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Phase Composition of Electrodeposited Fe–Zn Alloys

Ie. V. Kolesnyk

*SHEI 'Ukrainian State University of Chemical Technology',
8 Gagarin Avenue,
49005 Dnipropetrovs'k, Ukraine*

Presence of α -phase, $\text{Fe}_{75}\text{Zn}_{25}$, $\text{Fe}_3\text{Zn}_{10}$ and η -phase in electrodeposited Fe–Zn alloys is determined by the method of X-ray diffractometry. The phase proportion varies with the increase of zinc concentration in the sulphate electrolyte. Discovered formation of $\text{Fe}_{75}\text{Zn}_{25}$ phase during co-deposition of iron and zinc can be the cause of creation of previously revealed irregular surface relief with anomalously high roughness. Revision of $\text{Fe}_{75}\text{Zn}_{25}$ phase atomic composition is accomplished by the numerical method based on precise value of the crystal-lattice spacing and taking into account elastic strain caused by zinc atoms, which are dissolved in the α -Fe crystal lattice.

Методом рентгенівської дифрактометрії визначено наявність в електроосаджених стопах Fe–Zn α -фази, $\text{Fe}_{75}\text{Zn}_{25}$, $\text{Fe}_3\text{Zn}_{10}$ та η -фази. Співвідношення фаз змінюється з ростом концентрації цинку в сульфатному електроліті. Виявлене вперше формування фази $\text{Fe}_{75}\text{Zn}_{25}$ при сумісному електроосадженні заліза та цинку може бути причиною утворення виявленого раніше нерегулярного рельєфу поверхні з аномально високою шерсткістю. Уточнення складу фази $\text{Fe}_{75}\text{Zn}_{25}$ здійснено чисельною методою, виходячи з прецизійного значення періоду ґратниці та з урахуванням пружної деформації, яку зумовлено атомами Цинку, розчиненими в ґратниці α -Fe.

Методом рентгеновской дифрактометрии установлено наличие в электроосаждённых сплавах Fe–Zn α -фазы, $\text{Fe}_{75}\text{Zn}_{25}$, $\text{Fe}_3\text{Zn}_{10}$ и η -фазы. Соотношение фаз изменяется с ростом концентрации цинка в сульфатном электролите. Обнаруженное впервые формирование фазы $\text{Fe}_{75}\text{Zn}_{25}$ при совместном электроосаждении железа и цинка может быть причиной образования выявленного ранее нерегулярного рельефа поверхности с аномально высокой шероховатостью. Уточнение состава фазы $\text{Fe}_{75}\text{Zn}_{25}$ выполнено численным методом, исходя из прецизионного значения периода решётки и с учётом упругой деформации, которая обусловлена атомами цинка, растворёнными в решётке α -Fe.

Key words: Fe–Zn alloys, phase composition, electrodeposited alloys, coat-

ings.

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1. INTRODUCTION

Electrodeposited alloys of Fe–Zn system can be employed as corrosion-resistant coatings of steel sheet [1–3], for restoration of dimensions of machinery components worn during operation [4], and as a preliminary surface treatment of steel items before application of polymer, composite and other types of coatings [5].

As known, the phase composition of metallic materials significantly influences on their properties. In addition, it should be taken into account that phase composition of electrodeposited coatings frequently differs from the equilibrium one and greatly depends on electrolyte composition and deposition process parameters, namely, current density and temperature. In this respect, experimental investigations in this field remain quite urgent. The difference of phase composition from equilibrium phase diagram is noted for electrodeposited Fe–Zn coatings, for example, in [3, 6–8]. Crystallography and thermodynamics of phases of Fe–Zn system are described in [9] and [10] respectively. However, the majority of works devoted to electrodeposited Fe–Zn alloys are directed rather to electrochemical issues of alloys deposition than to investigations of their structure and phase composition.

Nevertheless, it should be noted that phase composition of alloys of Fe–Zn system, both electrodeposited [11–13] and obtained by annealing of hot-dip zinc coating on steel substrates [14–16], is quite thoroughly investigated in the range of high zinc concentrations as these alloys are employed as corrosion-resistant coatings. However, the other possible areas of application of electrodeposited Fe–Zn alloys mentioned above also require more thorough investigations of this system in the range of high iron concentrations. Analysis of literature sources shows that only several works address this issue, *e.g.*, [7, 17, 18].

Besides, the diffraction patterns of electrodeposited Fe–Zn alloys presented in [1, 11] indicate complexity of their phase composition, which along with low thickness of the coatings make complete phase identification difficult.

Therefore, the aim of this work is to determination phase composition of electrodeposited alloys of Fe–Zn system obtained at various ratios of zinc to iron concentrations in the electrolyte.

2. MATERIALS AND METHODS

Coatings of 15 μm thickness are deposited at the temperature 55–57°C and the cathode current density 10 A/dm² from sulphate iron-plating

electrolyte containing: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ —400 g/l, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ —100 g/l, pH = 2–3, in which zinc ions are additionally inserted in the range of concentration ratios from 1:80 to 40:80 (mass) relative to iron. Steel 08kp sheet with the thickness of 0.5 mm is used as a substrate. During deposition, a soluble iron anode is used.

Phase composition of the coatings is determined by the method of X-ray diffractometry with modernized DRON-type diffractometer in copper radiation without separation from the substrate due to sufficient coatings thickness.

For evaluation of concentration of zinc solid solutions in iron, the crystal lattice spacing is precisely calculated by the angular displacement of diffraction maxima relative to the maxima of pure electrodeposited iron. Based on the obtained values of the spacing, the concentration of solid solutions is numerically calculated according to the method suggested by Lubarda [19], which regards elastic deformation of crystal lattice caused by solute atoms. According to this method, the spacing of crystal lattice of a substitution solid solution can be determined by the formula

$$a = (a_1^3 + 4\pi R_1^3 x \gamma C k_1 / \theta_1)^{1/3},$$

where a_1 is spacing of crystal lattice of the solvent, R_1 is Seitz atomic radius of the solvent, x is atomic concentration of the solute element, k and θ_1 are coefficients, characterizing crystal lattice of solid solution (for b.c.c. being 2 and 1, respectively), γ and C —constants determined according to [20] with regard to the values of elastic moduli of the solvent and the solute element.

3. RESULTS AND DISCUSSION

The results of the investigations of phase composition of electrodeposited Fe–Zn alloys show that at low ratios of zinc to iron concentrations in the electrolyte (1:80) only solid solution of zinc in α -Fe (α -phase) is formed in the coatings (see Fig. 1, *a*), which is indicated by certain angular displacement of the diffraction maxima relative to the samples of pure electrodeposited iron without alloying, which had been previously investigated by the author in the work [21]. It should be noted that axial crystal orientation of $\langle 211 \rangle$, typical for pure electrodeposited iron, is less pronounced in this case. Similar fact of decrease of perfection of crystallographic texture due to insertion of zinc ions into iron-plating electrolyte was revealed by the author during investigations of coatings deposited from chloride electrolyte in the work [22].

It was found that further increase of zinc concentration in the electrolyte results in formation of additional phases. Thus, at zinc to iron concentration ratio being 5:80, the following phases were discovered in

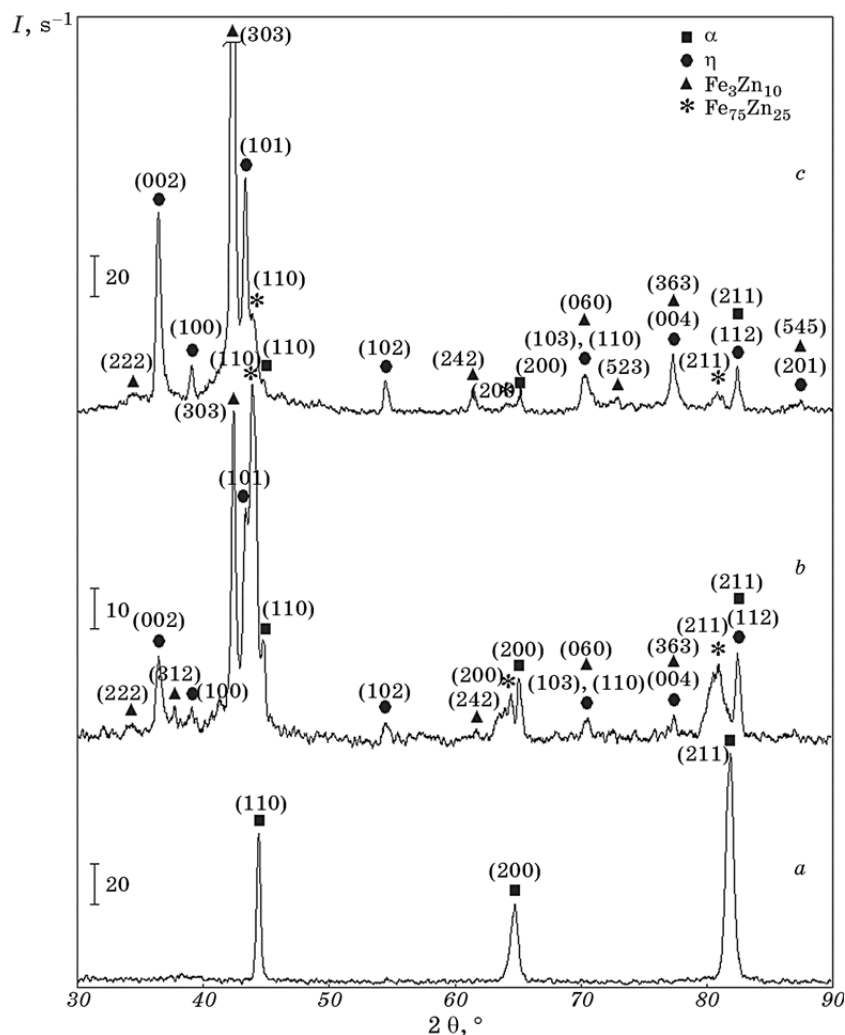


Fig. 1. Diffraction patterns of Fe–Zn alloys electrodeposited from electrolytes with Zn to Fe concentration ratio (mass): *a*—1:80, *b*—5:80, *c*—10:80.

the composition of electrodeposited coatings after thorough analysis of the obtained diffraction patterns (in descending order of diffraction maxima intensities): unknown phase with α -Fe crystal lattice; intermetallic $\text{Fe}_3\text{Zn}_{10}$ (Γ -phase), solid solution of iron in zinc (η -phase), and α -phase mentioned above (see Fig. 1, *b*).

Presence of α - and η -phases is typical for electrodeposited Fe–Zn alloys. Intermetallic $\text{Fe}_3\text{Zn}_{10}$ known in literature as Γ -phase possesses complex cubic lattice of Cu_5Zn_8 type [23] and had been found in electrodeposited Fe–Zn coatings before [24].

Angular position of the diffraction maxima of discovered unknown phase made possible a conclusion about crystal lattice of α -Fe, which is clearly seen from comparison of their positions with the ones of the maxima of identified α -phase. However, significant displacement of unknown phase maxima indicates the higher zinc concentration than in the α -phase. In addition, extremely strong axial crystal orientation of $\langle 110 \rangle$ in the found phase should be mentioned.

Discovered phase with crystal lattice of α -Fe is close by its composition to the phase $\text{Fe}_{67}\text{Zn}_{33}$ obtained by metallurgical method, described in [25]. As there are no mentions of detection of such phase in electrodeposited Fe–Zn alloys in literature sources, the author accomplished precise determination of the crystal lattice spacing by the positions of centroids of the diffraction maxima with consequent calculations of solid solution concentration with regard to elastic deformation of crystal lattice of α -Fe caused by solute zinc atoms. In order to minimize influence of residual inner stresses typical for electrodeposited coatings, on the calculations results, the angular positions of the maxima of electrodeposited pure iron coatings obtained from sulphate electrolyte at similar deposition conditions are used as reference data instead of conventional powder diffraction data, which is known to be obtained on samples without perceptible residual stresses. Accomplished calculations show that atomic composition of unknown phase is close to $\text{Fe}_{75}\text{Zn}_{25}$.

Increase of zinc to iron concentration ratio in the electrolyte to 10:80 causes no qualitative changes in phase composition of the coatings, but significantly alters phase proportion, which can be evaluated by intensities of the diffraction maxima (see Fig. 1, c). Thus, with the increase of zinc concentration, the amount of $\text{Fe}_{75}\text{Zn}_{25}$ phase decreases drastically. It is accomplished by growth of fractions of $\text{Fe}_3\text{Zn}_{10}$ and η -phase. Change of phase proportion in the coatings with the increase of zinc concentration in the electrolyte can be clearly seen in Fig. 2 imaging fragments of the diffraction patterns shown in Fig. 1 in the angular range of $40\text{--}46^\circ$, where the most intense maxima of the detected phases are located.

The further increase of zinc concentration in the electrolyte results in gradual decrease of the amounts of $\text{Fe}_{75}\text{Zn}_{25}$ and $\text{Fe}_3\text{Zn}_{10}$ phases in the coatings up to their complete disappearance. Thus, at zinc to iron concentration ratio being 40:80, phase composition of the coatings is represented solely by η -phase.

It should be mentioned that the coatings deposited from the electrolyte with the concentration ratio of 5:80 possess high surface roughness ($R_a = 4.5 \mu\text{m}$), while for the 1:80 and 10:80 ratios the values of R_a are 1.02 and 1.76 μm , respectively, and for the steel substrate without coating it is 0.93 μm . Based on this fact, the author suggested usage of the electrodeposited Fe–Zn alloy with high surface roughness as a sub-

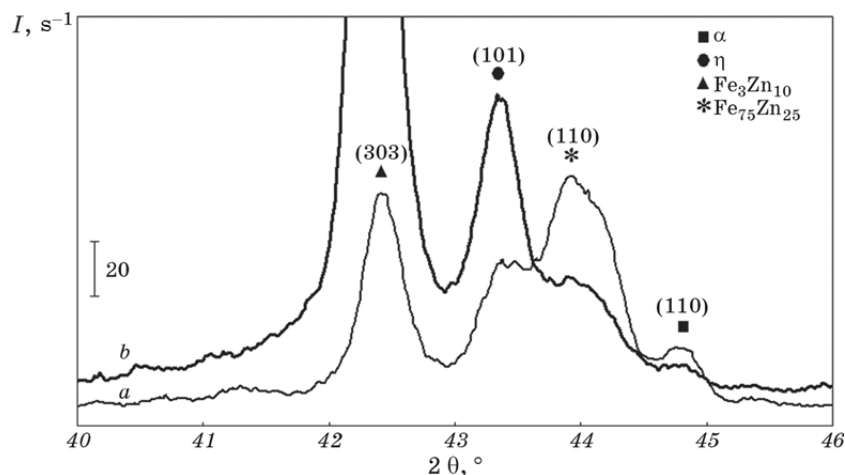


Fig. 2. Diffraction patterns of Fe–Zn alloys electrodeposited from electrolytes with Zn to Fe concentration ratio (mass): *a*—1:80, *b*—5:80.

layer before application of polymer, composite, or metallic coatings on metal items. Such method for surface preparation before application of coatings was protected by the patent [5] and confirmed its effectiveness, in particular, for enhancement of adhesion of phenyl on coatings to steel substrates [26].

Investigation results obtained in this work make possible to suppose that such anomalously high surface roughness of electrodeposited Fe–Zn alloys can be connected with formation of the found $\text{Fe}_{75}\text{Zn}_{25}$ phase, the diffraction maxima of which are the most intensive at the same zinc concentration (5:80). The further investigations will be directed to confirmation of this conclusion by means of scanning electron microscopy and X-ray spectrometry microanalysis.

Evaluation of the role of discovered strong preferred crystal orientation of $\langle 110 \rangle$ of $\text{Fe}_{75}\text{Zn}_{25}$ phase in formation of irregular surface relief with high roughness in Fe–Zn alloys coatings also may be the interesting direction of further investigations.

4. CONCLUSIONS

Presence of phases such as $\text{Fe}_{75}\text{Zn}_{25}$, $\text{Fe}_3\text{Zn}_{10}$, iron-based (α -phase) and zinc-based (η -phase) solid solutions in electrodeposited Fe–Zn alloys is determined by the method of X-ray diffractometry. The phase proportion varies with the increase of zinc concentration in the sulphate electrolyte.

Formation of $\text{Fe}_{75}\text{Zn}_{25}$ phase during co-deposition of iron and zinc is discovered for the first time. Refinement of $\text{Fe}_{75}\text{Zn}_{25}$ phase atomic

composition is accomplished by the numerical method with regard to precise value of the crystal lattice spacing and to elastic deformation caused by solute zinc atoms in crystal lattice of α -Fe.

It is found that formation of $\text{Fe}_{75}\text{Zn}_{25}$ phase with pronounced preferred crystal orientation of $\langle 110 \rangle$ can be the cause of creation of previously found irregular surface relief with anomalously high roughness.

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