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## Initial stages of electrocrystallization of nickel, iron and nickel-iron alloy on a glassy carbon electrode in an electrolyte based on a eutectic mixture of choline chloride and ethylene glycol

F.I. Danilov, D.A. Bogdanov, V.S. Protsenko

Ukrainian State University of Chemical Technology, Dnipro, Ukraine

The kinetics and mechanism of the initial stages of electrocrystallization of nickel, iron and nickel-iron alloy were characterized for the process of electrolytic deposition from a solution based on deep eutectic solvent ethaline (liquid mixture containing choline chloride and ethylene glycol at a molar ratio of 1:2, respectively). The theoretical model developed by Scharifker and Hills was used to interpret the obtained experimental data. It was shown that the electrodeposition of nickel and iron obeys the patterns of three-dimensional instantaneous and progressive nucleation, respectively. It was concluded that the formation of iron nuclei occurs at a significantly lower rate than in the case of nickel. The kinetics of the initial stages of Ni-Fe alloy deposition obeys the mechanism of instantaneous nucleation. Thus, in the case of electrolytic deposition from ethaline-based solutions on a glassy carbon electrode, nickel imposes on iron not only its own region of electrode potentials where alloy deposition occurs, but also the type of mechanism of nucleation in the course of codeposition.

**Keywords:** electrochemical crystallization, nickel, iron, alloy, deep eutectic solvent.

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### Introduction

Studying the electrochemical deposition of metal coatings from electrolytes based on the so-called deep eutectic solvents (DESS) is currently one of the key trends in modern electrochemical science [1,2]. Among the wide range of various metals and alloys that can be electrodeposited from this type of room-temperature ionic liquids, nickel, iron and nickel-iron alloy occupy a special place due to a unique combination of corrosion, protective, mechanical, electrocatalytic, magnetic and other properties of coatings [3–7]. Earlier [8], we considered the kinetics of codeposition of nickel and iron from the electrolyte based on a widespread representative of DESS, the so-called ethaline, which is a eutectic mixture of choline chloride and ethylene glycol. It was shown that the process of electrolytic deposition of Ni-Fe alloy from this electrolyte is accompanied by acceleration of the discharge of iron (II) ions. A mechanism based on the ideas previously reported by Zech et al. [9] was proposed to explain this effect. However, the patterns of the initial crystallization stages, the kinetics of which are extremely sensitive to the nature of the electrolyte used, was left out of consideration. Currently available data on the electrocrystallization stages of deposition of nickel and iron from DESS are rather limited and

contradictory [7,10–12]. In particular, electrocrystallization of nickel from an electrolyte based on reline (a DES, which is a eutectic mixture of choline chloride and urea) on a copper microelectrode obeys the patterns of three-dimensional instantaneous nucleation, the nature of which does not change with the introduction of nicotinic acid [10]. However, in the study of the initial stages of Ni electrocrystallization from the same electrolyte on a glassy carbon electrode and controlled water content in solution [11], it was found that both instantaneous and progressive nucleation mechanisms can be observed, depending on the selected potential applied to the electrode. Patterns of electrochemical nucleation of nickel in ethaline-based solutions are not described in the literature.

As for the deposition of iron, it was shown that the mechanism of progressive nucleation is realized in the ethaline-based solution on a glassy carbon electrode [7,12]. However, the process is sensitive to the chemical composition of the electrolyte (for example, in a solution with a reduced concentration of chloride ions, the process is not described by either the mechanism of progressive nucleation or instantaneous one). Since an electrolyte containing an ascorbic acid additive was used in our study [8] to prevent the oxidation of iron(II) ions by atmospheric oxygen, it remains unclear whether the conclusions about the electrocrystallization mechanism reported in

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works [7,12] can be extended *a priori* to the deposition process of iron from the electrolyte used in study [8]. Patterns of electrochemical nucleation during deposition of Ni–Fe alloy from DES-based electrolytes are not described in the literature known to us.

In view of the above, the aim of this work was to establish the patterns of the initial stages of electrochemical crystallization in the course of nickel, iron and nickel-iron alloy deposition from an electrolyte based on eutectic mixture ethaline containing the additive of ascorbic acid.

## Experimental

Electrolytes containing 0.5 M NiCl<sub>2</sub> (for deposition of individual nickel), 0.2 M FeCl<sub>2</sub>·H<sub>2</sub>O (for deposition of individual iron) or 0.5 M NiCl<sub>2</sub>+0.2 M FeCl<sub>2</sub>·H<sub>2</sub>O (for deposition of Ni–Fe alloy) in ethaline were used for coatings preparation. All electrolytes also contained an additive of ascorbic acid (2 g dm<sup>-3</sup>), which is introduced to prevent spontaneous oxidation of iron(II) ions caused by the interaction with atmospheric oxygen. The method of preparation of the electrolytes was described in detail in our previous publication [8]. It should be observed that, as found out earlier [8], the presence of water impurities in the electrolyte based on a DES can affect the kinetics and mechanism of electrochemical processes. That is why we used anhydrous nickel chloride salt and iron chloride monohydrate, rather than the more common and available suitable crystal hydrates with higher water content. According to our calculations, the introduction of water of crystallization via the addition of the specified amount of iron(II) chloride monohydrate increases the water content by 0.4 wt.%. Due to the hygroscopicity of the components of the solution, the electrolytes contained a certain amount of water, the total content of which did not exceed 1 wt.% (determined by the Fisher method).

A glassy carbon working electrode (∅ 3 mm) was used to record current transients, the surface of the electrode being polished and washed in hydrochloric acid solution before each experiment, then with distilled water and dried in an air stream. The experiments were performed in a common thermostated (60<sup>0</sup>C) three-electrode cell. The auxiliary electrode was either a nickel plate (in the study of electrocrystallization of nickel and nickel-iron alloy) or a steel plate (in the study of electrocrystallization of iron). The reference electrode was a platinum wire

immersed in a solution of 2.5 mmol dm<sup>-3</sup> K<sub>3</sub>[Fe(CN)<sub>6</sub>]+2.5 mmol dm<sup>-3</sup> K<sub>3</sub>[Fe(CN)<sub>6</sub>] in ethaline, which was at the same temperature as working electrode. The electrical contact of the solution in which the reference electrode was located and the solution in which the working and auxiliary electrodes were immersed was provided by the Luggin capillary.

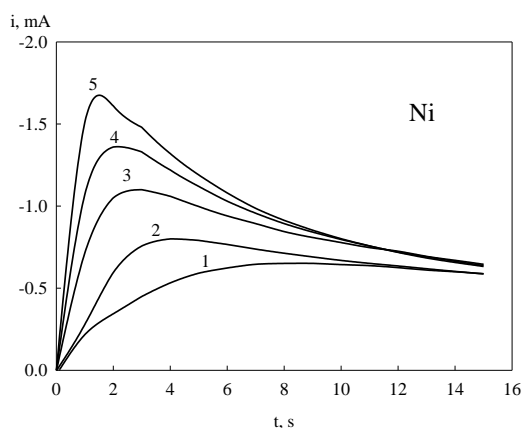
Current transients in the study of electrocrystallization were recorded in potentiostatic mode using the Potentiostat/Galvanostat/ZRRReference 3000 (Gamry, USA).

## Results and discussion

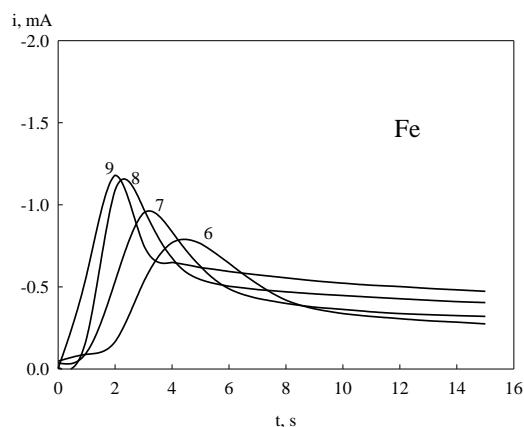
The experimentally registered current density transients for the initial stages of electrocrystallization of nickel, iron, and Ni–Fe alloy for different electrode potentials are shown in Fig. 1. All the obtained transients have a classical appearance: the initial increase in current after the imposition of the cathode electrode potential, reaching a certain maximum value of current density ( $i_{max}$ ), which corresponds to a certain point in time ( $t_{max}$ ), and a further decrease in current density. An increase in the current density at  $t_{max}<0$  is due to an increase in the surface concentration of the nuclei of the metal phase formed on the electrode. A decrease in the current density at  $t_{max}>0$  is determined by a decrease in the concentration of discharged metal ions due to diffusion limitations of their transport. In all cases, other things being equal, an increase in the cathodic polarization leads to an increase in the maximum current density ( $i_{max}$ ) and a decrease in the corresponding time ( $t_{max}$ ). It should be noted that the electrocrystallization of individual iron occurs at electrode potentials significantly more negative than in the case of individual nickel, which is fully consistent with the results of previous voltammetric studies [8]. Electrodeposition of the Ni–Fe alloy occurs at potentials close to the value inherent in nickel [8,13].

To quantify the obtained current transients, we used the known kinetic model developed by Scharifker and Hills [14]. This model describes two different mechanisms of formation of a monolayer of metal nuclei during electrodeposition on a foreign substrate: (i) instantaneous nucleation, when almost all nuclei are formed immediately after switching on the cathode current (this means a high rate of nucleation as compared with the rate of their

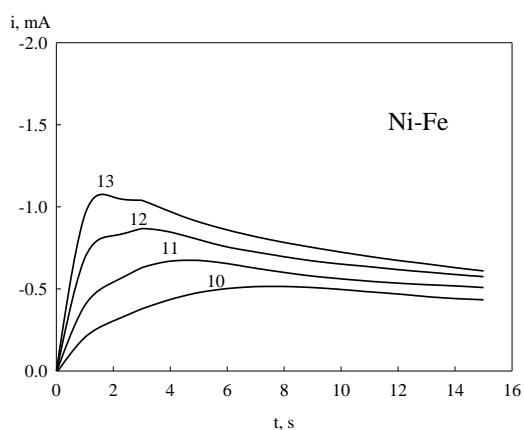
subsequent growth); and (ii) progressive nucleation, when the number of nuclei gradually increases over time during electrodeposition (this means a relatively low rate of nucleation).



a



b



c

Fig. 1. Current transients for the initial stages of electrocrystallization for deposition of Ni (a), Fe (b) and Ni-Fe (c) on a glassy carbon electrode at different values of the electrode potential (V): -0.89 (1); -0.92 (2); -0.95 (3); -0.98 (4); -1.01 (5); -1.21 (6); -1.23 (7); -1.25 (8); -1.27 (9); -0.86 (10); -0.89 (11); -0.92 (12); -0.95 (13)

Let us note that these two mechanisms are both ideal cases, and in practice a certain combination of these two extreme cases can be realized, when one of them prevails.

In order to determine which nucleation mechanism is valid for this particular case, it is customary to use the following kinetic equations in dimensionless form [14]:

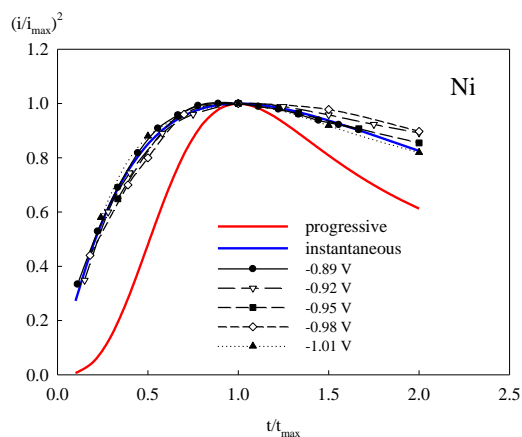
$$\left(\frac{i}{i_{\max}}\right)^2 = \frac{1.9542}{t/t_{\max}} \left\{ 1 - \exp\left[-1.2564\left(\frac{t}{t_{\max}}\right)\right] \right\}^2, \quad (1)$$

$$\left(\frac{i}{i_{\max}}\right)^2 = \frac{1.2254}{t/t_{\max}} \left\{ 1 - \exp\left[-2.3367\left(\frac{t}{t_{\max}}\right)^2\right] \right\}^2. \quad (2)$$

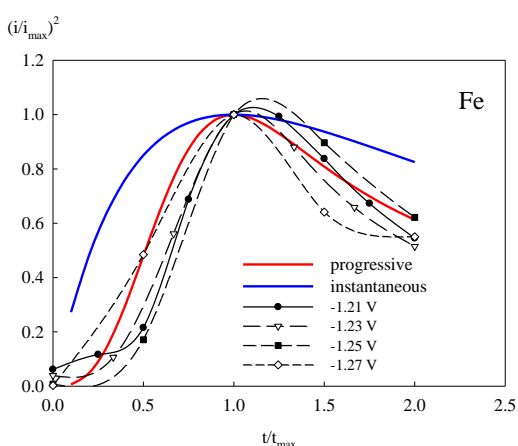
Equations (1) and (2) describe the kinetics of instantaneous and progressive nucleation, respectively. The graph plotted in dimensionless coordinates  $(i/i_{\max})^2$  vs.  $(t/t_{\max})$  according to Eqs. (1)–(2) yields two lines (Fig. 2), the appearance and location of which do not depend on the electrode potential. These two curves allow discriminating between two nucleation mechanism: if the dependence  $(i/i_{\max})^2$  vs.  $(t/t_{\max})$  plotted on the basis of experimental data approaches that reflected by Eq. (1), then a conclusion is made about the instantaneous mechanism of nucleation. If the obtained experimental data are more accurately reflected by the curve corresponding to Eq. (2), it indicates a progressive mechanism of nucleation.

Analysis of the obtained data shows that the electrocrystallization of individual nickel obeys the patterns of instantaneous nucleation (Fig. 2,a), which coincides with the mechanism reported for the nickel plating electrolyte based on reline [10]. Interestingly, the value of the deposition potential (in the studied range from -0.89 V to -1.01 V) has little effect on the appearance and location of these test curves in dimensionless coordinates  $(i/i_{\max})^2$  vs.  $(t/t_{\max})$ .

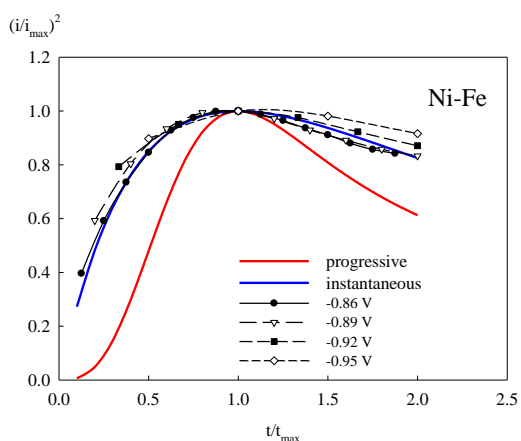
The electrocrystallization of individual iron on a glassy carbon electrode is fundamentally different. Although the scatter of the points of the corresponding curves  $(i/i_{\max})^2$  vs.  $(t/t_{\max})$  when varying the electrode potential is significantly larger (Fig. 2,b), the nature of the dependences allows us to draw a clear conclusion about the mechanism of progressive nucleation. This finding coincides with the conclusion made earlier in works [7,12].



a



b



c

Fig. 2. Experimental dependences  $(i/i_{max})^2$  vs.  $(t/t_{max})$  for the initial stages of electrocrystallization for the deposition of Ni (a), Fe (b) and Ni – Fe (c) on a glassy carbon electrode at different values of the electrode potential (black lines) and theoretical dependences  $(i/i_{max})^2$  vs.  $(t/t_{max})$  plotted according to Eqs. (1) and (2) for instantaneous and progressive nucleation (blue and red lines, respectively)

It follows from the observed differences in the mechanisms of the initial electrocrystallization stages of nickel and iron in ethaline that the formation of Fe nuclei occurs at a significantly lower rate than in the case of Ni. This may be due to both differences in the nature of these two metals and the conditions under which these processes occur (differences in the potentials of electrodeposition, surface charge, and structure and composition of the double layer).

Experimental data on the kinetics of electrochemical nucleation of the Ni–Fe alloy (Fig. 2,c) indicate the implementation of the mechanism of instantaneous nucleation. Thus, it can be argued that during codeposition of these two metals from ethaline solution on a glassy carbon electrode, nickel imposes on iron not only its potential region where deposition occurs, but also the nature of electrochemical nucleation mechanism described by Eq. (1). It is known that the mechanism of instantaneous nucleation is typical of the deposition of alloys–solid solutions [15], a typical representative of which is the nickel-iron alloy [4,8].

### Conclusions

Electrolytic deposition of nickel and iron from the electrolyte based on deep eutectic solvent ethaline on the surface of a glassy carbon electrode obeys the patterns of three-dimensional instantaneous nucleation and progressive nucleation, respectively. The nickel component of the alloy imposes its own mechanism of instantaneous nucleation during electrodeposition of Ni–Fe alloy from ethaline-based solution.

### Acknowledgments

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**Початкові стадії електрокристалізації нікелю, заліза і сплаву нікель-залізо на скловуглецевому електроді в електроліті на основі евтектичної суміші холін хлориду і етиленгліколю**

**Ф.Й. Данилов, Д.А. Богданов, В.С. Протченко**

Охарактеризовано кінетику і механізм початкових стадій електрокристалізації нікелю, заліза і сплаву нікель-залізо при електролітичному осадженні з розчину на основі низькотемпературного евтектичного розчинника ethaline (рідка суміш, що містить холін хлорид і етиленгліколь при молярному співвідношенні 1:2, відповідно) на скловуглецевому електроді. Для інтерпретації отриманих експериментальних даних використана теоретична модель, запропонована Шаріфкером і Хіллсом. Показано, що електролітичне осадження нікелю і заліза підкорюється закономірностям тримірної миттєвої і прогресивної нуклеації, відповідно. Зроблено висновок про те, що утворення зародків заліза відбувається із суттєво нижчою швидкістю, аніж у випадку нікелю. Кінетика початкових стадій осадження сплаву Ni-Fe підкорюється механізму миттєвої нуклеації. Отже при спільному електролітичному осадженні з розчину на основі ethaline на скловуглецевому електроді нікель "нав'язує" залізу не тільки свою ділянку електродних потенціалів, де відбувається сплавоутворення, але і тип механізму електрохімічної нуклеації.

**Ключові слова:** електрохімічна кристалізація, нікель, залізо, сплав, низькотемпературний евтектичний розчинник.

**Initial stages of electrocrystallization of nickel, iron and nickel-iron alloy on a glassy carbon electrode in an electrolyte based on a eutectic mixture of choline chloride and ethylene glycol**

**F.I. Danilov\*, D.A. Bogdanov, V.S. Protsenko**

**Ukrainian State University of Chemical Technology, Dnipro, Ukraine**

\* e-mail: fdanilov77@gmail.com

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