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Adhesion strength of electrodeposited Ni, Zn, and Fe coatings with copper substrates

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ABSTRACT

This paper presents the adhesive strength values of electrodeposited nickel, zinc, and iron coatings on copper substrates at various deposition parameters, including laser-assisted stimulation of the deposition process. One of the factors determined to be responsible for the adhesive strength of metal films with a metal substrate is the formation of a diffusion zone at the 'coating-substrate' interface. It is shown that an increase in adhesive strength is achieved due to the expansion of the diffusion zone and the formation of solid solutions. The decrease in adhesive strength at high overpotentials is associated with the release of hydrogen and the formation of intermediate phases.

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Adhesion strength; electrodeposited coatings; laser-assisted deposition; diffusion layer in the solid state

1. Introduction

The most essential characteristic of electrodeposited films and coatings is their strength of adhesion to the substrate. For protective coatings with high microhardness and wear resistance, it is necessary that they have high adhesion values.

Adhesion occurs between the surfaces of two dissimilar bodies in contact. In the case of electrodeposition, these are the substrate and the growing film. Adhesion is primarily determined by the interaction between the molecules (atoms) of these bodies. The mechanism of adhesion is very complex, and there are practically no fundamental studies in this area. These studies^{1–3} discuss the general issues of adhesion, including the strength of electrodeposited metal film adhesion to the substrate. The results cited in the scientific literature are reduced to the empirical dependences of the adhesive strength on the film production parameters: current density, electrolyte composition, and substrate type. The scientific literature presents no results of studying the mechanisms and processes that lead to a change in adhesive strength. However, a number of recent works^{4,5} present the results of a study relating to the effect of a diffusion transition layer on the adhesive strength. Therefore, understanding the phenomenon of adhesion is impossible without a comprehensive study of the diffusion processes occurring at the 'film-substrate' interface and their effect on the adhesive strength.

At present the technology of deposition without external influence (laser radiation, ultrasound, magnetic field, cavitation) does not meet many requirements for the preparation of functional materials.

This article presents and discusses the adhesive strength values of electrodeposited nickel, zinc, and iron coatings on copper substrates obtained at various deposition parameters, including laser-assisted deposition (LAD).

2. Electrodeposition and investigation of metal coatings

The deposition of metallic films of nickel, copper, zinc, and iron was carried out using direct current, unipolar, bipolar, and programmed pulsed current (Figure 1); the authors have carried out studies on modulated current deposition over a long period.⁶ Films were deposited from aqueous solutions of electrolytes of the following compositions, g L⁻¹: copper plating – CuSO₄·5H₂O – 250; H₂SO₄ – 75; nickel plating – Ni₂SO₄·7H₂O – 300, H₃BO₃ – 30, Na₂SO₄ – 50, iron plating – FeCl₂·4H₂O – 410–450, NaBr – 0.5, H₂SO₄ – 1.9; zinc plating – ZnSO₄·7H₂O – 250, Na₂SO₄ – 75, Al(SO₄)₃·30, pH – 4. The electrolyte temperature was maintained constant and equal to 295 K. The current pulse frequency rate (*f*) varied from 30 to 1000 Hz. The duty cycle of the current pulses (*Q* the ratio of the period to the pulse duration) varied from 2 to 50.

The average pulse current density (*j*) was selected for each material so that the coating had a good quality appearance, and this was 50 A m⁻², 100 A m⁻² and 150 A m⁻² respectively, for nickel, zinc, and iron. At these current densities, these electrolytes are not subject to concentration limitations, i.e. no 'burning' of films is observed and no surface defects (pitting, microcracks) occur. Pure metal plates were used as an anode for electrodeposition. This made it possible to maintain a constant concentration of ions of the crystallising metal, which had a positive effect on the repeatability of the experiments.

Copper foil was used as a substrate for electrodeposition. The foil for the substrates went through several stages of preparation. First, the substrates were subjected to mechanical and chemical polishing. The solution for chemical polishing was a 5% solution of nitric acid. Chemical polishing reduced the roughness and removed the work hardening formed after mechanical polishing. Then the substrates were degreased in a solution of Vienna lime, which consists

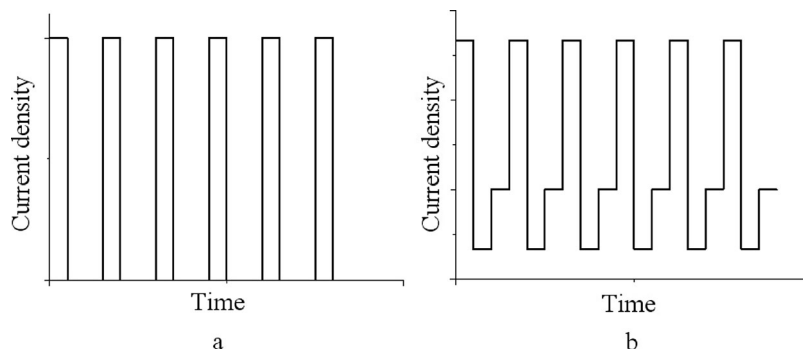


Figure 1. Forms of pulsed current used in the deposition of metal coatings: a – unipolar, b – bipolar.

of purified calcium oxide with small quantities of magnesium oxide and processing aids, and washed in distilled water.

Laser-assisted electrodeposition of metal films⁷ was carried out on a laser-electrolytic installation, the scheme of which is shown in Figure 2.

As an emitting source, the authors used a gas-discharge CO₂-laser with a power (*P*) of 25 W, and generation in a continuous mode at a wavelength (λ) equal to 10.6 μm . A laser beam 10 mm in diameter was directed to the cathode by a rotary mirror.

Experimental studies were also carried out on a solid-state ruby laser.^{8–10} Generation on ruby was carried out in a pulse-periodic regime at a laser emission wavelength of 694 nm, at a generation frequency of 10 Hz with an emission energy per pulse equal to 0.24–3.00 J, with a pulse duration of 4 ms and a focused laser beam with a radius of 0.5 mm. At radiant energies of 0.24 and 3.00 J, the laser emission intensity was 8107 W m⁻² and 95107 W m⁻², respectively.

In order to create the uniformity of the electric field created by the flow of charged ions, the electrodes were placed parallel to each other at a distance of 30 mm. To increase the emission power density in the irradiation zone, it was necessary to decrease the laser beam divergence angle. This was achieved by laser beam focusing. A working table was used to fix and position the cathode surface relative to the stationary focused laser beam.

The values of the electrode overpotential were recorded relative to a saturated silver chloride reference electrode of the EVL-1MH type.

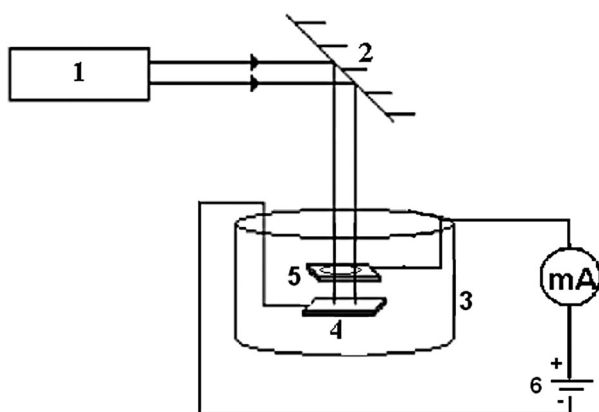


Figure 2. Test installation: 1 – Emitting source (gas discharge CO₂-laser: $\lambda = 10.6$ microns, $P = 25$ W), 2 – Rotary mirror, 3 – Electrolytic cell, 4 – Cathode, 5 – Anode, 6 – DC power supply.

To study the phase composition of the metal coatings, a DRON-2.0 diffractometer with scintillation registration of X-rays, was used.

Spectral microanalysis of the elemental composition of the surface and the 'film-substrate' interface was carried out using a REMMA 102-02 scanning electron microscope with a resolution of 5 nm.

Determination of the adhesion strength of the coatings was carried out according to the Jacquet method.¹¹ According to this method, a section of the coating is bent at a right angle and the force required to separate the coating from the substrate is determined perpendicular to the surface of the sample. Adhesion strength is expressed as a quotient of tearing or shearing force divided by the area of adhesion.

To implement this method, part of the substrate surface was covered with a conductive varnish. This ensured, on the one hand, the deposition of the coating on the entire substrate, and, on the other hand, reduced the adhesive strength of the part of the surface that was varnished with the substrate, which made it possible to bend back part of the coating.

3. Adhesion strength of the electrodeposited metal coatings

Figure 3 shows the dependences of the adhesive strength (σ_{adh}) of the nickel, zinc, and iron coatings with the copper substrate obtained at various cathodic overpotentials (η).

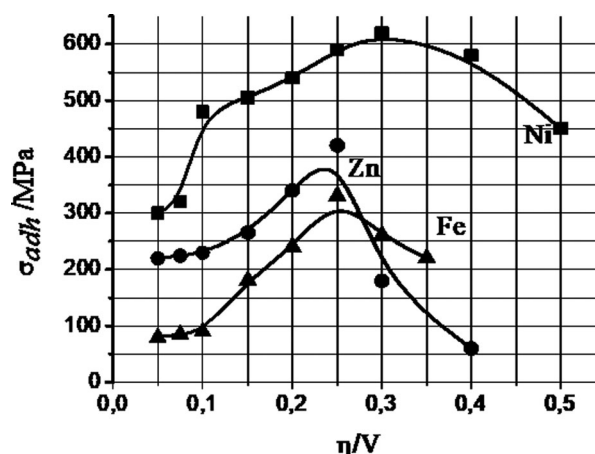


Figure 3. Dependences of the adhesive strength of the nickel, zinc, and iron coatings with the copper substrate obtained at various cathodic overpotentials.

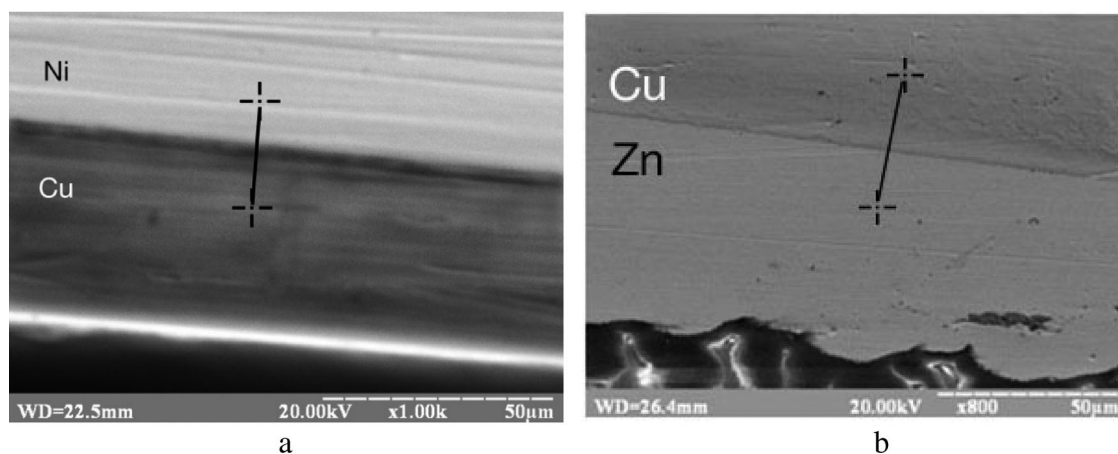


Figure 4. Photographs of the transverse section and the scanning path of the transition layer 'coating – substrate': a – Ni-Cu; b – Zn-Cu.

The dependences of the adhesion strength of coatings on cathodic overpotential (Figure 3) are complex in nature, which lies in the fact that at certain overpotential values the adhesion strength of coatings reaches a maximum value, and then decreases due to hydrogen evolution and the formation of passive films (thin

surface layers of hydride, oxide and hydroxide compounds).

The authors attribute the increase in adhesion values with the cathode overpotential rise to the penetration of adatoms of the coating metal into the substrate, i.e. to the formation of a diffusion layer at the 'coating-substrate' interface.

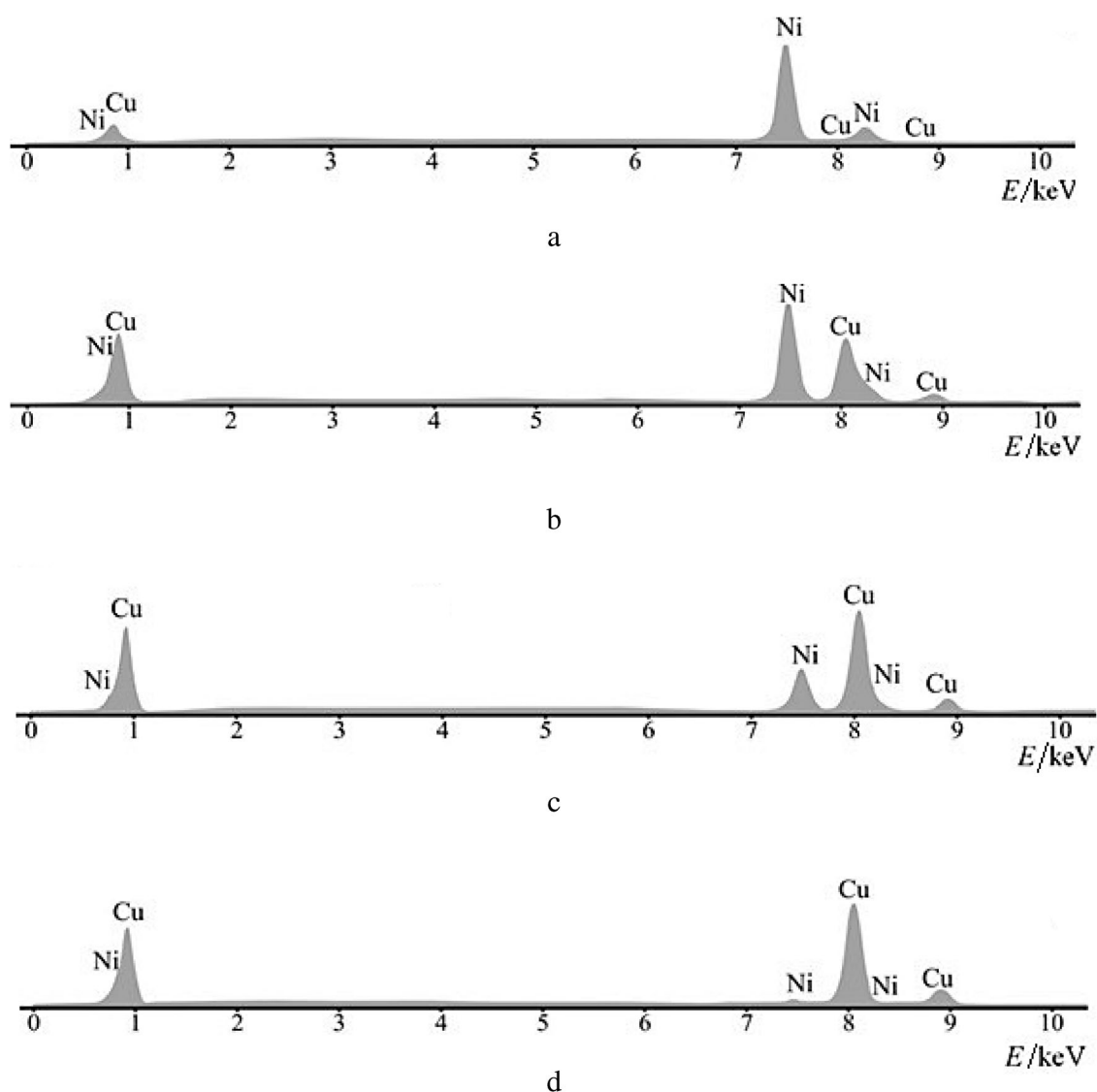


Figure 5. Spectra of the electron probe X-ray microanalysis of the 'coating-substrate' transition area, nickel coatings on the copper substrates obtained at direct current ($j = 0.5 \text{ A dm}^{-2}$, $\eta = 0.1 \text{ V}$). Depth of analysis a) $x = -0.5 \text{ μm}$; b) $x = 1 \text{ μm}$; c) $x = 1.5 \text{ μm}$; d) $x = 2 \text{ μm}$.

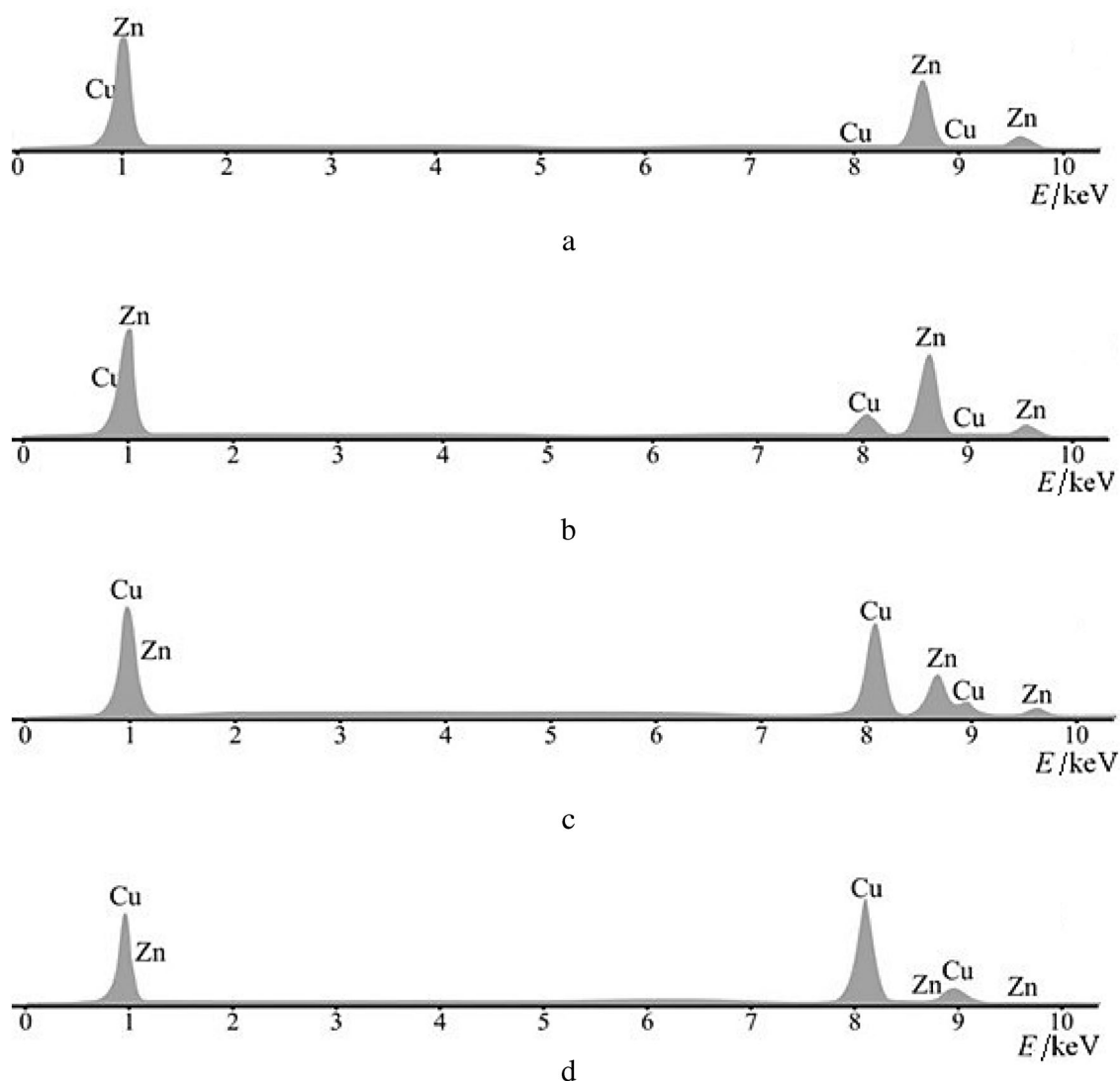


Figure 6. Spectra of the electron probe X-ray microanalysis of the 'coating-substrate' transition area, zinc films on the copper substrates obtained at direct current ($j = 1 \text{ A dm}^{-2}$, $\eta = 0.2 \text{ V}$). Depth of analysis a) $x = -0.5 \text{ }\mu\text{m}$; b) $x = 1 \text{ }\mu\text{m}$; c) $x = 1.5 \text{ }\mu\text{m}$; d) $x = 2 \text{ }\mu\text{m}$.

To determine the mechanism of adhesion and the effect of cathodic overpotential on the value of adhesive strength, the diffusion layer at the 'coating-substrate' interface has been studied.

The chemical composition of the cross-section of the coating-substrate interface was investigated from the depth of the substrate in the coating direction perpendicular to the interface with a step of $0.5 \text{ }\mu\text{m}$. Under various deposition conditions, the depth of detection of diffusing metal atoms did not exceed $6 \text{ }\mu\text{m}$. Further studies were carried out in the coating area at a depth of $4\text{--}6 \text{ }\mu\text{m}$ where no substrate atoms were detected. Figure 4 presents photographs of the boundary of the transition layer of the deposited nickel and zinc films on the copper substrate. Figure 4 shows the lines along which the study of the elemental composition was carried out.

The results of a qualitative analysis of the 'coating-substrate' transition layer at various coordinates (x) of the probe are presented in Figures 5 and 6, which show the electron probe X-ray microanalysis of the nickel and zinc films deposited with direct current on the copper substrates.

The results of the electron probe X-ray microanalysis (Figures 5, 6) show that the spectra contain lines corresponding to two elements: the crystallising material Ni or Zn and the substrate material Cu. Close to the interface on the side

of the growing films, the spectra contain the lines corresponding only to nickel (Figure 5a) and zinc (Figure 6a) atoms. With deeper scanning of the 'coating-substrate' transition layer, the spectra show an increase in the intensity of the lines corresponding to the substrate material (Figure 5b, c and Figure 6b, c), which indicates an increase in the concentration of atoms of the substrate material and a decrease in the concentration of atoms of the film material. Upon reaching a depth of $2.5 \text{ }\mu\text{m}$, no nickel atoms were detected in the films deposited with direct current (Figure 5d). For zinc deposited with direct current, the depth of the diffusion layer was $2 \text{ }\mu\text{m}$.

Analysing the results of the electron probe X-ray microanalysis, it can be concluded 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 and zinc diffuse into the substrate metal, forming a transitional diffusion layer. To determine the amount of the diffused nickel and zinc atoms, as well as the substrate depth to which the metal atoms penetrated, the authors carried out a quantitative chemical analysis of the 'coating-substrate' transition layer of the electrodeposited nickel and zinc films. The films studied were obtained from an aqueous solution of an electrolyte of a constant composition at various values of the cathode potential, which is determined both by the average

current density and by the type of current itself.⁶ In addition, the studies included the films obtained by laser-assisted electrodeposition. Based on the results obtained, it can be seen that during the electrocrystallisation of nickel and zinc on the copper substrate, a diffusion area is formed at the 'coating-substrate' interface. In this case, depending on the crystallisation conditions, nickel diffusion was 2–4 μm when the cathode potential changed from 0.1 V to 0.3 V. Zinc atoms penetrated to a depth of 1.5–2.5 μm when the potential changed from 0.2 V to 0.4 V.

Increased penetration depth of adatoms and expanded diffusion region leads to an increase in the values of the adhesive strength for the coatings: nickel – from 300 MPa to 620 MPa; zinc – from 220 MPa to 420 MPa; iron – from 80 MPa to 330 MPa.

A further increase in overpotential leads to a decrease in the adhesive strength values. This is due to two main factors affecting the decrease in adhesion. First, with an increase in the overpotential, a significant release of hydrogen occurs, which blocks the cathode surface and forms a passive film, which in turn leads to a decrease in the adhesive strength.¹² Secondly, in the diffusion layer at the 'coating-substrate' interface, not only a solid solution, but also various phases can form. So, for example, when zinc was deposited on a copper substrate under deposition modes with a low pulse frequency rate ($f = 30$ Hz) and a wide duty cycle ($Q = 32$), the authors found a CuZn_2 phase, which is hard and very brittle, in the diffusion layer (Figure 7). When it is formed, internal stresses increase,¹³

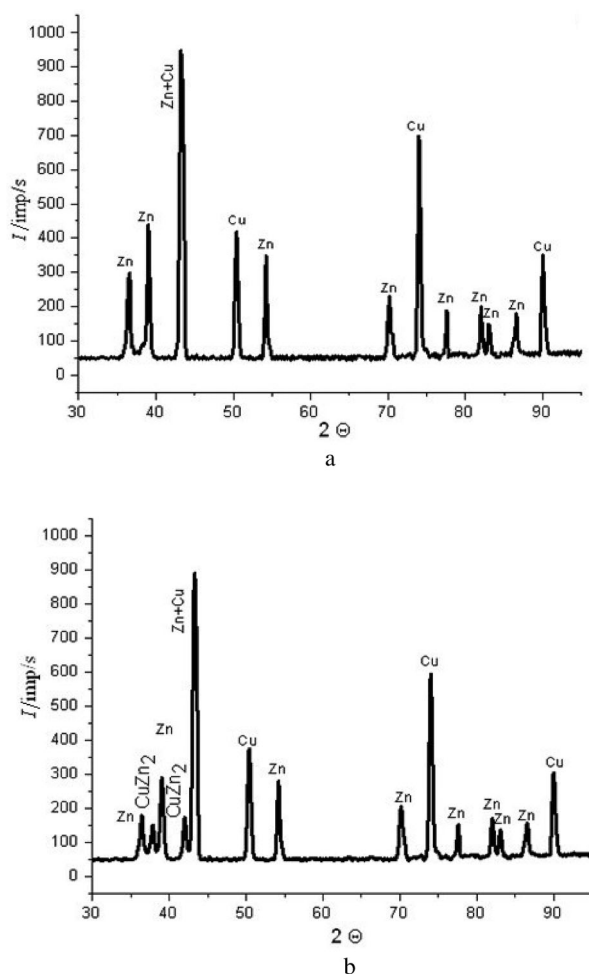


Figure 7. Diffraction patterns of the transition layer during zinc deposition on the copper substrate: a – direct current; b – LAD.

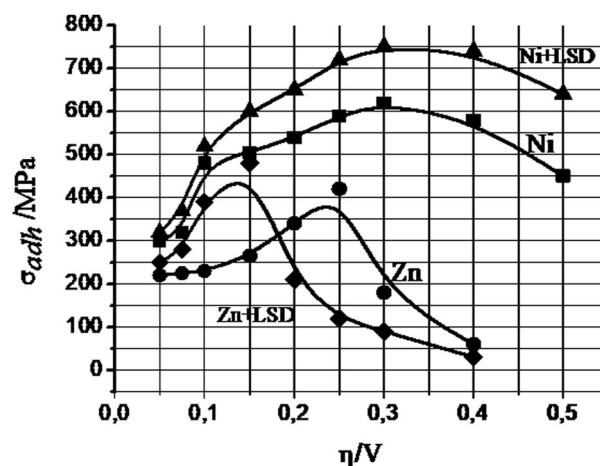


Figure 8. Dependences of the adhesive strength of nickel and zinc coatings with the copper substrate obtained at various cathodic overpotentials using laser-stimulated deposition.

which leads to microcracks and reduction of the film-substrate adhesion strength, in contrast to those metals where the formation of a continuous series of solid solutions is observed.

When nickel and iron are deposited on the copper substrate, a decrease in adhesive strength can be associated only with the evolution of hydrogen and the formation of a passive film, while, when zinc is deposited, both factors affect the decrease in adhesive strength. This is associated with a more pronounced decrease in the adhesive strength of zinc with the copper substrate.

The use of laser-assistance of the deposition process, as a rule, leads to an increase in adhesive strength. Figure 8 shows the dependences of the adhesion strength of nickel and zinc films with the copper substrate obtained by laser-assisted deposition and various overpotentials on the cathode.

Figure 8 shows that the use of laser-assisting of the nickel deposition on the copper substrate leads to an increase in the maximum adhesive strength from 620 MPa to 730 MPa. This is due to an increase in the energy of nickel adatoms resulting from the absorption of photon energy,^{14–18} which leads to the increased depth of the diffusion area to 4 μm at the 'coating-substrate' interface. During laser-assistance of the zinc deposition process, an increase in the maximum adhesive strength from 420 MPa to 485 MPa is also observed. However, in this case, the maximum adhesive strength shifts to the region of lower overpotential values from 0.25 V to 0.15 V, and a further decrease in the adhesive strength is more significant compared to the laser-assisted deposition mode. This is also associated with an increase in the diffusion area and the formation of various phases.

4. Conclusion

The conducted studies of electrodeposited nickel, zinc and iron coatings on copper substrates at various deposition parameters, including a laser-assisted deposition process, have shown that the value of adhesion strength strongly depends on the deposition conditions. It has been established that the value of adhesive strength, at the initial stage, increases with the rise in cathode overpotential for coatings: nickel – from 300 MPa to 620 MPa (0.05 ranging to 0.3 V); zinc – from 220 MPa to 420 MPa (0.05 ranging to 0.25 V); iron – from 80 MPa to 330 MPa (0.05 ranging to

0.25 V). This is due to an increase in the diffusion zone at the 'coating-substrate' interface. A further rise in the cathode overpotential leads to a decrease in the adhesion strength for the coating: nickel – 480 MPa; zinc – 50 MPa; iron – 220 MPa. The decrease in adhesive strength at high overpotentials is associated with (a) the release of hydrogen, which blocks the cathode surface and forms a passive film, (b) the formation of intermediate phases.

The application of the laser-assisted deposition process leads to an increase in the adhesion strength of the coatings. Thus the maximum adhesion strength of nickel coatings on copper substrate increases from 620 MPa to 730 MPa, zinc coatings – from 420 MPa to 485 MPa. When exposed to laser radiation, the energy of adsorbed atoms increases due to absorption of photon energy. This leads to an increase in the depth of the diffusion zone at the 'coating-substrate' interface and, consequently, to an increase in the adhesive strength values.

With the encouraging and informative data obtained from Ni and Zn deposits on copper, further studies are being carried out on Fe deposits on copper including the spectral microanalysis of the elemental composition of the interfaces between electrodeposited iron films and copper substrates.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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References

1. A.D. Zimon: *Adgeziya plenok i pokrytiy*, Moscow: Chemistry, 1977, **352**. (in Russian). <https://www.twirpx.com/file/1660241/>
2. E. Kinlok: *Adgeziya i Adgeziyiy; Nauka i Tehnologiya*, Moscow: Mir, 1991, **484**. (in Russian). <https://knigogid.ru/books/39906-adgeziya-i-adgeziy-nauka-i-tehnologiya>
3. V. M. Konstantinov, G. A. Tkachenko and A. V. Kovalchuk: *Metallurgiya: respublikanskiy mezhvedomstvennyiy sbornik nauchnyih trudov*, 2014, **35**, 272–281. (in Russian). <https://rep.bntu.by/bitstream/handle/data/15609/%d0%a1.%20272-281.pdf?sequence=1&isAllowed=y>
4. N. N. Zaveryuhina: *Pisma v Zhurnal teoreticheskoy fiziki*, 2010, **36**(16), 82–88. (in Russian). <http://journals.ioffe.ru/articles/viewPDF/14122>
5. V. V. Dudkina: *Vestnik Dnepropetrovskogo natsionalnogo universiteta zheleznodorozhnogo transporta*, 2013, **44**(2), 83–91. (in Russian). <http://stp.diit.edu.ua/article/download/12245/12785/0>
6. V. A. Zabudovsky, N. V. Fedotava and E. F. Shtapenko: *Transactions of the IMF*, 1996, **74**(3), 106–107. doi:10.1080/00202967.1996.11871107
7. V. A. Zabudovsky, V. V. Dudkina and E. F. Shtapenko: *Lambert academic publishing, saarbrücken*, 2014. (in Russian). <https://eadnurt.diit.edu.ua/uk/bitstream/123456789/11210/1/Zabudovsky.pdf>
8. V. V. Dudkina, V. O. Zabudovsky and E. F. Shtapenko: *Fizyka i khimiya tverdogo tila*, 2011, **12**(2), 332–336. (in Ukrainian). http://irbis-nbuv.gov.ua/cgi-bin/irbis_nbuv/cgiirbis_64.exe?C21COM=2&I21DBN=UJRN&P21DBN=UJRN&IMAGE_FILE_DOWNLOAD=1&Image_file_name=PDF/PhKhTT_2011_12_2_11.pdf
9. V. A. Zabudovsky, E. P. Shtapenko and V. V. Dudkina: *The Physics of Metals and Metallography*, 2015, **116**(3), 256–260. https://eadnurt.diit.edu.ua/uk/bitstream/123456789/3849/1/Shtapenko_Zabudovsky_Dudkina.pdf
10. V. A. Zabudovsky and V. V. Dudkina: *Physics and Chemistry of Solid State*, 2012, **13**(4), 898–902. (in Ukrainian). https://eadnurt.diit.edu.ua/uk/jspui/bitstream/123456789/1737/1/zabud_dudk.pdf
11. P. M. Vyacheslavov and N. M. Shmeleva: *Metodyi ispytaniy elektroliticheskikh pokrytiy*, Leningrad, Mashinostroenie, 1977, 88. (in Russian). <https://www.twirpx.com/file/1352206/>
12. V. S. Kshniakyn, A. S. Opanasiuk and K. O. Diadiura: *Osnovy fizychnoho materialoznavstva: navchalnyi posibnyk*, Sumy, Sumskiy derzhavnyi universitet, 2015, 466. (in Ukrainian). https://essuir.sumdu.edu.ua/bitstream-download/123456789/39057/1/fiz_materialoznavstvo.pdf
13. E. F. Shtapenko, V. A. Zabudovsky and V. V. Tytarenko: *J. Surf. Invest.*, 2018, **12**(2), 377–382. doi:10.1134/S1027451018020362.
14. V. V. Tytarenko, V. A. Zabudovsky and E. F. Shtapenko: *Fizika i himiya obrabotki materialov*, 2018, **3**, 34–42. (in Russian). DOI: 10.30791/0015-3214-2018-3-34-42
15. V. A. Zabudovsky, V. V. Tytarenko and E. P. Shtapenko: *Trans. IMF*, 2017, **95**(6), 337–341. <http://www.tandfonline.com/doi/full/10.1080/00202967.2017.1355463>
16. V. O. Zabudovsky, V. V. Dudkina and E. P. Shtapenko: *Nauka ta prohres transport, Visnyk Dnipropetrovskoho natsionalnogo universytetu imeni akademika V. Lazariana*, 2013, **47**(5), 70–76. (in Ukrainian). DOI:10.15802/stp2013/17968
17. V. O. Zabudovsky and V. V. Dudkina: *Metallofizika i Noveishie Tekhnologii*, 2012, **34**(1), 77–86. (in Russian). http://irbis-nbuv.gov.ua/cgi-bin/irbis_nbuv/cgiirbis_64.exe?C21COM=2&I21DBN=UJRN&P21DBN=UJRN&IMAGE_FILE_DOWNLOAD=1&Image_file_name=PDF/MPhNT_2012_34_1_9.pdf
18. Y. Yilin, Z. Jinqui, Y. Peixia and A. Maozhong: *Materials Reports*, 2022, **36**(3), 20080209–9. <https://doi.org/10.11896/cldb.20080209>