# Influence of Laser Irradiation on Metal Electrodeposition

By M. Bratoeva & S. Gurkovsky

The aim of the current investigation is to discover new potentialities of the electrochemical deposition of metals and alloys simultaneously with laser irradiation. A manifold increase in the rate of deposition has been observed. Laser irradiation decreases the alkalinity relative to nonirradiated tests. This type of electrochemistry offers not only means of maskless production of circuit boards, but new possibilities to plate difficult-to-access and overshadowed parts of cathodic surfaces.

One of the methods to intensify the process of electrodeposition of metals is laser irradiation. It is clear from the literature<sup>1-10</sup> that the influence of laser irradiation on the electrodeposition of metals has been investigated very actively in Belgium, Germany, Holland, Israel, Russia, the USA and Japan. It has been established that the increase of the deposition rate by laser irradiation results from the increase of temperature on the metal/solution boundary surface. This initiates three effects: intensive stirring of the electrolyte, increase of the charge exchange rate, and shift of the rest potential. Despite the great number of publications on the practical application of laser electrochemistry, there is a lack of data concerning the influence of laser irradiation on the process of electrodeposition of metals.

The aim of the current investigation is to discover new potentialities of the electrochemical deposition of metals and alloys with laser irradiation. The methods used include plating with simultaneous laser irradiation, measuring the acidity of the cathodic electrolyte layer (pH<sub>s</sub>) in the course of laser irradiation,<sup>10</sup> determination of the rate of deposition, and SEM investigations.



Fig. 1—Schematic diagram of pH<sub>s</sub>measurement during laser irradiation: 1 - laser; 2 - pH-meter; 3 - microelectrode; 4 - glass electrode; 5 thermocorrection electrode; 6 - rubber gasket; 7 - glass capillary; 8 calomel reference electrode; 9 - glass diaphragm; 10 - sample; 11 electrolytic cell; 12 - potentiostat.

#### Experimental Procedure

Copper, brass, steel, kovar, ceramics and glass-fiber-resin were used as substrates with surfaces of one cm<sup>2</sup>. A specially constructed quartz cell was used. Irradiation was accomplished by a Nd-pulsed laser and an Ar-continuous laser. Coatings obtained were: Ni, Fe, Co, Ni-Fe, Co-Ni-Fe, Ni-Mo, Cu, Zn, Sn-Pb, Ag and Au. The laser beam was directed to the cathode surface through the electrolyte. The total distance of the laser beam was fixed by an optical system. The duration of pulses was seven msec. The laser power density was 106 W/cm2. The polarization measurements were conducted in a 100-mL three-electrode cell. A potentiostat, coupled to an oscilloscope and a current amplifier with memory, were utilized for the electrochemical measurements. The change of concentration of reacting ingredients during the electrolytic process from C in the bulk of electrolyte to the cathode surface layer,  $C_s^{o}$ , was determined by measuring pH<sub>c</sub> (Fig. 1).

## Discussion

Measurement of pH<sub>s</sub> is necessary for study of the mechanism and kinetics of electrochemical reactions and physicochemical properties of the coatings: pH =  $-\log a_{H30}^{*}$ . The microglass electrode acts as a Luggin capillary, with tip welded to the glass electrode with diameter up to 0.1 mm. Its operation is a function of the input impedance of the pH meter. The capillary functions as a classical glass electrode. It is filled with 0.1 N HCl before welding, and a silver wire, anodically treated in 0.75 N HCl, is fixed inside it. Its calibration curve (pH-E) has been traced vs. a saturated calomel electrode





Fig. 3—pH<sub>s</sub> changes vs. time during Fe plating: —• without laser; — with laser; (×) 0.1; ( $\bullet$ ) 0.5; ( $\bigcirc$ ) 1 A/dm<sup>2</sup>.

(SCE). The top of the capillary contacts the cathodic surface in the range of the double layer. The reproducibility of the results is checked by three consecutive measurements at each of the investigated points.

The polarization curves were measured potentiostatically in the course of periodic irradiation by laser beam. The resulting current pulses of the cathodic polarization curve of Co-Ni-Fe alloy coatings are shown in Fig. 2. As can be seen, the cathodic current increases at each applied potential. Considerable acceleration of the rate of the electrolytic process is typical for the curve with peaks resulting from the laser irradiation. A comparison of the deposition currents for samples with and without laser irradiation are shown in Table 1.

It should be noted that at lower current values, without any laser irradiation on the cathode surface, there is no alloy electrodeposition. The laser irradiation brings about electrodeposition in the laser-induced areas. The alloy is deposited at higher current densities on the cathode, but in the laser-induced zone, the thickness of the coating is larger compared to that on the periphery, as established in the profiles. The coating thickness measured with a profilograph is shown in Table 2. The observed plateau on the polarization curve, conditioned by limiting current, is caused by the reduction of dissolved oxygen in the electrolyte. This is a result of performing the experiments in air.

Curr	nont
mA	
0.1	0.2
0.6	0.8
0.7	3.25
1.1	6.65
1.4	0 1
	Cur m without laser 0.1 0.6 0.7 1.1



Fig. 4—pH schanges after 50 sec vs. current density during Co-Ni-Fe alloy plating: Temp  $^{\circ}C$ : ( $\bigcirc$ ) 20; ( $\bigcirc$ ) 30; ( $\bigcirc$ ) 40; (e) 50; (o) 60.



Fig. 5—SEM photo of Ni-Mo alloy coatings: (1) without laser; (2) with Ndpulsed laser irradiation.

The investigation of electrolyte acidity in the near cathodic layer (pH<sub>s</sub>) vs. time after disconnection of the current (Fig. 3) and the cathode current density (Fig. 4) during iron plating, shows a lower grade of alkalization of the cathodic electrolytic layer by laser irradiation compared with that without laser irradiation.

Alteration of pH<sub>a</sub> is complete up to the 30<sup>th</sup> second after current disconnection and maintains a constant value, ±0.2 pH. To gain a better understanding of the process taking place in different laser-induced conditions, the study was completed with a morphological investigation of the coatings. The deposits obtained were examined by SEM. These investigations show that deposits, obtained by conventional plating, have a crystalline structure. The powerful pulsed laser irradiation leads to change of the structure, expressed as recrystallization processes. The structure of Ni-Mo alloy coatings (Fig. 5) obtained by laser beam is characterized mainly by the presence of fine crystalline formations, usually a favorable factor. In most of the cases, the coatings are not uniform. Crystalline aggregation and packing can be observed at the center of laser beam. The crystalline mass is less at the periphery of the spot and nodules had formed on the surface.

Table 2

Coating Thickness		
	Thickness, µm	
	with laser irradiation	without laser irradiation $\tau = 5 \min$
Coating	$\tau = 7$ msec	$\mathbf{D}_{\rm L} = 1  \mathrm{A}/\mathrm{dm}^2$
Ni-Mo	3.21	
Cu	5.82	2.21
Со	13.48	-
Zn	13.07	1.43
Ni	4.14	1.03
Sn-Pb	3.83	-



Fig. 6—Substrate of  $Al_2O_3$  ceramic for magnetic head with continuous laser-induced plating.

Figure 6 shows ultra-thin traces of Cu and Fe-Ni alloy (permalloy) for magnetic heads electrodeposited simultaneously with laser irradiation. In this case, preliminary treatment of the ceramic substrates in aggressive media has been completely eliminated. A defective circuit board with Cu and Sn-Pb multilayers is shown in Fig. 7. By laser irradiation only on the damaged parts, it is possible to restore the board.

The results obtained show that coatings can be deposited in the zone of laser irradiation. The quality of these coatings depends on the following factors:

- 1. *The laser equipment*—The laser beam influence appears to be determinative. The choice depends on the plating zone and the practical application.
- 2. *Power density of laser beam*—By irradiation at lower power, it is necessary to increase the time of exposition. This produces coatings not only in the irradiated area, but in other parts of the substrate. Increase of laser power allows shortening the time of deposition and localizing of the plating to the desired part of the substrate.
- 3. *Type of electrolyte*—The color of the electrolyte must match the wavelength of the laser beam for maximum absorption. The electrolyte is to be filtered and continuously renewed at the zone of irradiation.
- 4. Surface of the substrates—Substrate surfaces must be clean, with  $5-55 \,\mu m$  roughness, for better reflection of the laser beam.
- 5. *Plating current*—The optimal current must be smaller than the current without irradiation.

## Findings

This investigation established the possibility of plating Ni, Fe, Co, Ni-Fe, Co-Ni-Fe, Zn, Sn-Pb, Ag and Au coatings on substrates of copper, steel, kovar, ceramics and glass-fiberresin. A manifold increase of the rate of deposition was observed. Laser irradiation decreases the alkalinity relative to the non-irradiated tests. This type of laser electrochemistry offers not only means of maskless production of circuit boards, but new possibilities to plate difficult-to-access and overshadowed parts of cathodic surfaces, as well as to save on materials in short supply. Laser application in the process of electrodeposition quickly compensates for the expense of



Fig. 7—Circuit board for restoration with laser-induced plating.

laser equipment and has other economic advantages.

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#### References

- 1. L.T. Romankiw, Oberfläche-Surface, 25(8), 238 (1984).
- 2. F. Friedrich, Ch.J. Raub, Metalloberfläche, 38(6), 237 (1984).
- 3. A.A. Eremenko et al., Quantum Electronics, 11(8), 1677 (1984).
- 4. J. Zahavi et al., Proc. INTERFINISH '84, Jerusalem, 173 (1984).
- C.W. Draper, P. Maszoldi, *Laser Surface Treatment of Metals*, D/BIL, NATO, SAD, 577 (1986).
- 6. A.D. Davidov, *Electrochimia*, **30**(8), 945 (1994).
- 7. M. Bratoeva et al., Bulgarian patent, 40 083 (1985).
- 8. M. Bratoeva et al., Bulgarian patent 42 779 (1986).
- 9. M. Bratoeva et al., Bulgarian patent 446 351 (1987).
- T.M. Ovchinnikova, B.A. Ravdel, K.Y. Tikhonov & A.L. Rotiniyan, Methods and Results of Investigation of Acidity in the Zone of Reactions, Gorkii, Ed., Gorkii Univ., 53 (1977).

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