Laser surface treatment of copper

C. PANAGOPOULOS, A. MICHAELIDES
Laboratory of Physical Metallurgy, National Technical University of Athens, Zografou Campus, 15773, Athens, Greece

Copper specimens were irradiated with a KrF excimer laser. The surface morphology and structure of laser-treated copper was examined using optical and electron microscopy. Using X-ray diffraction, the residual stress on the copper surface layers was found to change from tensile to compressive as a result of laser treatment. The surface roughness of the copper was observed to be a function of laser power density. The corrosion resistance of the laser-treated copper was also studied in an NaCl solution.

1. Introduction

A laser beam can be used in several ways in order to improve the surface properties of various metallic and ceramic materials. Carbon dioxide, ruby, argon and yttrium-aluminium-garnet (YAG) lasers are currently used in research investigations and industrial processes related to the science and engineering of materials. With the aid of powerful lasers, several metallurgical processes have been applied for the surface treatment of various metallic materials, e.g. surface melting, cladding and surface alloying, transformation hardening, laser-assisted chemical and physical vapour deposition and welding [1]. However, recently, an additional laser, the excimer laser, has been developed which is not yet widely used by the scientific and industrial community. The most recent applications of the excimer laser in the technological field of surface metallurgy are listed below.

Tosto [2] studied the effect of excimer laser radiation on thin sheets of pure copper. Tosto calculated and also observed the generation of shock waves in the sheet of copper as a result of laser radiation; this observation could be the base for the industrial machining of thin sheets of copper.

O'Neill and Steen [3] observed an enhanced absorption of CO_2 radiation on copper and aluminium surfaces as a result of the simultaneous interaction with an excimer laser (KrF).

Badekas *et al.* [4] studied the influence of excimer laser radiation on an aluminium alloy (Al–4% Cu) surface properties. They found that laser surface treatment changed the magnitude and especially the sign of the residual stress in the surface layers of the alloy from tensile to compressive. They also observed that the laser treatment of the alloy increased the microhardness in the top surface layers (30 μm).

Ursu *et al.* [5] studied the change in the metallic surface microrelief as a result of multiple pulses of a powerful ultraviolet laser. They showed that the structure produced depends on the laser power density, the number of laser pulses, the type of irradiated metallic material, the state of the metallic surface and the ambient gas during the laser treatment.

2. Experimental procedure

Specimens with dimensions of 3.0 cm × 1.0 cm × 0.1 cm were cut from a pure copper (99.9%) sheet. These specimens were mechanically polished with SiC paper (150 M). Afterwards the specimens were painted with a black ink to increase the absorption of radiation during the laser treatment of copper.

The copper specimens were irradiated, in atmospheric air, with a Lambda Physik excimer laser using a KrF gas mixture with wavelength $\lambda = 248$ nm and photon energy of 332 mJ/pulse. The laser beam pulse had a lorentzian shape and scanned a copper specimen, as indicated in Fig. 1. The specimen area which was irradiated with the excimer laser was 1.2 cm × 1.0 cm. Each copper specimen was irradiated under different conditions. These conditions were determined by changing the following lasing parameters: (1) power density, (2) pulses per step, (3) number of scannings, i.e. the number of successive passes of the laser beam over the same area of the copper specimen. All the treatments were performed with 30% overlapping of successive laser pulses.

The surface morphology of the copper specimens after laser treatment was examined using optical and scanning electron microscopy (Jeol 133). The laser- and non-laser-treated copper specimens were examined with a Philips diffractometer with CoK_α radiation ($\lambda = 0.1791$ nm) and an iron filter. The surface roughness of laser-treated copper specimens was also studied with a Mahr Perthen profilometer. The corrosion resistance of the laser- and non-laser-treated copper was examined in 0.4 M NaCl solution at pH = 5 and 290 K. The data presented in this study are the average values of five independent experiments.

3. Results and discussion

Figs 2 and 3 show the surface of copper laser-treated with 170 and 200 MW cm^{-2} power density, respectively. Both surfaces were laser-treated three times. From these figures, the appearance of "valleys" and "hills" is noticable on the surface of the laser-treated

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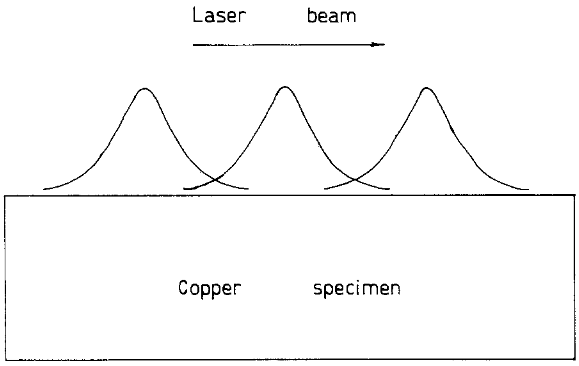

Figure 1 Schematic drawing of laser scanning of the copper specimen.

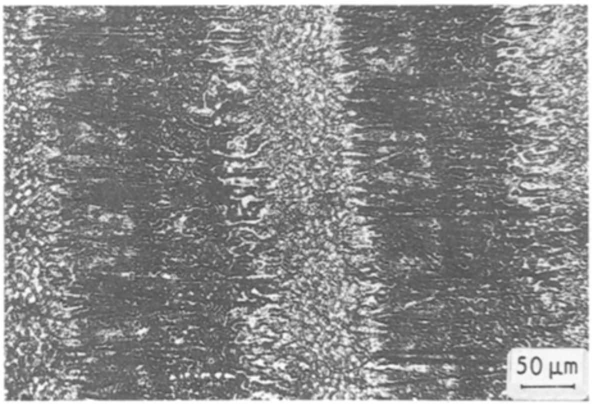

Figure 2 Plan view of copper laser-treated with 170 MW cm^2 power density and three laser scans.

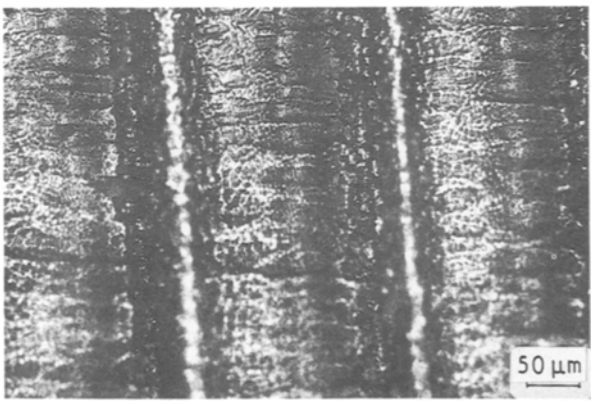

Figure 3 Plan view of copper laser-treated with 200 MW cm^{-2} power density and three laser scans.

copper. The "valleys" (light areas) correspond to the maximum value of the incident power and the "hills" (dark areas) correspond to the overlapping area of two successive laser power waves. The dark areas can be attributed to the thicker copper oxides formed during laser irradiation of copper, whereas the light areas correspond to the thinner copper oxides formed during the laser irradiation of the copper specimens.

The formation of these "valleys" and "hills' is enhanced by the creation of plasma on the copper surface during its excimer laser irradiation. For laser power densities lower than 165 MW cm^{-2}, the characteristic "valleys" and "hills" were not observed on the

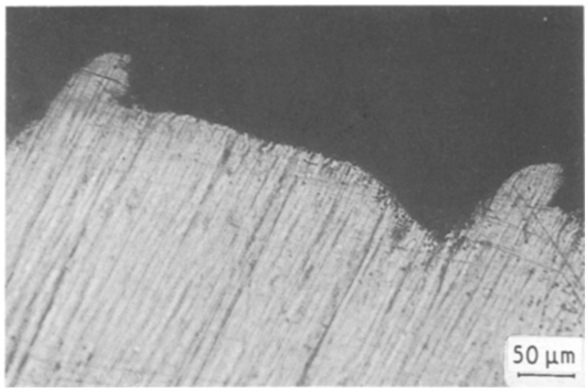

Figure 4 Transverse section of a copper specimen treated with an excimer laser.

copper surface due to the non-creation of plasma during excimer laser treatment of copper [5].

On examining Figs 2 and 3, the succession of "valleys" (light areas) and "hills" (dark areas) is observed to be smoother in Fig. 2 than in Fig. 3; in addition, the width of the "hills" is larger in Fig. 2 than in Fig. 3. This observation can be attributed to the higher power density used for laser-treated copper specimen shown in Fig. 3.

In both figures the creation of characteristic ripples can also be observed. This phenomenon might be caused by the following reasons:

(a) the use of laser power densities greater than that required for the laser melting of copper, 50 MW cm^{-2} [5], and the remelting of copper surface layers during the laser-treatment procedure;

(b) the formation of solidified convection currents on the copper surface during the rapid solidification of copper surface layers as a result of laser treatment.

Fig. 4 shows the transverse section of a laser-treated copper specimen. The characteristic "valleys" and "hills' on the copper surface are clearly observed.

Fig. 5 shows the transverse section of a laser-treated copper specimen. In this figure, the laser-affected zone, with average width of 15 µm, can be seen and for a depth larger than 15 µm the heat-affected zone can also be seen. As observed, the depth of the laser-affected zone is not uniform; this must be due to the non-uniform heat transfer from the top to the deeper layers of copper during its laser irradiation as a result of various defects existing in the surface layers of copper.

Fig. 6 shows the roughness of laser-treated copper as a function of laser power density for one and three scans, respectively. For laser power densities lower than 165 MW cm^{-2} the roughness of the laser-treated copper specimen is observed to be independent of the power density and the number of laser scans. For power densities higher than 165 MW cm^{-2} and lower than 320 MW cm^{-2} the surface roughness of copper irradiated with three scans is always higher than the surface roughness of copper specimen irradiated with only one scan.

For copper treated with more than one laser scan the increase of surface roughness is due to fact that the initial laser scan acts as a pretreatment for the next

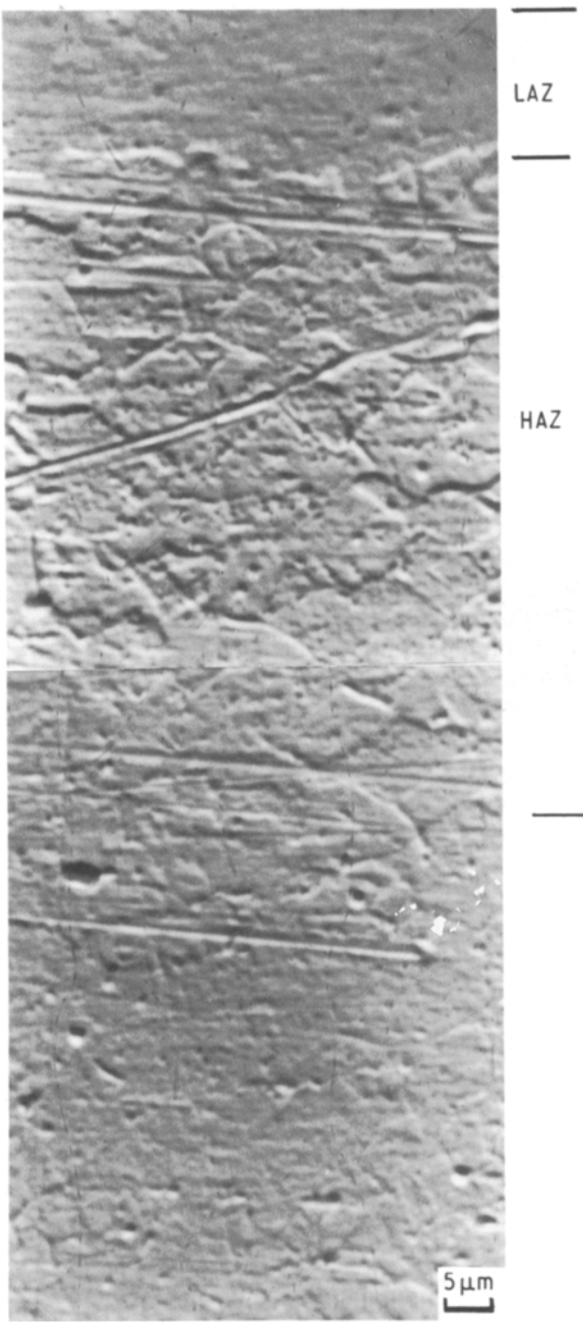

Figure 5 Transverse section of a copper specimen treated with an excimer laser: the magnification of this figure is much higher than the magnification of Fig. 4.

laser scans that follow. In such processes, the initial laser scans significantly decrease the copper reflectivity, resulting first in a higher absorption by the copper specimen and second in an increase of surface roughness. In the laser power density range 165–250 MW cm^{-2}, an abrupt increase in surface roughness of copper for one laser scan and especially for three laser scans is observed, Fig. 6. For power densities higher than 250 MW cm^{-2}, the drastic decrease in surface roughness of laser-treated copper might be attributed to the fact that the existing plasma is detached from the copper surface due to the high density of laser irradiation; an indirect result of this phenomenon is the expected decrease in laser energy absorption by the copper specimen surface.

If a strain which is assumed to be isotropic, is applied to the crystallites lying on the plane layers

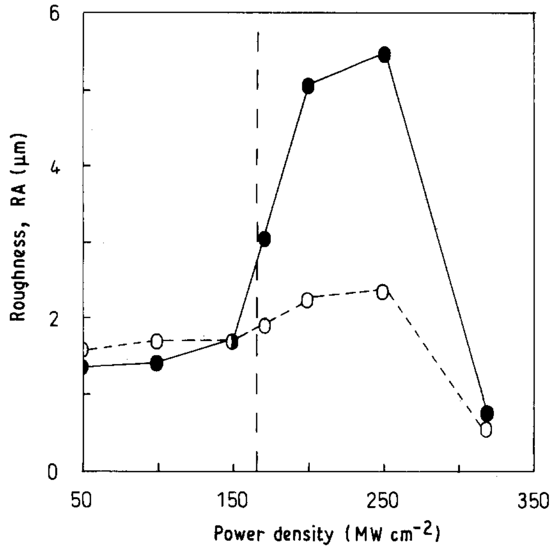

Figure 6 Surface roughness of laser-treated copper as a function of incident laser power density, for 20 pulses and (○) one scan, or (●) 3 scans.

parallel to a metal surface, a change in the interplanar spacing of those crystallites is observed with the result that the average stress in these surface layers is given by [4]

$$\sigma = \frac{E}{2\nu}(\sin\theta_{exp} - \sin\theta_{th})/\sin\theta_{exp} \qquad (1)$$

where σ is the residual stress of the surface layers, E the Young's modulus of the metallic material, ν Poisson's ratio of the metallic material, θ_{exp} the experimental diffraction angle from a plane of the metallic material, and θ_{th} the theoretical diffraction angle from a plane of the metallic material.

During laser treatment of a metallic material, a strain is applied to the surface layers of this material resulting in a shift of the diffraction peaks from their theoretical values in the X-ray diffraction spectrum of this material. But, an additional shift is expected to appear in the diffraction peaks of the metallic material as a result of surface roughening after the laser treatment of this material, i.e. as in Fig. 4.

In order to determine the shift of the diffraction peaks due solely to the laser treatment of copper, an artificial roughening on the copper surface was performed by selective chemical etching of copper, in which the surface roughness of the copper had comparable values with that of a laser-treated copper specimen. This procedure produced a shift of the diffraction peaks of copper, by about 0.2°, to lower angles than the angles of the diffraction peaks from the as-received material. This shift was subtracted from the shift observed for the laser-treated copper (0.5–0.6°) in order to obtain the shift of diffraction peaks due solely to the strain induced by the laser treatment of copper.

Fig. 7 shows the two diffraction peaks of copper, (1 1 1) and (2 0 0), before and after laser treatment of copper and the peaks expected from the ASTM data. From this figure, a shift to higher diffraction angles than those theoretically expected is observed for the as-received copper specimen; on the contrary, a shift to lower diffraction angles than those theoretically

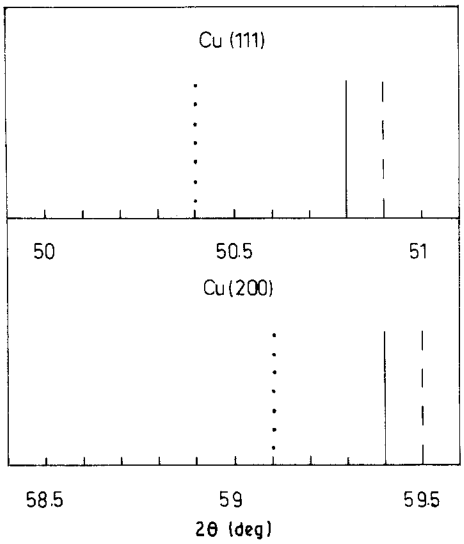

Figure 7 X-ray diffraction angles for the (1 1 1) and (2 0 0) diffraction planes of copper; (——), from ASTM data, (– – –), from as-received copper, (· · ·) from laser-treated copper.

expected is observed for the laser-treated copper specimen.

Using values of 110 GPa for the Young's modulus and 0.35 for Poisson's ratio of copper, and finding the values of $\sin\theta_{exp}$ and $\sin\theta_{th}$ and introducing all these values into Equation 1, the residual stress in the surface layers of the laser- and non-laser-treated copper for each family of recording planes, can be obtained (Table I, Fig. 8). From the results given in this table and Fig. 8, a change in the magnitude and the sign of the surface residual stress on the copper, from tensile to compressive, might be noted as a result of excimer laser treatment of copper.

A non-laser-treated copper specimen, and two copper specimens laser treated, with 100 and

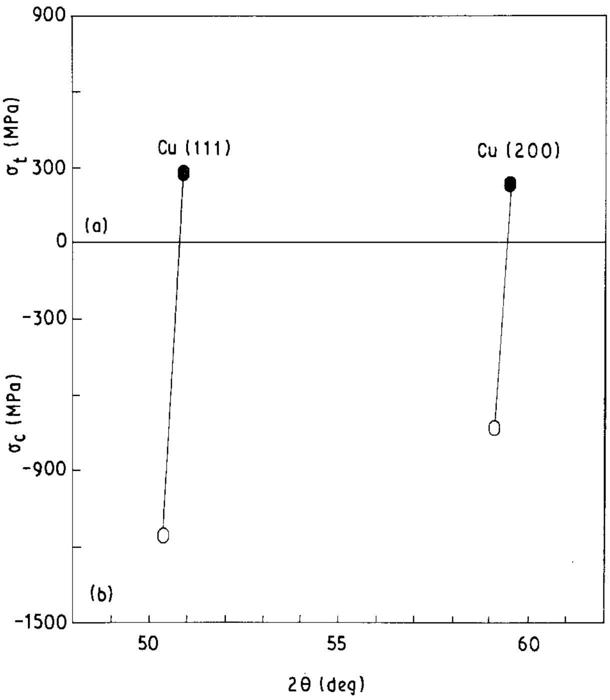

Figure 8 Residual stress as a function of the diffraction angle for (a) as-received copper, and (b) laser-treated copper.

TABLE I Calculated residual tensile and compressive stress for the as-received and laser-treated copper as a function of some X-ray diffraction parameters

	Diffracting plane	$2\theta_{th}$ (deg)	$2\theta_{exp}$ (deg)	4 (2θ) (deg)	ρ (MPa)
As-received	Cu (1 1 1)	50.8	50.9	+ 0.1	+ 288
	Cu (2 0 0)	59.4	59.5	+ 0.1	+ 240
Laser-treated	Cu (1 1 1)	50.8	50.4	− 0.4	− 1165
	Cu (2 0 0)	59.4	59.1	− 0.3	− 725

200 MW cm^{-2} laser power density, were immersed in a 0.4 M NaCl aerated solution, of pH 5 at 290 K and the corrosion potentials of those specimens was monitored as a function of immersion time, Fig. 9. In the case of the non-laser-treated copper specimen, the potential seems to be constant for the period 0–10 min, evidence that the corrosion rate is constant, and up to 1500 min, seems to decrease slightly with increasing time, which means that the corrosion rate of this specimen increases with increasing corrosion time.

In the case of a copper specimen laser-treated with 200 MW cm^{-2} the corrosion potential is approximately constant up to 10 min, then decreases slightly with increasing time up to 150 min, and then becomes approximately constant up to 1500 min. This change

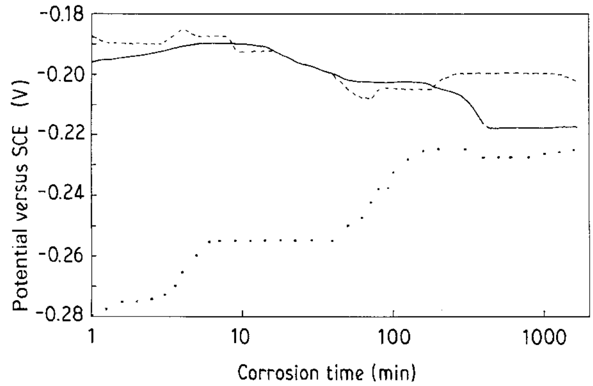

Figure 9 Plot of corrosion potential versus time for (——) the as-received copper specimen, and copper specimens laser-treated with (– – –) 200 MW cm^{-2} and (· · ·) 100 MW cm^{-2} power density.

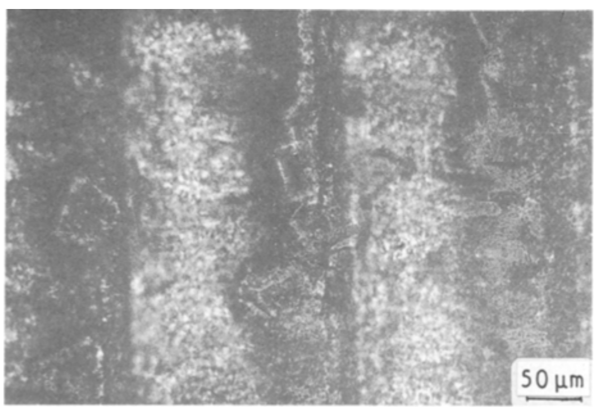

Figure 10 Corrosion pits on the surface of copper laser-treated with 200 MW cm^{-2}.

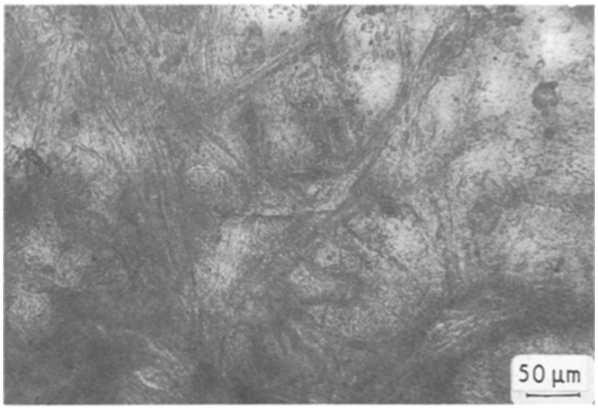

Figure 11 Corrosion products on the surface of copper laser treated with 100 $MW\,cm^{-2}$.

in corrosion potential with time, indicates that during the period in which the corrosion potential is constant, the corrosion rate is constant; on the other hand, when the corrosion potential of laser-treated copper decreases, the corrosion rate increases. The nature of corrosion of this laser-treated copper specimen might be localized corrosion or pitting, Fig. 10.

In the case of copper laser-treated with 100 $MW\,cm^{-2}$, the corrosion potential of the specimen, between 0 and 1500 min, shows successive regions of passivation and dissolution. Therefore, the possible corrosion mechanism of this copper specimen might be caused by the known phenomenon of dissolution–precipitation. Localized areas of precipitated corrosion products can be seen in Fig. 11 during the corrosion of the copper specimen.

4. Conclusions

1. The surface of laser-treated copper showed a succession of "valleys" and "hills".
2. The surface roughness of the copper was found to depend on the laser power density.
3. The residual stress in the copper surface layers was observed to change from tensile to compressive as a result of laser treatment.
4. The corrosion behaviour of laser-treated copper specimens was found to be a function of laser power density incident on the copper specimens.

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Received 3 December 1990
and accepted 10 April 1991