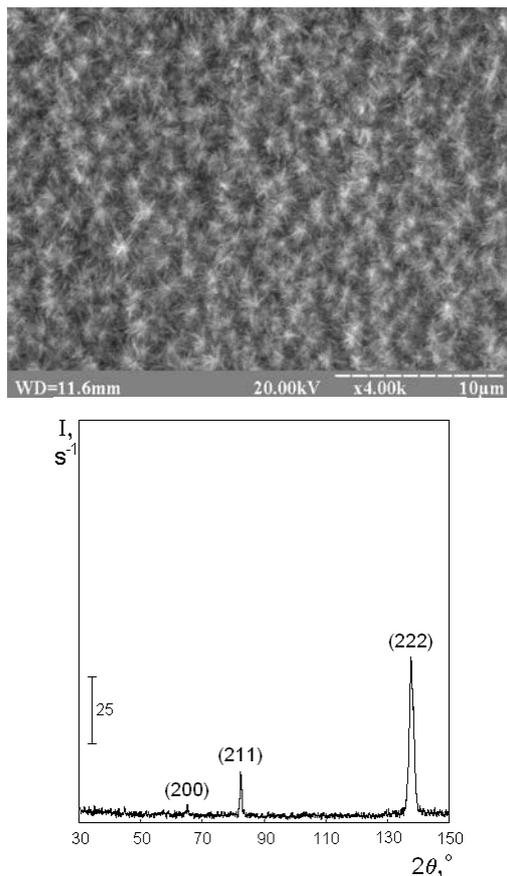


Fig. 4. Surface morphology (a) and X-ray diffractogram (b) of electrodeposited Fe-Ni alloy (50 μm) electrodeposited from the electrolyte with 20 g/l of Ni

4. Conclusions

The main common regularities of influence of nickel and chromium on structure formation of electrodeposited iron are the formation of solid solutions and fine structures as well as the identical character of change of microhardness of the alloyed iron coatings. The main specific regularities of influence of nickel are the formation of strong $\langle 111 \rangle$ axial texture and a fundamental change in surface morphology of the coatings from fine crystal structure with clear cut to the formation of spherulites, while the insertion of chromium in the electrolyte nearly does not change the $\langle 211 \rangle$ axial texture of electrodeposited iron.

The essential difference between the characters of the dependences of the average content of an alloying element in the coating on its concentration in the electrolyte is established for nickel and chromium. This dependence for nickel-alloyed coatings is of an exponential type, while for the chromium-alloyed coatings it is close to a logarithmic type, which is caused by a significant difference in the deposition rates of nickel and chromium at their different concentrations in the electrolyte.

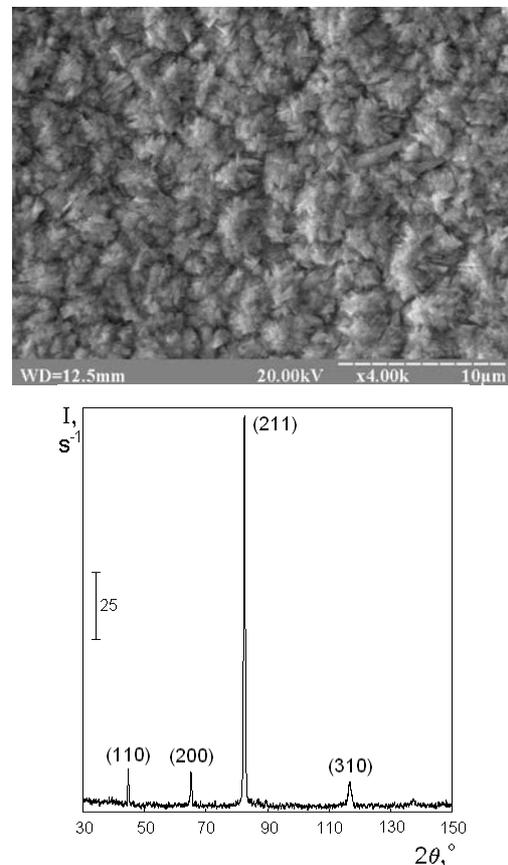


Fig. 5. Surface morphology (a) and X-ray diffractogram (b) of electrodeposited Fe-Ni alloy (50 μm) electrodeposited from the electrolyte with 20 g/l of Cr

5. Literature

- Likhachev V.A., Restoration of worn machine parts by the method of cold iron-plating, *Galvanotekhnika i Obrabotka Poverkhnosti*. 14 (2006) 14-18. (In Russian)
- Pleshka E.D., Iron coatings from multicomponent methyl sulfate chloride electrolyte, *Surface Engineering and Applied Electrochemistry*. 44 (2008) 264-270.
- Kolesnyk Ie., Influence of metal ions in iron-plating solution on structure formation of electrodeposited iron-based coatings, *Chimia*. 67 (2013) 575.
- Nakamura K., Umetani M., Hayashi T., Electrodeposition of iron-rich Ni-Fe alloys from sulphate and chloride baths, *Surface Technology*. 25 (1985) 111-119.
- Kolesnyk Ie.V., Features of structure formation of electrodeposited alloys Fe-Ni, *Scientific Bulletin of National Mining University*. 137 (2013): 62-66. (In Russian)
- Wang F., Watanabe T., Preparation and characterization of the electrodeposited Fe-Cr alloy film, *Materials Science and Engineering A*. 349 (2003): 183-190.
- Kolesnyk Ie.V., Velychko M.T., Features of structure formation of electrodeposited Fe-Cr coatings, *Metaloznastvo ta Termichna Obrobka Metaliv*. 63 (2013) 64-68. (In Russian)
- Sziráki L., Kuzmann E., El-Sharif M., et al., Electrochemical behavior of electrodeposited strongly disordered Fe-Ni-Cr Alloys, *Electrochemistry Communications*. 2 (2000) 619-625.
- Sziráki L., Kuzmann E., Chisholm C.U., et al., Characterization of the passive films on electrodeposited Fe-Ni-Cr alloys in borate solution at pH 8.4, *Central European Journal of Chemistry*. 5 (2007) 931-950.

10. Adelhani H., Arshadi M.R., Properties of Fe-Ni-Cr alloy coatings by using direct and pulse current electrodeposition, *Journal of Alloys and Compounds*. 476 (2009) 234-237.
11. Kolesnyk Ie.V. Joint effect of chromium and nickel on surface morphology and preferred crystal orientations of electrodeposited iron-based coatings, *Metallofizika i Noveishie Tekhnologii*. 37 (2015) 347-354.
12. Kolesnyk Ie.V., Bagliuk G.A. Comparative analysis of structure and properties of electrodeposited iron and Fe-Cr-Ni alloy coatings, *Metaloznavstvo ta obrobka metaliv*. 1 (2016) 23-28. (In Ukrainian)
13. Kolesnyk Ie.V. Phase composition of electrodeposited Fe-Zn alloys, *Metallofizika i Noveishie Tekhnologii*. 37 (2015) 257-264.
14. Kolesnyk Ie.V. The laws governing structure formation in Fe-Zn alloys electrodeposited from sulfate electrolytes, *Surface Engineering and Applied Electrochemistry*. 51 (2015) 235-239.