Diffusion at the Film−Substrate Interface during Nickel Electrocrystallization on a Copper Substrate

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Received June 10, 2017

Abstract—The results of experimental studies of the diffusion layer at the interface between a nickel electrolyte film and a copper substrate are presented. Studies have shown that in the transition layer, diffusion of the deposited metal into the substrate material occurs. The depth of the diffusion layer and, consequently, the concentration of interstitial nickel atoms strongly depend on the electrocrystallization conditions: 2 μm in the constant-current mode and 4 μm under laser-assisted deposition. The diffusion coefficient of nickel adatoms in polycrystalline copper is 8.3×10^{-16} m²/s in the constant-current deposition mode and 3.3×10^{-13} m²/s under laser-assisted deposition.

INTRODUCTION

The physics of the film state of a substance is of interest, first, because new specific effects may occur in films that are not observed in bulk samples. The most typical effect is the dependence of various physical characteristics of films on their dimensions; in particular, diffusion processes are accelerated in films [1]. However, despite numerous studies [2, 3], quantitative data on diffusion processes in binary systems are very limited in publications. In addition, when studying diffusion processes in film systems, it is rather difficult to separate the contributions of different processes.

From the entire existing set of diffusion mechanisms in the case of electrocrystallization, two main ones can be distinguished: diffusion along grain boundaries (grain-boundary diffusion) and diffusion in the grain volume (bulk diffusion). Bulk diffusion can occur in different ways: by vacancies or by atomic exchange mechanisms. Typically, bulk diffusion is accompanied by the formation of new phases in systems in which they are possible [4]. However, there is no generally accepted point of view on many questions concerning the peculiarities of diffusion processes in crystalline materials.

In most works dealing with the direct measurement of diffusion parameters, a large scatter of experimental data on values of the diffusion coefficients and the energy of its activation in metals is observed. This is associated with various technological modes of structure formation, different concentrations of uncontrol-
lable impurities, or other factors. For these and other reasons, there is no detailed understanding of the specific features of the physical mechanisms of diffusion processes occurring in crystalline materials. It was demonstrated by studies of the diffusion permeability of metals that the values of the grain-boundary diffusion coefficients (D_b) are several orders of magnitude larger than the bulk diffusion coefficient (D_v) [5]. For example, for the diffusion of copper in nickel, $D_b = 5.06 \times 10^{-15}$–$2.2 \times 10^{-14}$ m²/s and $D_v = 1.4 \times 10^{-34}$–$3.7 \times 10^{-31}$ m²/s with a temperature change from 398 to 443 K; for the diffusion of cobalt in titanium, $D_b = 8.4 \times 10^{-15}$–$4.1 \times 10^{-14}$ m²/s and $D_v = 1.56 \times 10^{-20}$–$4.8 \times 10^{-19}$ m²/s with a temperature change from 423 to 473 K; and for the diffusion of silver in copper, $D_b = 2 \times 10^{-14}$ m²/s and $D_v = 2.2 \times 10^{-20}$ m²/s at 423 K.

In the study of self-diffusion in nickel, only grain-boundary diffusion was observed [6], and bulk diffusion can be considered "frozen" [7]. Anomalously high values of the coefficients of grain-boundary diffusion were also found in a number of experimental studies of nanocrystalline metals with an average grain size of ~10 nm in comparison with conventional polycrystals [8]; some of the materials were obtained by condensation.

However, the majority of the work is devoted to investigation of the diffusion mechanisms that occur during isothermal annealing. During electrocrystallization, diffusion processes occur in the formation of a growing film at the initial stages of nucleation.
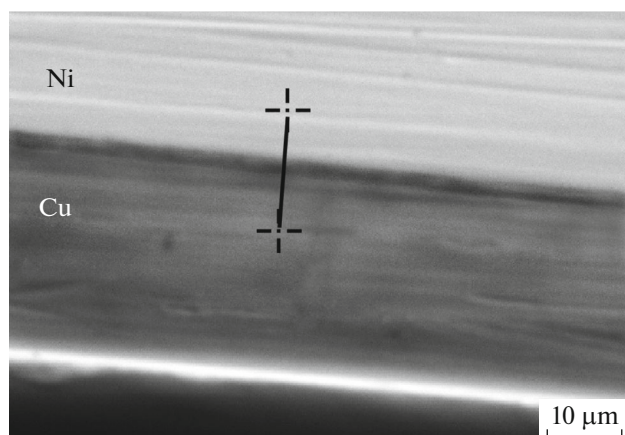
Fig. 1. SEM image of the transverse section and directions of scanning of the Ni–Cu film–substrate transition layer.

In the process of electrocrystallization, which occurs with large overvoltages supplied to the cathode, a direct embedding mechanism is observed, when each adatom located on the substrate is the center of growth of a new phase [9]. In addition, the adatom can diffuse into the substrate [10, 11], thereby forming, for example, a continuous series of solid solutions, which consists of atoms of the substrate and atoms of the metal crystallizing on the substrate. Therefore, studying diffusion processes at the film–substrate interface is of interest, both in terms of theory and practice.

In the present paper, we present the results of experimental studies of the diffusion layer at the boundary between a nickel electrolyte film and a copper substrate. The coefficients of diffusion of nickel adatoms into polycrystalline copper are determined, and the results are compared to those obtained by other authors.

EXPERIMENTAL

Nickel films 15–20 μm in thickness were deposited with the use of a constant and pulsed current over 2 h. An aqueous electrolyte solution consisting of 300 g/L of $NiSO_4 \cdot 7H_2O$, 30 g/L of H_3BO_3, and 50 g/L of $Na_2SO_4 \cdot 5H_2O$, with pH 6 and a temperature of $T = 300$ K was used in the electrodeposition process. The repetition rate of the current pulses (f) was varied in the range from 30 to 1000 Hz. The current pulse density (Q is the ratio of the pulse period to duration) was varied from 2 to 32. The average density of the constant and pulsed current (j) was 0.5–1 A/dm², which enabled a variation in the overvoltage at the cathode (η) within 0.1–0.3 V. The laser-assisted deposition of nickel films was carried out using a laser-electrochemical unit assembled on the basis of a gas-discharge CO_2 laser with a wavelength of $\lambda = 10.6$ μm and a power of 25 W under continuous generation [12].

Copper plates were used as the substrate for electrodeposition. The substrates underwent mechanical and chemical polishing in a 5% nitric-acid solution. Chemical polishing reduced the roughness and removed the hardening formed after mechanical polishing. Then the substrates were degreased in a solution of Vienna lime and washed in distilled water. The thickness of the deposited films was 20–50 μm.

The elemental composition of the film–substrate transition layer was determined by micro-X-ray spectral analysis using a PEMMA-102-02 scanning electron microscope with a resolution power of 5 nm. We examined the end faces of the substrate with the deposited film, polished mechanically and chemically, using reverse current pulses in the final stage, which allowed not only polishing of the end surface, but also the removal of particles of another metal from the end surface, possibly trapped by mechanical polishing. These procedures increased the reliability of micro-X-ray spectral analysis of the film–substrate transition layer.

To obtain a quantitative estimate of the strength of adhesion (σ) of the coatings to the substrate, the samples were examined using a PMT-3 microhardness tester by indenting a diamond pyramid into the interface between the film and substrate at the lateral section [11].

RESULTS AND DISCUSSION

To determine the structure of the transition layer at the film–substrate interface, elemental chemical analysis was carried out for the presence of nickel and copper atoms. Studies were conducted in the direction perpendicular to the interface with 0.5-μm steps. The area of the investigation extended to 4–6 μm on either side of the interface, depending on the conditions of deposition of the films. A SEM image of the interface of the transition layer and the direction along which the elemental composition was investigated are presented in Fig. 1.

The results of qualitative micro-X-ray spectral analysis of the film–substrate transition layer for different probe coordinates (x) [13] are shown in Fig. 2. Nickel films on copper substrates were obtained in the constant-current deposition mode. Two main elements were analyzed, of which the growing film and the substrate consisted. Scanning was carried out from the side of the deposited film to the depth of the substrate.

It is seen in Fig. 2 that there are lines in the spectra corresponding to two elements: a crystallizing material (Ni) and a substrate material (Cu). Near the interface, only nickel atoms are present in the growing film (Fig. 2a). With further scanning of the film–substrate transition layer into the bulk of the substrate, an increase in the intensity of the lines corresponding to the substrate material is observed in the spectra (Figs. 2b and 2c), which indicates an increase in the
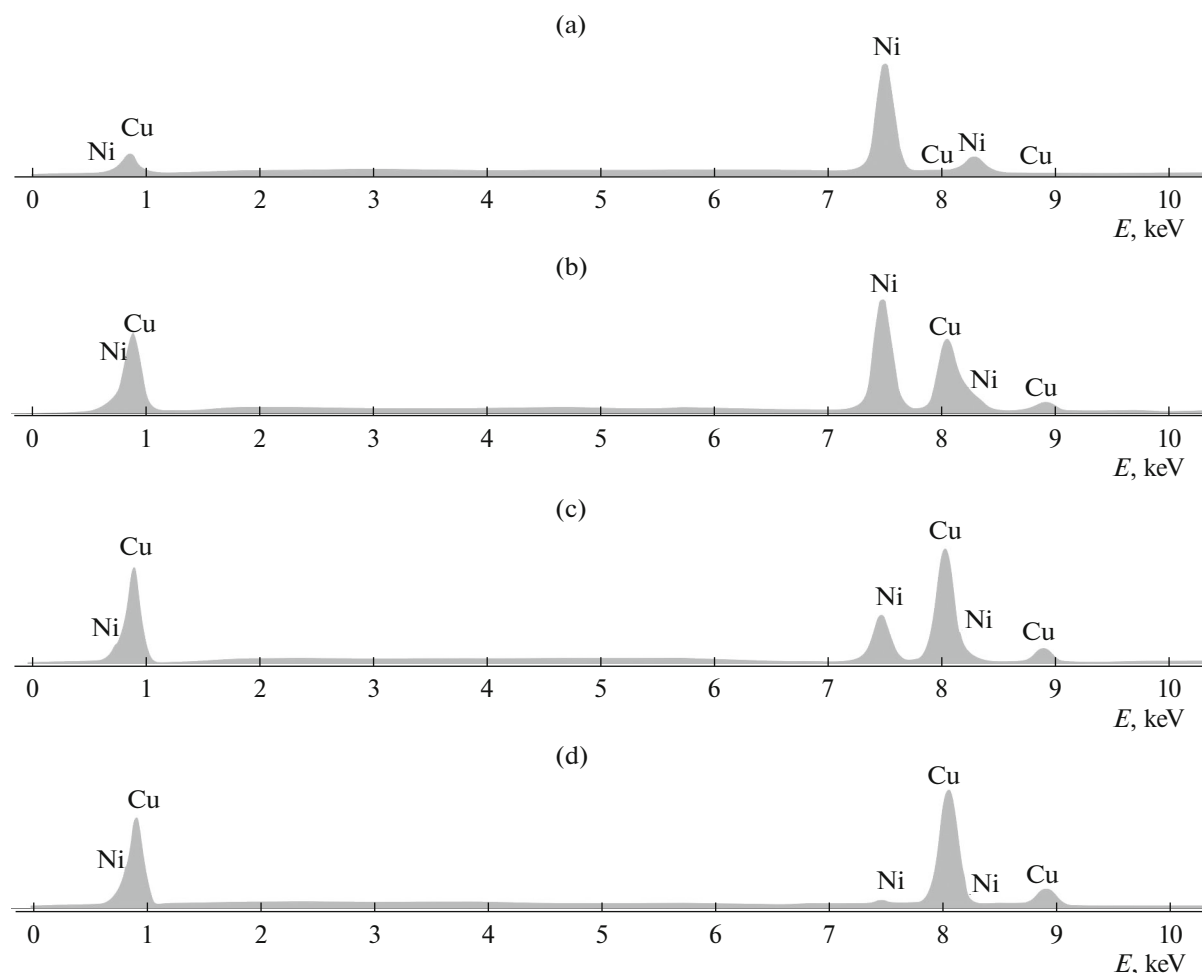
Fig. 2. Results of micro-X-ray spectral analysis of the transition region between a nickel film and a substrate, obtained at constant current ($j = 0.5$ A/dm^2, $\eta = 0.1$ V) at different probe coordinates x: (a) −0.5, (b) 1.0, (c) 1.5, and (d) 2.5 µm.

concentration of atoms in the substrate material and a decrease in the concentration of atoms in the film material. When the substrate depth is 2.5 µm, atoms of the film material were not detected in the samples deposited at constant current (Fig. 2d). It follows that during electrodeposition, there is a diffusion interaction between the coating elements and the surface of the base metal, as a result of which nickel diffuses into the substrate metal, forming a transition diffusion layer.

Quantitative chemical analysis of the film–substrate transition layer was carried out to determine the amount of diffused nickel atoms and the depth of their penetration into the substrate. We studied the films obtained under different deposition conditions: with constant composition of the aqueous electrolyte solution and with different values of the cathode potential (η), which is determined by the average current density (j) and the type of current itself [14]. The results of chemical analysis of the transition diffusion region of nickel

films on copper substrates obtained under different deposition conditions are presented in Table 1.

It follows from the results that the electrocrystallization of nickel on a copper substrate leads to the formation of a diffusion region at the film–substrate interface. Depending on the conditions of crystallization, the diffusion of nickel was 2−3.5 µm when the cathode potential was varied from 0.1 to 0.3 V. The application of laser-assisted deposition expands the diffusion layer to 4 µm. This can be explained by an increase in the energy of nickel adatoms due to the absorption of monochromatic laser radiation by metal ions.

In addition, an increase in the adhesion strength of the coatings to the substrate can be proof of the diffusion interaction between the coating elements and the substrate surface, as a result of which nickel diffuses into the substrate metal, forming a transition diffusion layer. For example, overvoltage supplied to the cathode from 0.1 to 0.3 V increases the adhesion strength from 300 to 620 MPa, and the penetration depth of

Table 1. Concentration (C) of nickel diffusing into the copper substrate under different deposition conditions

Deposition conditions	x, μm									
	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
	C, at %									
Constant current $j = 0.5$ A/dm^2, $\eta = 0.1$ V	100	55.7	10	2.6	0.65	0	0	0	0	0
Pulsed current $j = 0.5$ A/dm^2, $f = 50$ Hz, $Q = 32$, $\eta = 0.3$ V	100	67	31	12	5	1.6	1	0.5	0	0
Constant current with laser stimulation $j = 0.5$ A/dm^2, $\eta = 0.1$ V	100	78	42	19	9	2.8	1.9	1.08	0.5	0

nickel adatoms increases from 2 to 3.5 μm; the use of laser-assisted deposition increases the adhesion strength to 700 MPa, and the depth of penetration reaches 4 μm.
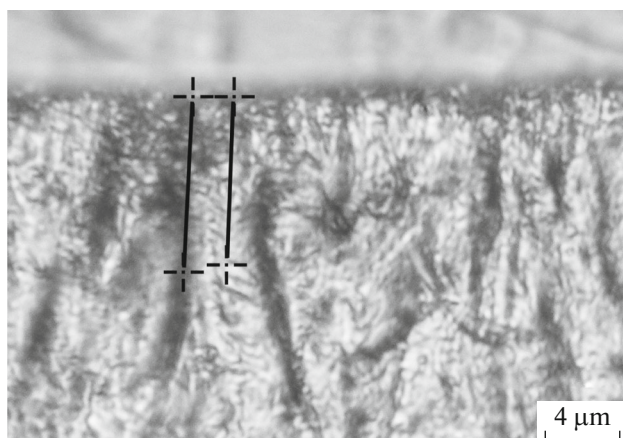
Fig. 3. SEM image of the transverse section and direction of scanning of the copper substrate.
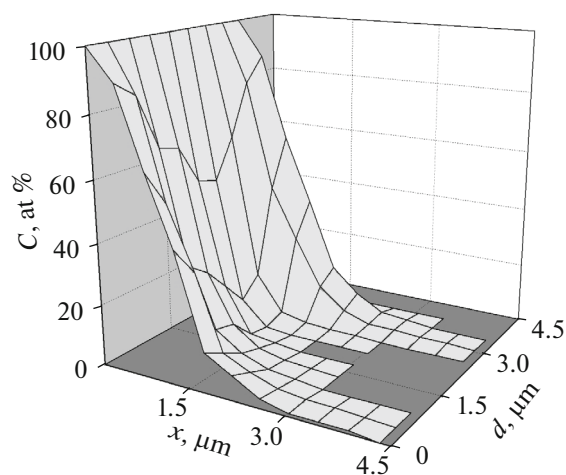
Fig. 4. Nickel concentration in the copper grain near the film–substrate interface, obtained at constant-current deposition; d is the grain thickness, and x is the depth of diffusion.

To reveal the mechanism of the penetration of nickel adatoms into the copper substrate, the elemental composition of the copper substrate over its depth was studied in various regions: at grain boundaries and in grains. To determine the areas of research, the end sections were etched in a 10% solution of nitric acid before the structure was manifested in the cross section of the copper substrate (Fig. 3). The selection of regions for study is based on the determination of changes in the concentration of nickel over the depth of the substrate, both for the grain boundaries and for the grains themselves.

Figures 4 and 5 show the distribution of nickel in a grain with the thickness d: from one grain boundary to the other and into the bulk of the substrate for different deposition conditions. It is seen that there are at least two ways of penetration of adatoms deep into the copper substrate during electrocrystallization. These are, first, grain boundaries (grain-boundary diffusion) and, second, grains (bulk diffusion) where solid solutions are formed.

To determine the diffusion coefficient (D), the distribution of nickel in the diffusion zone was plotted as a function of $\log C = f(x^2)$ (Fig. 6), where C is the nickel concentration in the range of 0–100 at %, and x is the depth of diffusion. The diffusion coefficients were determined by the known method [15], using equation

$$D = \frac{1}{4\tau \tan \alpha}, \qquad (1)$$

where τ is the time of the diffusion-stimulating action, and α is the slope of the dependence of $\log C = f(x^2)$ (Fig. 6).

The time τ of the diffusion-stimulating effect was determined experimentally as the time during which the growing film covered the entire surface of the cathode. In the mode of electrodeposition at constant current, τ was 300 s; in the pulsed mode of electrodeposition, it was 20 s; and in the transition to the mode of electrodeposition at constant current with the use of laser-assisted deposition, τ decreased to 10 s.
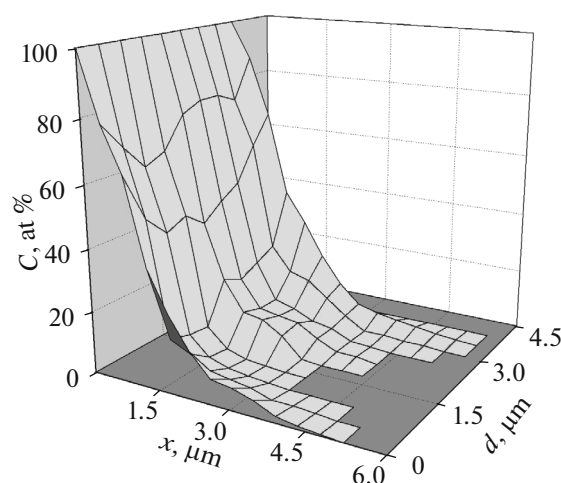
Fig. 5. Nickel concentration in the copper grain near the film−substrate interface, obtained at constant-current laser-assisted deposition; d is the grain thickness, and x is the depth of diffusion.

Fig. 6. Logarithmic dependencies of the nickel concentration in the diffusion region after deposition in (*1*) the constant-current mode (j = 0.5 A/dm^2, η = 0.1 V), (*2*) the pulsed-current mode (j = 0.5 A/dm^2, f = 50 Hz, Q = 32, η = 0.3 V), and (*3*) the constant-current mode with laser stimulation (j = 0.5 A/dm^2, η = 0.1 V).

Two sections—I and II—can be distinguished in the above-mentioned dependences (Fig. 6), differing in slopes, which probably can be explained by different diffusion mechanisms. By comparing Figs. 4 and 5, it can be assumed that in Section I diffusion is carried out in accordance with two basic mechanisms: grain-boundary and bulk, and in section II, only the grain-boundary mechanism takes place.

The diffusion coefficients of nickel in copper, calculated from Eq. (1) for different deposition conditions, and the results obtained in other works are listed in Table 2. It is seen that the values of the diffusion coefficient (D) obtained in the present study are in good agreement with the results obtained by other authors. A large spread in the values of D is associated, in one case, with the size factor and the thickness of the layers [1], and in other cases, with the temperature at which diffusion occurred [16, 17].
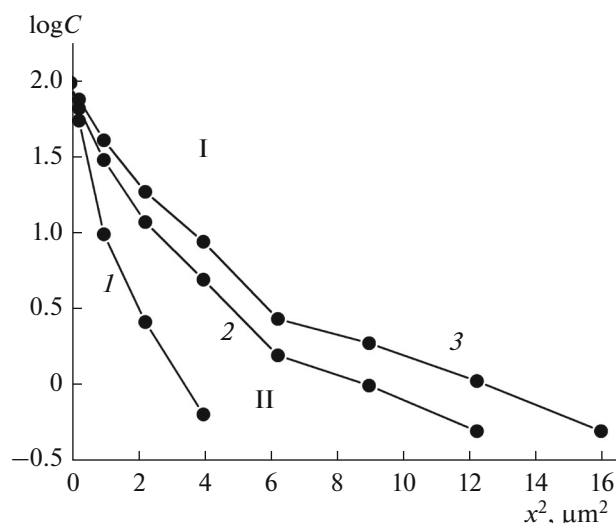
A significant difference between the observed diffusion from self-diffusion at high temperatures is that during electrodeposition, diffusion takes place at low temperatures: 293 K for constant-current deposition and 351 K for laser-assisted deposition. At these temperatures, the diffusion coefficients are 10^{-22}–10^{-20} m^2/s [17]. However, the adatoms of the deposited substance have a much higher energy than the thermal-motion energy kT [18].

CONCLUSIONS

Studies of the transition layer at the film−substrate interface, formed upon the electrodeposition of nickel films onto a copper substrate, showed that in this

Table 2. Values of the diffusion coefficient of nickel in copper

Deposition conditions	D, m^2/s				
	section		reference		
	I	II	[1]	[14]	[15]
Constant current	8.3×10^{-16}	2×10^{-15}			
Pulsed current	4.3×10^{-14}	1.5×10^{-13}	10^{-17}–10^{-7}	10^{-22}–10^{-10}	10^{-20}–10^{-14}
Constant current with laser stimulation	10^{-13}	3.3×10^{-13}			

layer, the deposited metal diffuses into the substrate material. The depth of the diffusion layer and, consequently, the concentration of embedded nickel atoms strongly depend on the electrocrystallization conditions: 2 μm in the constant-current mode and 4 μm under laser-assisted deposition. The values obtained for the diffusion coefficient of $8.3 \times 10^{-16} - 3.3 \times 10^{-13}$ m^2/s indicate a high mobility of nickel adatoms in polycrystalline copper and strongly depend on the deposition conditions, more precisely, on the energy of the deposited adatoms. A large spread in the values of the diffusion coefficient is probably associated with different diffusion mechanisms.

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Translated by O. Zhukova