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STRUCTURE, PHASE TRANSFORMATIONS, AND DIFFUSION

Diffusion at the Boundary between the Film and Substrate upon the Electrocrystallization of Zinc on a Copper Substrate

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Abstract—In this paper, we present the results of experimental investigations of the diffusion layer formed at the film–substrate interface upon the electrodeposition of zinc films on a copper substrate. The investigations have shown that, in the transient layer, the deposited metal is diffused into the material of the substrate. The depth of the diffusion layer and, consequently, the concentrations of the incorporated zinc atoms depend strongly on the conditions of electrocrystallization, which vary from 1.5 μm when using direct current to 4 μm when using direct current in combination with laser-stimulated deposition (LSD). The X-ray diffraction investigations of the transient layer at the film–substrate interface have shown that, upon electrocrystallization using pulsed current in rigid regimes with the application of the LSD, a $CuZn_2$ phase is formed in the diffusion layer. This indicates that the diffusion of zinc into copper occurs via two mechanisms, i.e., grain-boundary and bulk. The obtained values of the coefficient of diffusion of zinc adatoms in polycrystalline copper are equal to 1.75×10^{-15} m^2/s when using direct current and 1.74×10^{-13} m^2/s when using LSD.

Keywords: film–substrate interface, diffusion transient layer, diffusion coefficient, energy of adatoms

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INTRODUCTION

The formation of a new phase on a substrate upon electrocrystallization is of significant interest from the point of view of studying diffusion processes in binary systems. The initial stages of electrocrystallization mainly affect the formation of the texture; size of crystallites; amount of defects; and, consequently, the mechanical properties of electrodeposited films [1]. In particular, the corrosion resistance and adhesion mainly depend on the nature of the transient layer between the substrate and the film, the structure of which is completely determined by the initial stages of crystallization [2]. Therefore, the study of diffusion processes at the film–substrate interface is of interest from both the theoretical and practical viewpoints.

Among the known mechanisms of diffusion [3] upon electrocrystallization, two main mechanisms can be distinguished, i.e., diffusion along the grain boundaries (grain-boundary diffusion) and diffusion through vacancies, via the mechanism of atomic exchange. Usually, the bulk diffusion is accompanied by the formation of new phases in systems in which they are possible. However, currently, there is no common viewpoint in the literature on many problems concerning the occurrence of diffusion processes in crystalline materials.

In most works devoted to the direct measurements of diffusion parameters, a large spread is observed in the experimental data on the diffusion coefficients and activation energies for diffusion in metals. This is related to differences in the technological regimes of the formation of the structure, different concentrations of uncontrollable impurities, and other factors.

The majority of works are devoted to investigating the mechanisms of diffusion that occur upon isothermal annealing. Upon electrocrystallization, the diffusion processes occur upon the formation of the growing film at the initial stages of nucleation. In this case, an adatom can diffuse into the substrate [4], thereby forming a new phase, which consists of atoms of the substrate and atoms of the metal that crystallizes on the substrate.

In this paper, we give the results of experimental investigations of the diffusion layer at the film–substrate interface for zinc films electrodeposited on a copper substrate. The values of the coefficients of diffusion of zinc adatoms in the polycrystalline copper have been determined.

EXPERIMENTAL

The zinc films were prepared using direct and pulsed electrical current, as well as by applying the method of laser-stimulated deposition (LSD). For the electrodeposition of zinc films, an aqueous electrolytic solution of the following composition was used: $ZnSO_4 \cdot 7H_2O$, 250 g/L; $Na_2SO_4 \cdot 5H_2O$, 75 g/L;

$Al(SO_4)_3$, 30 g/L (pH 4; $T = 300$ K). The frequency of the repetition of current pulses (f) varied from 30 to 1000 Hz. The relative pulse duration (period of the pulse to the duration of the pulse) varied in the range of 2–32. The average density of the direct and pulsed current (j) was 1–3 A/dm^2, which made it possible to change the overvoltage at the cathode (η) in the limits of 0.1 to 0.3 V. The laser–electrochemical setup for the LSD was constructed based on a ruby solid-state laser radiating in the pulse-periodic regime with a wavelength of 694 nm at the intensity of 70 kW/cm^2 [5].

As the substrates for the electrodeposition, plates of polycrystalline copper were used. The substrates were subjected to mechanical and chemical polishing. As the solution for chemical polishing, the 5% aqueous solution of nitric acid was taken. After polishing, the substrates were degreased in a solution of Vienna lime and washed in distilled water. The thickness of the films deposited was 5–20 μm. The choice of copper as the substrate material was caused by the fact that zinc forms intermediate phases with copper [6].

The chemical composition of the film–substrate transient layer was determined by electron microprobe analysis using a PEMMA-102-02 scanning electron microscope with a resolution of 5 nm. The butt ends of the substrate with the deposited film were subjected to mechanical and chemical polishing. At the last stage of the chemical dissolution, treatment by backward pulses of current was added, which not only polished the butt surface, but also removed particles of the other metals that could fall onto it in the course of the chemical polishing. This made it possible to enhance the reliability of the electron microprobe analysis.

To investigate the phase composition of metallic films, a DRON-2.0 diffractometer was used with a scintillation detector of X-rays. The survey was performed in copper radiation.

RESULTS AND DISCUSSION

Electron Microprobe Analysis of the Film–Substrate Transient Layer

To study diffusion in solids, a large number of physical and physicochemical methods have been developed to date [7]. These methods are based mainly on the measurements of the distribution of concentration of the diffusing substance in the sample under study depending on the time and temperature of diffusion annealing or some other external action.

To determine the structure of the transient layer at the film–substrate interface, the elemental chemical analysis for the presence of atoms of the deposited material and atoms of the substrate material has been performed. The investigations were carried out in the direction perpendicular to the interface with a step of 0.5 μm. The region of the investigation became extended for 4–6 μ into both directions from the interface, depending on the conditions of the deposition of the films. Figure 1 displays the photo of the boundary of the transient layer and the line along which the investigations of the elemental composition were performed.

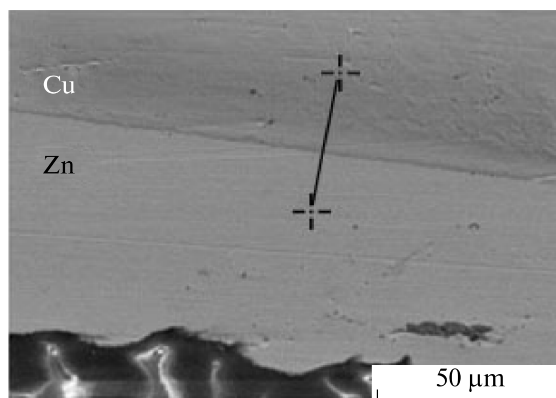

Fig. 1. Photos of the transverse section and paths of scanning the substrate–film transient layer.

The results of the qualitative integral analysis of the film–substrate transient layer are shown in Fig. 2. Spectra of the electron microprobe analysis of zinc films obtained by deposition onto copper substrates using direct current are given for different coordinates x of the probe. The analysis was performed for two main elements of which the growing film and substrate consisted. The scanning started from the deposited film and continued into the substrate. The origin $x = 0$ corresponds to the film–substrate interface.

It can be seen from the figures that the spectra contain lines corresponding to two elements, i.e., the crystallizing material Zn and substrate material Cu. Near the interface, on the side of the growing films, lines are present in the spectra that correspond only to zinc atoms (Fig. 2a). Upon the further scanning of the film–substrate transient layer into the depth, the intensity of the lines that correspond to the material of the substrate increases in the spectra (Figs. 2b, 2c). This indicates an increase in the concentration of atoms of the substrate material and a decrease in the concentration of atoms of the film material. At a depth of 2 μm, no zinc atoms have been revealed in films deposited using the direct current (Fig. 2d). The analysis of the above spectra suggests that, upon electrodeposition, a diffusion interaction takes place between the elements of the coating and the surface of the main metal; as a result, the zinc atoms diffuse into the metal of the substrate to form a transient diffusion layer.

Table 1 gives the results of the chemical analysis of the transient diffusion region of the zinc films on copper substrates obtained under different deposition conditions. The averaging was performed on five samples obtained under identical conditions; in addition, each sample was scanned along three directions in the transient layer.

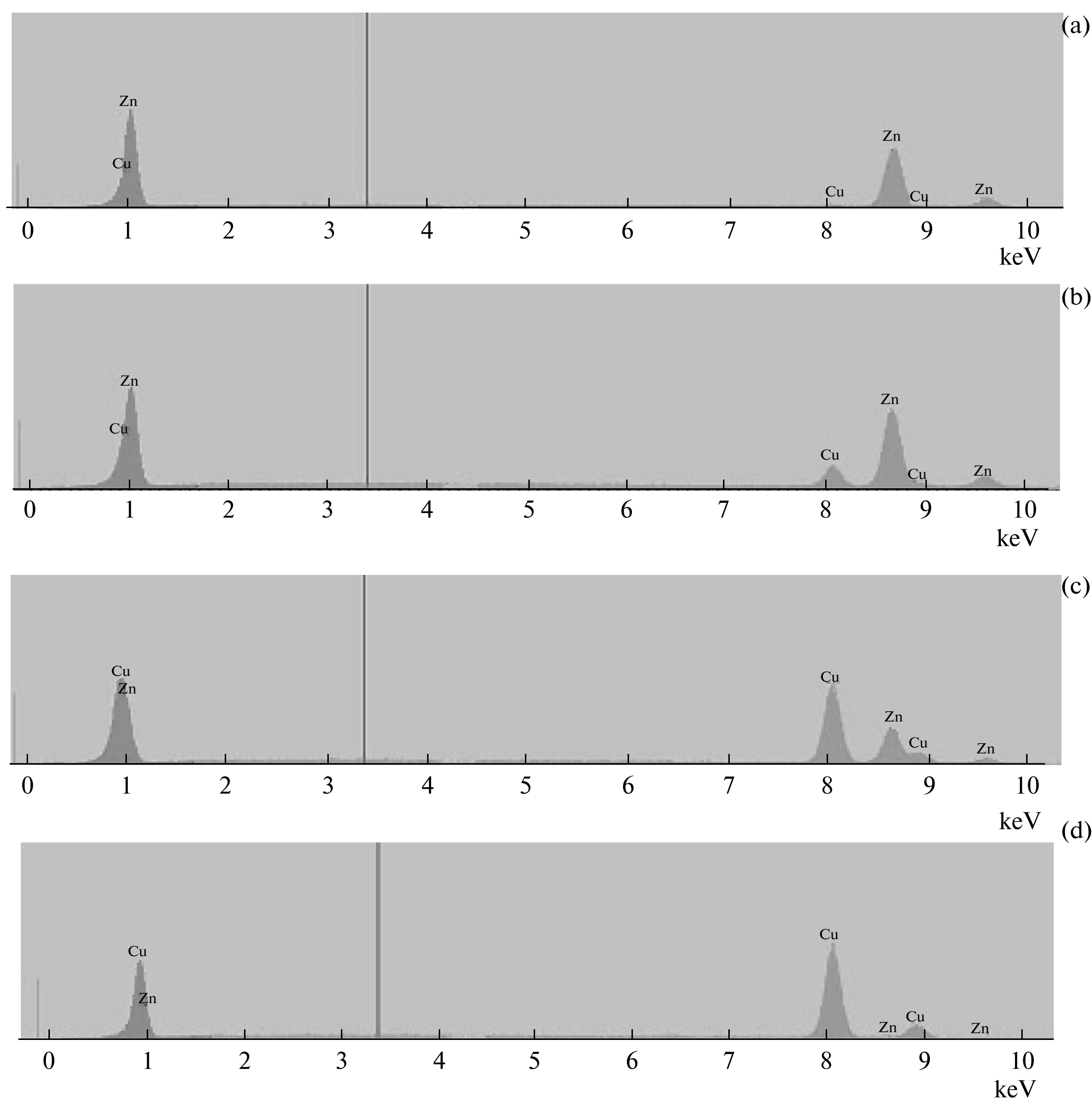

Fig. 2. Spectra of the electron microprobe analysis of the film–substrate transient region of the zinc films on copper substrates obtained using direct current ($j = 1$ A/dm^2, $\eta = 0.2$ V): (a) $x = -0.5$ μm; (b) $x = 1$ μm; (c) $x = 1.5$ μm; and (d) $x = 2$ μm.

It can be seen from the results presented in Table 1 that the zinc atoms penetrate to a depth from 15 μm in the case of the electrocrystallization using direct current ($j = 1$ A/dm^2, $\eta = 0.2$ V) to 2.5 μm upon deposition using the pulsed current in the rigid regime ($j =$ 1 A/dm^2, $f = 30$ Hz, $Q = 64$, $\eta = 0.4$ V). The use of the LSD leads to an extension of the diffusion layer at the film–substrate interface to 4 μm. This is explained by the increase in the energy of the zinc adatoms due to the absorption of the monochromatic light of the laser radiation.

According to the phase diagram [6], various solid-solution phases can be formed in the Zn–Cu system. According to [8], β and ε phases are clearly revealed in the diffusion layer upon the thermal diffusion of zinc into copper. Based on the data on the concentration (C, at %) of zinc that diffuses into the copper substrate (Table 1), different phases can be formed at the film–substrate interface. To check this, X-ray diffraction studies of zinc films on the copper substrate have been performed. For these investigations, 5-μm-thick zinc films have been prepared. At this thickness, the X-ray diffraction patterns contain lines of the material of the substrate (Cu) and of the material of the film (Zn). The X-ray diffraction patterns of the transient layer formed at the film–substrate interface upon the deposition of zinc onto a copper substrate are given in Fig. 3.

It can be seen from the figures that, when depositing zinc onto a copper substrate using the direct current, the X-ray diffraction patterns contain lines corresponding only to copper and zinc (Fig. 3a). This

Table 1. Concentrations C (at %) of zinc diffusing into the copper substrate under various deposition conditions

Deposition conditions	x, μm	−1	−0.5	0	0.5	1	1.5	2	2.5	3	3.5	4	4.5
Direct current, $j = 1$ A/dm^2, $\eta = 0.2$ V	Zn, at %	100	99.5	99	40	2	0.5	0					
	Cu, at %	0	0.5	1	50	98	99.5	100					
Pulsed current, $j = 1$ A/dm^2, $f = 1000$ Hz, $Q = 2$, h = 0.3 V	Zn, at %	100	99	9	83.5	42	2	0.4	0				
	Cu, at %	0	1	1	16.5	58	98	99.6	100				
Pulsed current, $j = 1$ A/dm^2, $f = 30$ Hz, $Q = 64$, $\eta = 0.4$ V	Zn, at %	100	99	99	92.5	56	13	5	0.5	0			
	Cu, at %	0	1	1	7.5	44	87	95	99.5	100			
LSD, Direct current, $j = 1$ A/dm^2, $\eta = 0.2$ V	Zn, at %	100	99	99	94	60	17	12	6	3	1	0.5	0
	Cu, at %	0	1	1	6	40	83	88	94	97	99	99.5	100

indicates that no intermetallic compounds are formed in the diffusion layer at the film–substrate boundary and the diffusion occurs exclusively via the grain-boundary mechanism. These results were obtained upon deposition using pulsed current in a soft regime. Figure 3b shows an X-ray diffraction pattern obtained from the diffusion layer grown via LSD; it can be seen that it contains lines that do not belong to either copper or zinc. The identification of phases that can appear in the diffusion layer is difficult, first of all, because of the small amount of these phases and, second, because of the coincidence of the interplanar spacings [9]. However, the additional lines present make it possible to identify them as lines obtained from the $CuZn_2$ phase [10]. Similar results were obtained from the films deposited using pulsed current in a rigid regime; in this case, the $CuZn_2$ phase was also found in X-ray diffraction patterns. These results indicate that, at the film–substrate interface, the diffusion of zinc into copper occurs not only through the grain-boundary mechanism, but bulk diffusion also takes place, which leads to the formation of the above phase.

Coefficients of Diffusion upon Electrodeposition

The experimental determination of the diffusion coefficients D usually is reduced to an analysis of the dependence of the concentration of a diffusing element C on the depth of penetration x [7]. To determine the diffusion coefficient D, we have constructed the dependences of the distribution of atoms of the growing film in the diffusion zone as a function $\log C = f(x^2)$. The diffusion coefficients were determined by the method suggested in [11] by the formula

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

where τ is the time of the action that stimulates diffusion; and α is the slope of the $\log C = f(x^2)$ dependence. The angle α was determined experimentally. In our case, the time τ of the stimulating action was determined experimentally as the time in which the growing film covered the entire surface of the cathode.

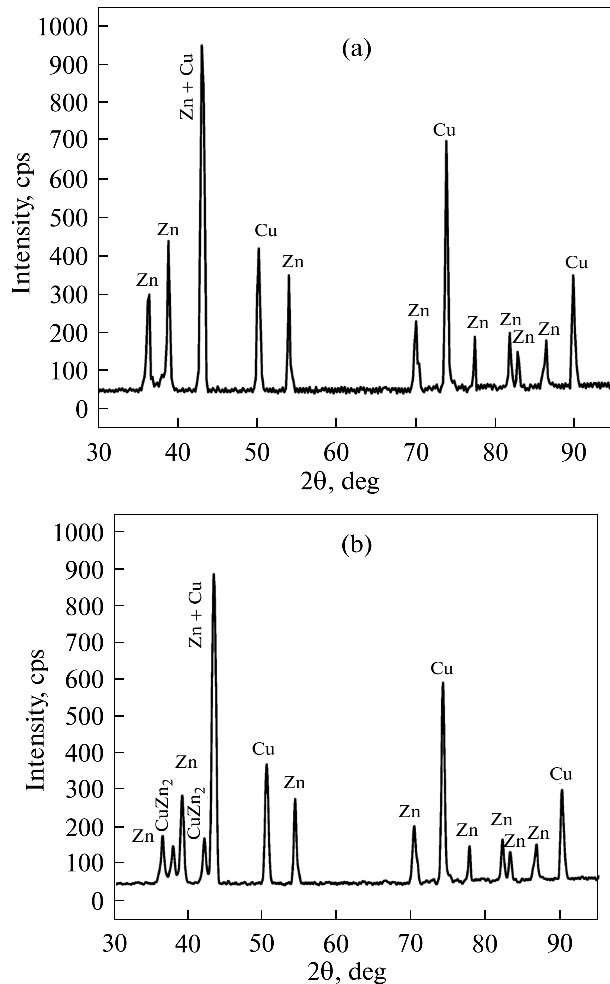

Fig. 3. X-ray diffraction patterns of the transient layer formed at the film–substrate interface upon the deposition of zinc onto a copper substrate: (a) direct current, $j = 1$ A/dm^2, $\eta = 0.2$ V; (b) LSD, direct current, $j = 1$ A/dm^2, $\eta = 0.2$ V.

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

Deposition conditions	τ, s	D, m^2/s	D, m^2/s ref [3]	D, m^2/s ref [12]
Direct curren, $j = 1$ A/dm^2, $\eta = 0.2$ V	140	$(1.75 \pm 0.2) \times 10^{-15}$	10^{-10}–10^{-12}	4×10^{-15}
Pulsed current, $j = 1$ A/dm^2, $f = 1000$ Hz, $Q = 2$, $\eta = 0.3$ V	60	$(7.25 \pm 0.7) \times 10^{-15}$		
Pulsed current, $j = 1$ A/dm^2, $f = 30$ Hz, $Q = 64$, $\eta = 0.4$ V	15	$(4.53 \pm 0.4) \times 10^{-14}$		
LSD, direct current, $j = 1$ A/dm^2, $\eta = 0.2$ V	10	$(1.74 \pm 0.2) \times 10^{-13}$		

Figure 4 displays the logarithmic dependences of the concentration of zinc atoms in the diffusion layer of the copper substrate for different conditions of deposition on x^2 (Table 1).

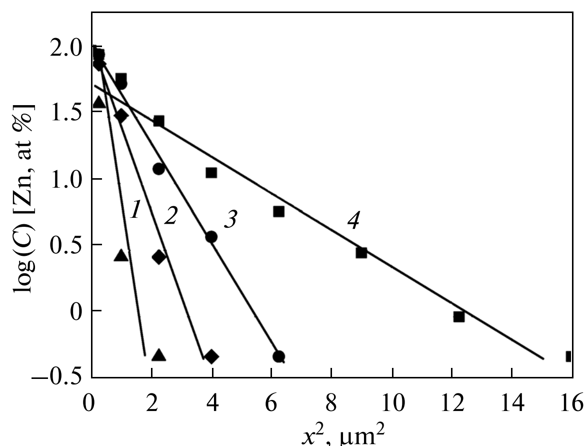

Fig. 4. Logarithmic dependences of the concentration of zinc in the diffusion region: (*1*) direct current, $j = 0.5$ A/dm^2, $\eta = 0.1$ V; (*2*) pulsed current, $j = 0.5$ A/dm^2, $f =$ 1000Hz, $Q = 2$, $\eta = 0.2$ V; (*3*) pulsed current, $j = 0.5$ A/dm^2, $f = 50$ Hz, $Q = 32$, $\eta = 0.3$ V; and (*4*) LSD, direct current, $j = 0.5$ A/dm^2, $\eta = 0.1$ V.

Table 2 contains our values of the coefficients of zinc diffusion in copper calculated by formula (1) for different conditions of deposition and the results obtained by other researchers.

CONCLUSIONS

The investigations of the transient layer at the film–substrate interface, which is formed upon the electrodeposition of zinc films on a copper substrate, have shown that, in the transient layer, the diffusion of the deposited metal into the material of the substrate occurs. The depth of the diffusion layer and, consequently, the concentration of the incorporated zinc atoms strongly depend on the conditions of electrocrystallization. It changes from 1.5 μm when using a direct current to 4 μm when using direct current with the application of LSD.

The X-ray diffraction studies of the film–substrate transient layer have shown that upon the electrocrystallization using a pulsed current in rigid regimes and LSD, a $CuZn_2$ phase is formed in the diffusion layer. This indicates that the diffusion of zinc into copper occurs via grain-boundary and bulk mechanisms. The application of direct and pulsed currents using soft regimes of deposition does not lead to the formation of additional phases in the diffusion layer, which indicates the occurrence of only a grain-boundary mechanism of diffusion.

The obtained values of the coefficients of diffusion (1.75×10^{-15} to 1.74×10^{-13} m^2/s) agree well with the results of other investigations (10^{-10} to 10^{-12} m^2/s [3] and 4×10^{-15} m^2/s [11]).

REFERENCES

1. V. V. Povetkin and I. M. Kovenskii, *Structure of Electrolytic Coatings* (Metallurgiya, Moscow, 1989) [in Russian].
2. N. A. Kostin, V. S. Kublanovskii, and V. A. Zabludovskii, *Pulsed Electrolysis* (Naukova Dumka, Kiev, 1989).
3. B. S. Bokshtein, *Diffusion in Metals* (Metallurgiya, Moscow, 1978).
4. E. P. Shtapenko, "Formation of a continuous series of solid solutions in the transitional layer "substrate–film" upon electrocrystallization," Fiz. Khim. Tverd. Tila **8**, 422–425 (2007).
5. V. Zabludovskii, V. Dudkina, and E. Shtapenko, *Laser-Stimulated Electrodeposition of Metals* (Lambert Academic, Saarbrücken, 2014).
6. N. P. Lyakishev, *Phase Diagrams of Binary Metallic Systems: A Handbook*, Ed by N. P. Lyakishev (Mashinostroenie, Moscow, 1996) [in Russian], Vol. 1.
7. I. A. Sluchinskaya, *Fundamentals of Materials Science and Technology of Semiconductors* (Mir, Moscow, 2002) [in Russian].
8. A. A. Popov, *Theory of Transformations in Solid State* (UGTU-UPI, Ekaterinburg, 2004) [in Russian].
9. L. I. Mirkin, *Handbook on X-ray Diffraction Analysis of Polycrystals* (GIFML, Moscow, 1961) [in Russian].
10. *JCPDS – Joint committee on powder diffraction standards* (A Pennsylvania Non-Profit Corporation 1601, Park Lane, Swarthmore, Pa, 1998).
11. Method of determination of diffusion coefficients in film materials, RF Patent no. 2212027.
12. Yu. R. Kolobov, A. G. Lipnitskii, M. B. Ivanov, and E. V. Golosov, "Role of diffusion-controlled processes in the formation of structure and properties of metallic nanomaterials," Komp. Nanostrukt., No. 2, 5–24 (2009).

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