Laser-enhanced electrodeposition of nickel coatings

V. A. Zabludovsky, V. V. Tytarenko* and E. Ph. Shtapenko

Optimal conditions for a laser-enhanced electrodeposition of nickel coatings have been specified. Comparative results of structure and mechanical properties of electrically deposited nickel coatings produced by a laser-enhanced galvanostatic method and without laser emission were analysed. It was found that laser medium wave IR radiation has a local thermal effect on the process of electrodeposition and stimulates formation of a nickel coating structure which is of a more equilibrium state, less defective and has reduced internal stress in the area of local laser heating. Studies of plating rate showed a 1.4 times increase for nickel coatings in conditions of laser-enhanced electrodeposition due to reduction of common cathode overpotentional and increase of cathode metal efficiency, that involves generation of a more coarse microcrystal structure. Results of studies of the laser radiation effect on structure and properties of nickel coatings show potential for increased adhesion of electrodeposited coatings with a copper substrate.

Keywords: Laser radiation; Electrodeposition; Structure; Properties; Nickel films; Equilibrium electrochemical crystallisation

Introduction

At the present time the problem of increasing durability and corrosion resistance, improvement of protective and decorative properties of materials remains real. One way to solve this problem lies in electroplating of the surface.[1–3] Microelectronics progress leads to development of new and improved processes of making thin-film materials which are characterised with a specified package of physical properties.

For some time past the process of electrodeposition stimulated by laser radiation aimed at acceleration of the process of electrometallisation has been a subject of heightened interest for the metal coatings industry.[4] Manufacture of microelectronics devices comprises processes of making comprehensive metal-coated structures which demand several highly complicated stages in production of masks, photolithography process, etc. It entails the implementation of rather difficult monitoring of a process and higher production cost. Development of a laser-based plating process is a promising technology to be applied for prompt and selective coating.

This work is aimed at the study of the combined effect of cathodic overpotentional and laser medium wave IR radiation on the process of electrodeposition, structure and properties of nickel coatings.

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Materials and methods

A laser electrolytic installation was used to produce nickel coatings, shown schematically in Fig. 1. The test installation is based on a 25 W power gas discharge continuous wave lasing CO_2-laser with wavelength $\lambda = 10.6$ micrometres. An aqueous electrolyte comprised of (g L^{-1}) $Ni_2SO4{\cdot}7H_2O$ – 300, H_3BO_3 – 30, Na_2SO_4 – 50; at pH = 6 was used for electrodeposition of nickel coatings in galvanostatic mode (at a constant cathode current density 0.5 A dm^{-2}).

The current density of 50 A m^{-2} for electrodeposition of the nickel coatings was not a random selection. According to large body of researches,[5–8] this value of current density is known to be optimum for generation of quality coverings from simple sulphate nickel-plating electrolyte under normal conditions. This current density does not impose any concentration restrictions for the said electrolyte, i.e. no so-called burning of deposits is observed.

Copper was used as the cathode (4 in Fig. 1) during the process of electroplating. The substrate was pre-processed by polishing mechanically using a paste based on chromium oxide and diamond paste. Five per cent nitric acid solution was used for chemical polishing. The chemical polishing reduced roughness and removed strain hardening resulting from mechanical polishing. Following this the substrates were degreased in Vienna lime to remove etching sludge and washed with distilled water. The anode (5) was a pure nickel plate that allowed the maintaining of a constant concentration of nickel ions, giving a positive effect on repeatability of tests. To ensure uniformity of electric field generated by the stream of charged ions of electrodepositing metal the electrodes were arranged in parallel each other.

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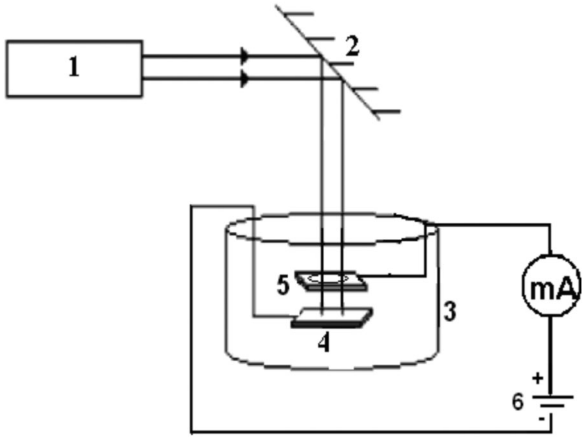
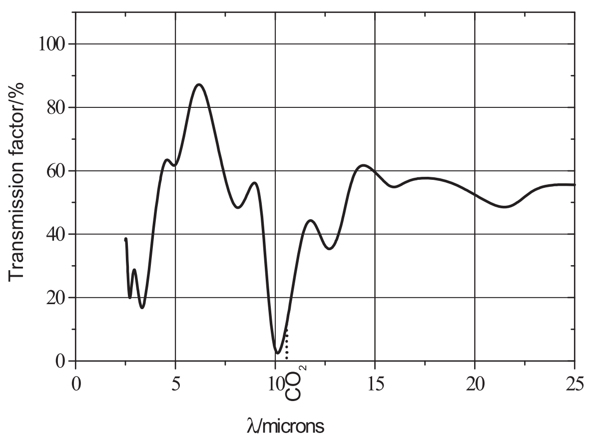


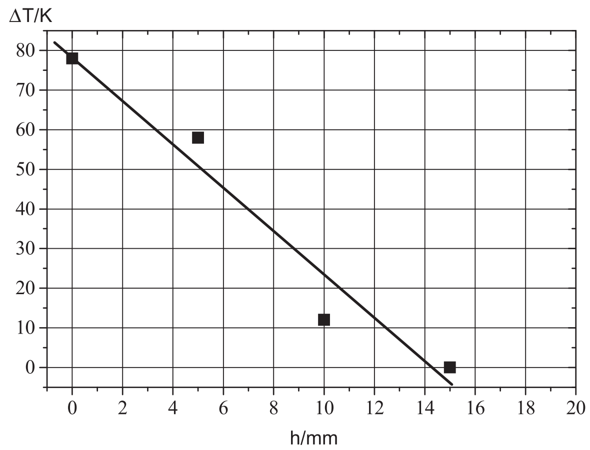
1 Test installation: 1 – Emitting source (gas discharge CO_2-laser: $\lambda = 10.6$ micrometres, $P = 25$ W), 2 – Rotary mirror, 3 – Electrolytic cell, 4 – Cathode, 5 – Anode, 6 – DC power supply

The transmittance spectra of the aqueous electrolyte solutions in the IR range were recorded by a spectrophotometer, SPECORD M 80 supplied by Ruta Engineering, Chernovtsy (Ukraine). Thickness of electrolyte solution layer in a bath was 5 mm.

The temperature of the electrolyte solutions in the cathode region was measured by a copper-constantan thermocouple. According to the standard GOST 6616-53 thermocouples made of copper and constantan wire comprising two thermal junctions can be used to measure low temperatures (from –180°C to 200°C). Measurement accuracy of 0.5°C in temperature ranges from –40°C to 125°C can be achieved. Metallographic studies of structure were fulfilled using a microscope 'Zeiss Neophot-21' at magnification power x600. Microhardness of coatings was measured by a hardness device PMT-3 at indenter force 0.1 N. Phase composition, lattice spacing and fine texture were examined an X-ray diffractometer DRON-2.0 with Co-radiation. Lattice spacing was determined by visible maximum of diffraction line (311) taking into account its width and correction for photography.[9] Mean value of mosaic blocks (coherent dispersion areas) and size of microdistortions were defined by the method of approximation.[10] Annealed nickel was used as a reference. Dislocation density was evaluated through actual physical diffraction line broadening.



2 Spectral transmission graph of nickel electrolyte water solution



3 Temperature variation vs. solution layer thickness in the field of radiation

Results and their discussion

Selection of aqueous electrolyte solution for nickel plating was based on the results of the investigation of transmission spectrum and distributions of temperature through thickness of solution layer in the radiation field.

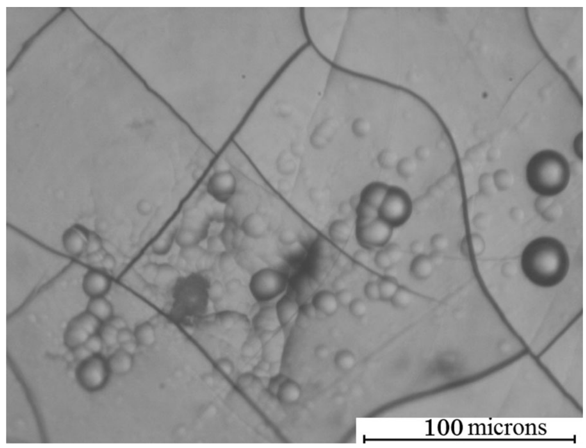
Measurement of transmission capacity of electrolyte water solutions in the middle IR-range (Fig. 2) showed that water solutions have low transmission capacity in this optical band, and for CO_2-laser wavelength $\lambda = 10.6$ micrometres, the transmission factor came to 10%.

To prove the hypothesis regarding the local thermal effect,[11–16] sounding of electrolyte solutions i.e. measuring of solutions temperature variation in conditions of the laser radiation effect was fulfilled with the help of a copper-constantan thermocouple[17] (Fig. 3).

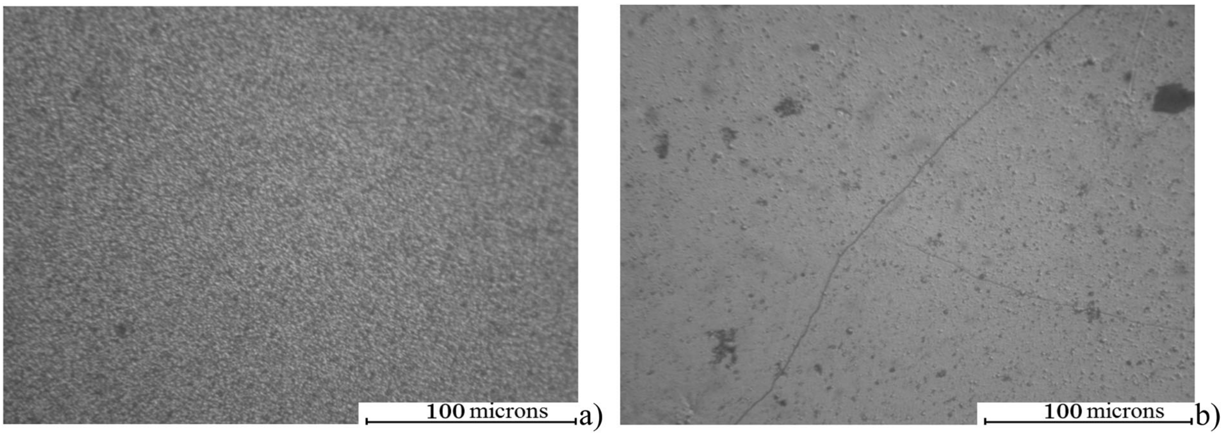
On the basis of electrolyte solutions transmission spectrum study and temperature distribution in the cathode radiation area, the following conditions of electrodeposition were selected:

– nickel was electroplated subject to external enhancement by gas discharge CO_2-laser operating in medium IR-band;
– optimum thickness of electrolyte solution layer above the substrate was 5 mm.

Analysis of electrodeposited nickel surface morphology showed that use of external laser exposure of cathode area



4 Morphology of DC electroplated nickel surface in galvanostatic mode, $j = 50$ A m^{-2}

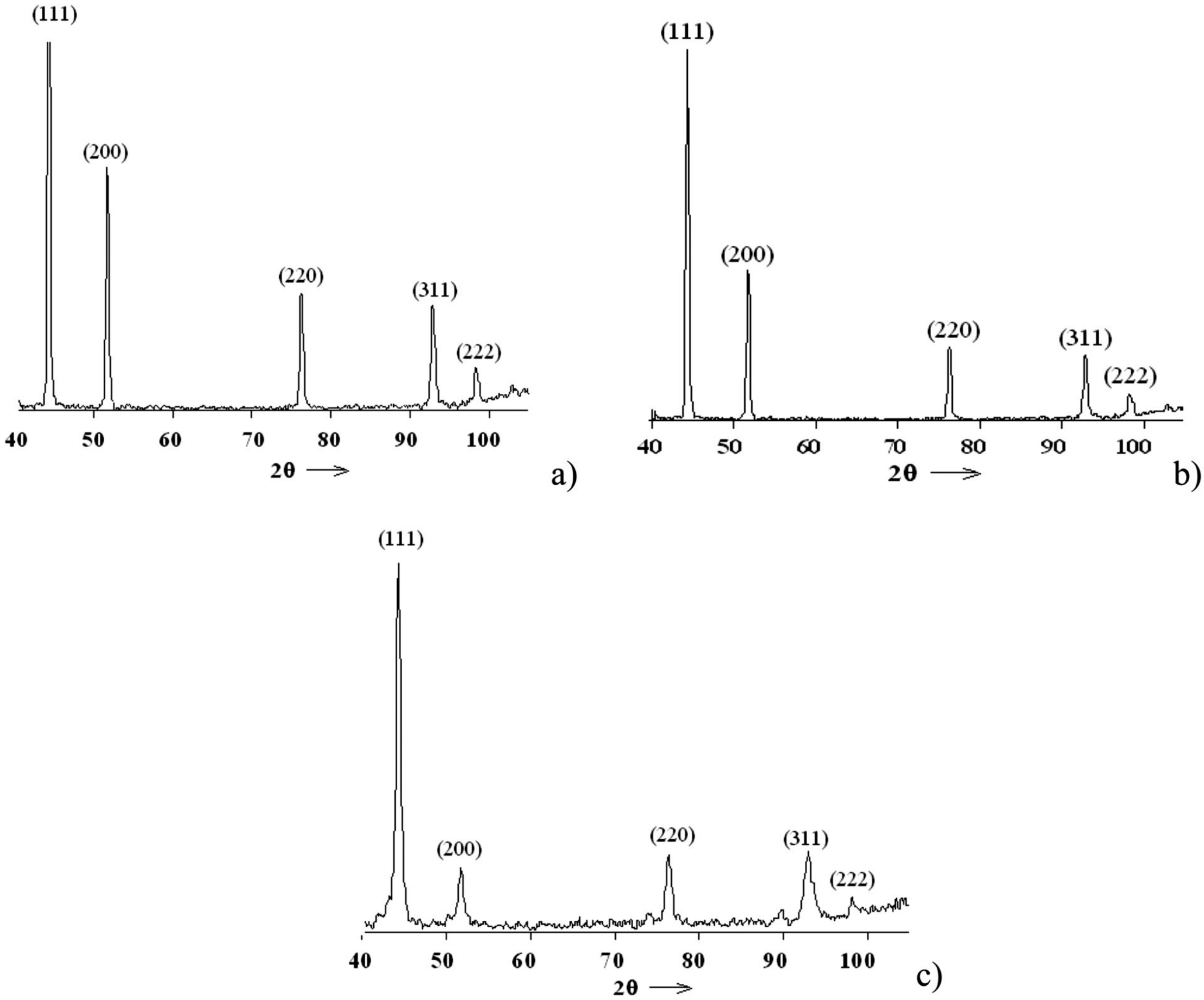


5 Morphology of laser-enhanced electroplated nickel surface in galvanostatic mode, $j = 50$ A m^{-2}: *a* in radiation zone; *b* out of radiation zone

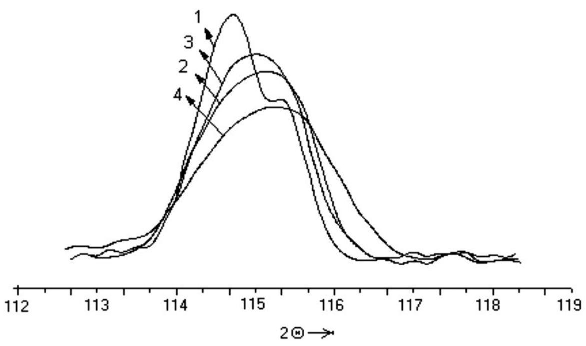
in the process of electrodeposition resulted in transformation of surface morphology in comparison with coatings produced by direct current (DC) application without laser exposure.

The process of DC cathodic nickel reduction from sulphate electrolyte is accompanied by release of hydrogen which passivates the cathode surface due to adsorption across its whole surface. Analysis of DC galvanostatically electroplated coatings (at constant current density 50 A m^{-2}), showed formation of surface blisters which appear like ‘frozen’ gas bubbles and represent such superficial defects. Figure 4 shows that the frozen hydrogen bubbles are internal stress concentrators and one of the factors promoting coatings cracking.

In galvanostatic laser-enhanced electrodeposition mode nickel coating internal stress in the radiation field decreases. In the field of radiation the coating is matte, with a rather developed surface structure (Fig. 5a). In



6 X-ray analysis of nickel coatings phase composition: *a* reference; *b* laser-enhanced mode; *c* DC



7 **Shift of the maximum and variation of nickel diffraction line profile (311) *vs.* change of electrodeposition mode: (1) reference; (2) DC; (3) laser-enhanced (area of the sample exposed to radiation); (4) laser-enhanced (area of the sample not exposed to radiation)**

the transition section from radiated area to non-radiated zone of the sample cracks occurred in the nickel coating that testifies to increase in internal stress (Fig. 5b). The morphology of the surface behind the radiation zone is similar to the one for nickel obtained in DC mode (Fig. 4).

X-ray diffraction analysis of phase structure shows that in the nickel coatings produced by both DC and laser radiation single-phase coatings are generated with the nickel face-centred cubic lattice. No nickel hydrides and/or hydroxides in the recovered coatings were found (Fig. 6).

Diffraction patterns of electrodeposited nickel coatings differ considerably from reference diffraction patterns. First of all, it concerns the line intensities (200) and (220) that can indicate formation of axial growing texture with crystallographic indexes [111] for galvanostatic electrodeposition mode.

Diffraction lines (311) for nickel coatings produced in both electrodeposition modes are wider in comparison with the reference because of available crystal lattice defects arising in the course of coating growth (Fig. 7). The largest widening of line (311) occurs for the sample received in DC mode at current density 50 A m^{-2} that can be associated with the poorest equilibrium conditions of structure formation. Minimal widening of line (311) corresponds to the laser-exposure electrodeposited sample subject to the same current density, but higher equilibrium conditions of crystallisation.

For confirmation of this fact, the fine texture of produced nickel coatings was investigated. Results of analysis of nickel coatings fine texture produced by DC and laser-enhanced electrodeposition methods are presented in Table 1.

The reported reduction of lattice parameter and increase of dislocations density also were caused by formation of defective structure in coatings plated in galvanostatic mode.

Table 2 Nickel coatings adhesion strength *vs.* electrodeposition conditions

Deposition modes	$T_{solution}$/K	*n*
DC	293	2.5
DC	351	5
Laser-enhanced electrodeposition	351	8

Lessening of the degree of imperfection of nickel crystal lattice leads to increase in expansion of X-rays coherent dispersion area, observed in the electrodeposited coatings at laser radiation of cathode (Table 1). Analysis of fine texture showed that DC-produced coatings include stacking faults, so called intrinsic defects. Laser-enhanced electrodeposited nickel coatings have reduced concentration of stacking faults. Change of coatings structure affects physical and chemical properties of films, e.g. microhardness (Table 1).

The results of the investigation of fine texture and microhardness confirm that laser radiation promotes the formation of greater equilibrium structure in nickel coatings electrodeposited in galvanostatic mode.

Investigation of the electroplated nickel coating rate disclosed that transition from DC electrodeposition mode without laser radiation to laser-enhanced electrodeposition showed an increase of electrodeposition rate from 0.0011 to 0.0015 μm s^{-1} which is associated with reduction of general cathode overpotential and increase of output of metal i.e. plating current efficiency, thus ensuring a more macro-crystalline structure is formed.[18,19]

Results of research focused on laser radiation effect on structure and properties of nickel coating have indicated the possibility of increase of electrodeposited coatings adhesion with a copper substrate.

Tests of adhesion of 15–20 micrometre nickel coating to the substrate were performed by the bend method of samples folding over-double (until breakdown). The tests showed peeling of DC electrodeposited coatings (formed from nickel-plating electrolyte solution at 293 K) along the overall line of fracture. When the temperature of the nickel-plating electrolyte solution increased by 58 K samples showed the coating peeling along 50–60% of the line of fracture. Laser-enhanced plated samples had neither cracks nor peelings until complete copper substrate bending fracture. Table 2 includes results of determination of coatings adhesion strength. Number of bending cycles (*n*) is a factor characterising the adhesion of coatings.

Measurement of nickel coatings adhesion with a substrate performed by the method of making a grid of scratches confirm the low adhesion of coatings with substrate DC electroplated at temperature 293 K, and show evidence of increase of adhesion strength of laser-enhanced electrodeposited coatings. Thus, if a grid of crossed scratches is scored on coatings electrodeposited at temperature 293 K the coatings are damaged and

Table 1 Effect of electrodeposition galvanostatic modes on lattice spacing (a), size of mosaic blocks (D), dislocations density (ρ), micro distortions (Δa/a) and microhardness ($H_μ$) for nickel coatings

Deposition modes	a/nm	D/nm	$ρ \times 10^{13}/m^{-2}$	$Δa/a/ \times 10^{-3}$	$H_μ$/MPa	Metal cathode efficiency/%
DC	0.3514	89	12.6	2.7	3800 ± 40	63
Laser-enhanced electrodeposition (in radiation zone)	0.3520	138	5.2	1.1	2800 ± 30	86
Laser-enhanced electrodeposition (out of radiation zone)	0.3516	100	10.0	2.4	3500 ± 30	

separated from a substrate. Increasing of temperature of nickel-plating electrolyte solution by 58 K leads to improvement of electrodeposited coatings adhesion with a substrate: peeling at points in the crossed scratches is less intensive than in the previous case. Testing of laser-enhanced electrodeposited coatings showed no peeling in crossed scratches points.

Thus, laser radiation of the cathode area during electrodeposition of metal coatings promotes increase of adhesion strength with a substrate. Results of adhesion strength tests of coatings give grounds to assume that during the process of laser-enhanced electrodeposition diffusion interaction between coating elements and the base metal surface takes place. This is thought to contribute to increased coating adhesion strength with a substrate and will be a subject of the authors' further research.

Conclusions

Analysis of investigations into structure, mechanical properties and fine texture of laser-enhanced electrodeposited nickel coating showed that decrease of microhardness in a radiation area, decrease of lattice spacing of laser-enhanced electrodeposited nickel and change of nickel coating fine texture parameters result from formation of greater equilibrium structure.

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