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# Enhancement of the corrosion resistance of copper metal by laser surface treatment

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## Abstract

In this work, the copper metal was treated using Nd:YAG laser with energy 1Joul to enhance corrosion resistance and improve surface properties. The copper metal has many applications in industry as well as water, oil and gas pipes. The same conditions, (laser power density, scan speed, distance between paths, medium gas-air) were applied in the laser surface treatment, After laser treatment, the samples microstructures were investigated using optical microscope (OM) to examine micro structural changes due to laser irradiation. Specimen surfaces were investigated using atomic force microscopy (AFM), X-ray diffraction (XRD), macro hardness, and corrosion test before and after laser treatment to examine the surface properties changes as a result of laser irradiation, and X-ray fluorescence (XRF). Results showed that laser irradiation enhances the corrosion resistance of the metal copper. Corrosion rates as low as 0.550 mpy for laser treated samples were obtained in comparison to 0.699 mpy obtained for the untreated samples. The corrosion protection afforded by laser treatment is attributed mainly to the grain refinement of the top surface layer. This layer is found to consist of nano-scale grains. Higher hardness and lower average roughness due to laser surface treatment.

**Key words**

*ND-YAG Laser, copper, corrosion protection, surface treatment.*

**Article info.**

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# تعزيز مقاومة التأكل لمعدن النحاس بواسطة المعالجة الليزرية السطحية

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## الخلاصة

في هذا العمل معدن النحاس تمت معالجته بليزر نديموم الياك بطاقة 1 جول، لتعزيز مقاومة التاكل وتحسين الخصائص السطحية. معدن النحاس له العديد من التطبيات الصناعية بالاضافة الى انابيب الماء والنفط والغاز. نفس الظروف (كثافة القدرة وسرعة المسح ومسافة المسار والوسط هواء) تمت بها عملية المعالجة السطحية بالليزر.بعد المعالجة بالليزر تم التحقق من التركيب المايكروي باستخدام المجهر الضوئيلمعرفة التركيب المايكروي كيف تغيرت نتيجة الليزرزسطح العينة تم فحصه باستخدام XRD, AFM والتصلد المايكروي والتأكل لمعدن النحاس قبل وبعد المعالجة الليزرية. النتائج بينت ان المعالجة الليزرية عززت مقاومة النحاس. معدل التأكل اقل من 0.550 mpy للعينات المعالجة باليزر بالمقارنة مع 0.699 mpy للعينات الغير معالجة. تعزى حماية من التآكل التي يوفرها العلاج بالليزر بشكل رئيسي إلى صقل الحبوب للطبقة السطحية العلوية. وجد ان هذه الطبقة تتكون من حبيبات بمقياس النانو. وبصلادة أعلى وانخفاض متوسط الخشونة بسبب المعالجة السطحية بالليزر.

## Introduction

Corrosion of the metals is one of the most serious problems throughout the world. Several techniques have been used to protect metals from corrosion among them, Laser surface treatment of materials is an important technique because it offers a possibility to enhance various properties such as the surface strength, hardness, roughness, coefficient of friction, chemical resistance, and corrosion of various materials. [1]. Laser surface treatment is a thermal process that has an advantage over conventional furnace treatment. It is based on the heating caused by the light adsorption of the surface layer and the cooling ensured by the high conductivity of the material. The adsorbed laser energy results in a thin surface layer with desired properties while the bulk of the material is unaffected. [2]. Application of laser technology in metal surface-modified takes advantage of heat energy from the laser beam to change the materials' surface characteristics. The laser process has got from the above advantages over the common methods which involve local heating of the surface without changing the substrate material properties, accuracy mechanics of operation [3]. Treating the alloy surface with laser irradiation can form a solid layer in which precipitates are dissolved and redistribute of alloying elements takes place; according to the level of micro separate reach in the solid layer, the change in corrosion resistance of the metal is obtained after leaser surface treatment [4]. Copper and its alloys are widely used in variety of products that enable and enhance our everyday lives. They have excellent electrical and thermal conductivities, exhibit good strength and formability [5]. Copper, along with gold and rare meteoric alloys, is one of the few metals that are found in nature in the metallic state and is the only noble metal used as an engineering material. Today, a considerable variety of copper alloy materials are in use in a wide range of environments and many different forms of copper corrosion are known. Corrosion involves alteration of both the material and the environment and both factors are important for copper alloys. The copper is extremely well documented due to its use in industry after aggressive environment exposure [6]. One way to improve the surface properties of materials is the laser surface engineering. Laser surface engineering encompasses several applications that are mainly related to enhancing one of the surface dependent properties, like hardness, friction, fatigue and resistance to wear, corrosion, etc. [7].

The present study aims to utilize laser surface melting to improve the corrosion resistance of copper surface by pulse Nd:YAG laser beam irradiation and focused on the surface modifications without effect on the bulk properties.

## Experimental

The specimens prepared as a disk with 2cm diameter length of each plated bar was cut using diamond cutting wheel. Using grinding wheel machine type metallographic Lapping/ Polishing machine (UN 1 POL-820) all specimens were grinded using different grinding paper grades (120, 240, 320.600, 800, and 1200). Specimens were polished using polishing wheel with proper cloth and diamond emulsion (6 µm), obtaining surface free from scratches. The specimens cleaned thoroughly with solvent, then rinsed in distilled water to remove any traces of the cleanser.

## Corrosion and structural tests

### Electrochemical cell

Cyclic polarization techniques for corrosion studies were performed with working M_Lab 200 electronic Germany bank potentiostat in a double glass wall three-electrode corrosion cell with a 1 cm$^2$ surface area. The surface of the holder was exposed to the test solution acts as a working electrode, a saturated calomel electrode and high purity of platinum rod with 10 cm length were applied as reference and counter electrode respectively. For the copper sample, the corrosion tests were performed in a 3.5% NaCl solution and 25 ℃ temperature.

### Atomic force microscopy (AFM)

The Atomic Force Microscope (AA3000 model) or surface morphology analysis has been employed to characterize the external surface roughness that has been categorized as one of the most important surface features. The film thickness measurement is performed carefully scratching the film in the symbolic area. The physical action of AFM include a cantilever beside a sharp tip which is deeply sensitive to small forces, and which causes contact with the sample surface.

### Surface treatment by laser

A MED-810 model, pulsed ND: YAG laser with lasers wavelength 532 nm was usage for laser processing of the copper. The laser pulse frequency, pulse duration, and pulse energy were 1 Hz, <10ns and 1000 mJ, respectively. The spot size was 1 cm$^2$ and the space between the samples to the laser source was 9 cm.

### Harness test

The Rockwell hardness test (XRock-150A model) of the specimens was measured before and after laser surface treatment under a load of 100 g with effect time of 15 s. The laser surface technique produced a self-quenching effect on the surface of copper and gave change in the microstructure. Due to it, the hardness of the copper surface was improved. It should be noted that laser can only harden the surface about 10ns average depth with pre-determined parameters such as energy and power density [8].

## Results & discussion

The chemical composition analysis of copper was carried out using (XR-F) are listed in Table 1, where the values of compositions give high purity of copper metal.

*Table 1: Analytical chemical compositions of the copper metal.*

| Metal | Analysis (wt. %) |
|---|---|
| Cu% | 98.41 |
| Zn% | 0.0040 |
| Ni% | 0.0987 |
| P% | 0.0012 |
| Al% | 0.0410 |
| Mg% | 0.025 |
| Si% | 0.0012 |
| Fe% | 0.1336 |
| Cr% | 0.0595 |
| Ag % | 1.226 |

Both Figs. 1 and 2 view the effect of 3.5% NaCl concentration to create the corrosion medium at room temperature and the corrosion behavior of copper before and after laser surface treatment. The values of corrosion current and corrosion rate were listed in Table 2 for after and before laser surface treatment for copper.

The result appear that the corrosion rates for sample that has been treated by laser is lower than the untreated copper. Furthermore, laser surface treatment causing a considerable increase in the corrosion resistance of the copper as compared with the basis specimen many times. This back to the formation of passive layer on the surface, this layer improves the corrosion resistance.

The decrease in corrosion rate can be explained by the resolidification of metal surface in which the precipitates (alloying elements and impurities if exist) are dissolved and redistributed in an original alloying matrix according to the rapid melting and resolidification.

After the sample corrosion test, it was found a large number of inhomogeneous small cavities was noticed through the optical microscope. These were randomly distributed on the sample surface. They created due to form the corrosion attacks.In case of the laser treatment, the effect of power density on the surface is due rapid melting followed by rapid solidification which result the formation of a different microstructure from bulk metals [9]. From polarization corrosion curves there is no pitting corrosion, which indicates more homogeneous and chemically stable phase and series as an effective barrier to protect the matrix against corrosion process, further improve the behavior by reducing cavities due to the dissolved particles [10].

For that the surface after LST in most often free from alloying elements; furthermore the microstructure is being more homogenous.

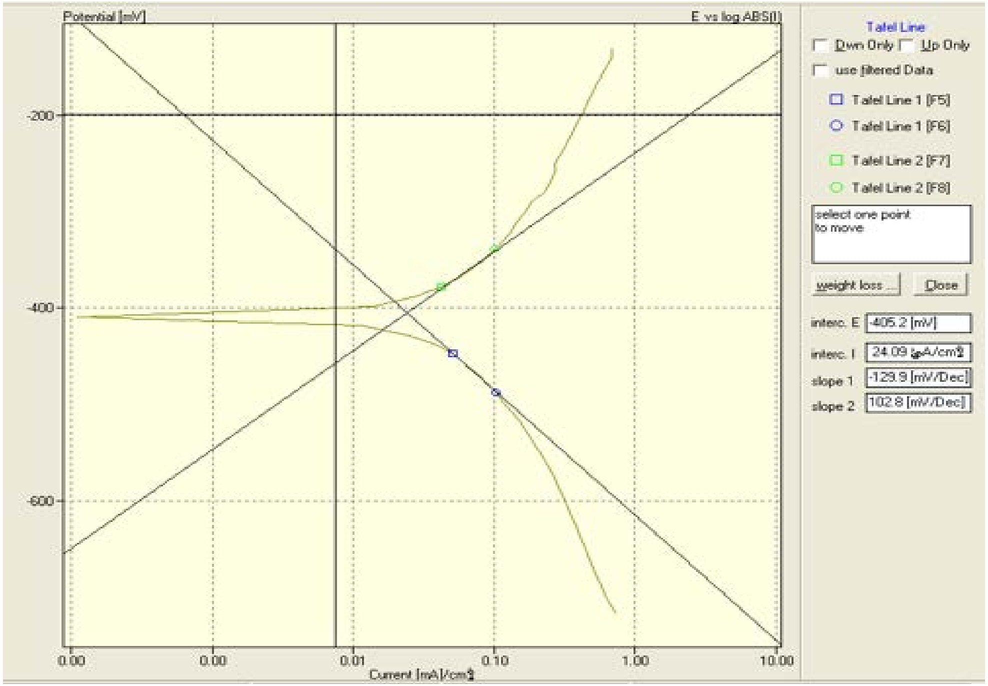
The corrosion rate is calculated by using the Eq.(1) [11].

$$\text{CR (mpy)} = \frac{0.13\ \text{I} \times \text{E.W}}{\rho} \qquad (1)$$

I: corrosion current, µA/cm.

E.W.: Equivalent weight of the specimen in g. / equivalent.

ρ: Density of specimen was 8.96 g/cm$^3$.



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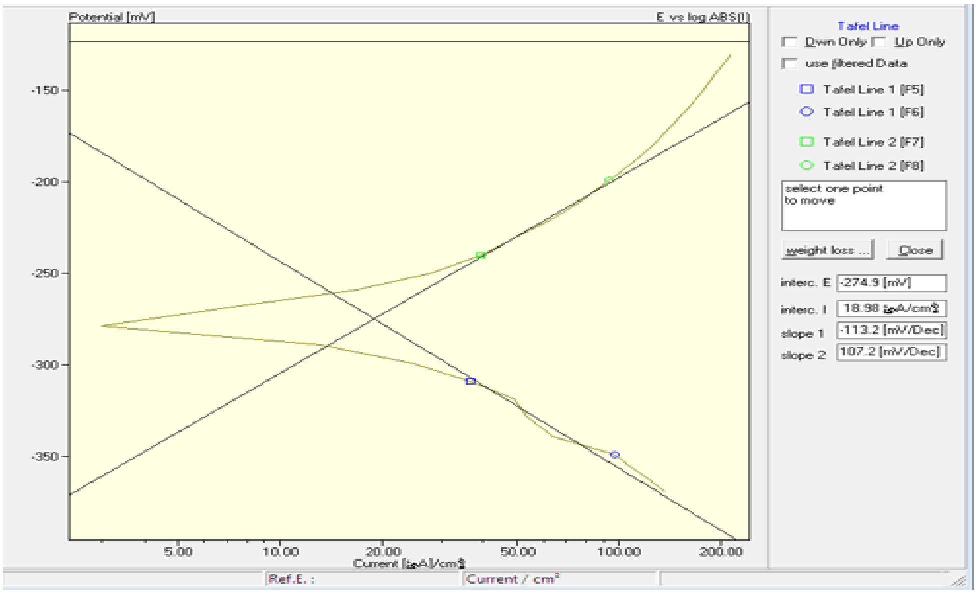
slope 2 102.8 [mV/Dec]

*Fig.1: Polarization curve for copper before LST at 25 ℃and 3.5%NaCl.*



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interc. I 18.98 [µA/cm²]
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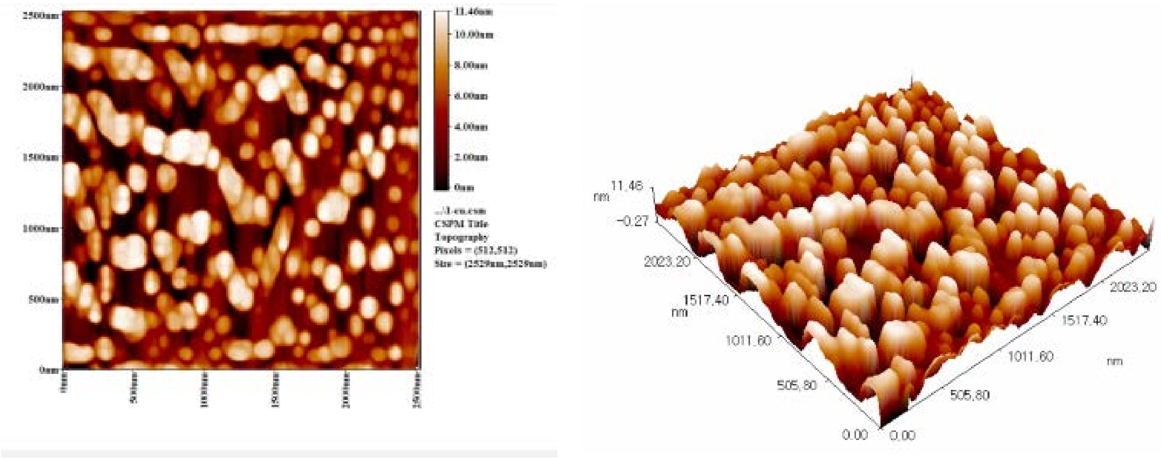
slope 2 107.2 [mV/Dec]

*Fig.2: Polarization curve for copper after LST at 25ĉ and 3.5% NaCl.*

*Table 2: Corrosion kinetic parameters for samples before and after LST.*

| Copper sample | Nacl Con. | $E_{corr}$ mv. | $i_{corr}$ μA.cm$^{-2}$. | C r mpy. |
|---|---|---|---|---|
| Before LST | 3.5 | -405.2 mv | 24.09 | 0.699 |
| After LST | 3.5 | -274.9 mv | 18.98 | 0.550 |

Atomic Force Microscopy (AFM) are emerging as fundamental tools to deeply investigate morphology and structural properties at micro and sub-micrometric scale. In order to evaluate the roughness of the surface sample before and after the leaser treatment was investigated using AFM. Process was resolute by AFM as shown in Figs. 3 and 4. The AFM image revealed that a roughness average decrease after laser surface treatment and that owing to increase the corrosion resistance on the copper surface and this back to laser re-melting is proved to improve the surface quality of copper, the rapid cooling in laser surface treatment process result in refined microstructure, a decrease in surface roughness increases the corrosion resistance agree with [12].



(a) (b)

*Fig.3: AFM Surface scans of copper surface before LST, a. (3D) View. b. (2D) View. Section analysis showing roughness parameters.*

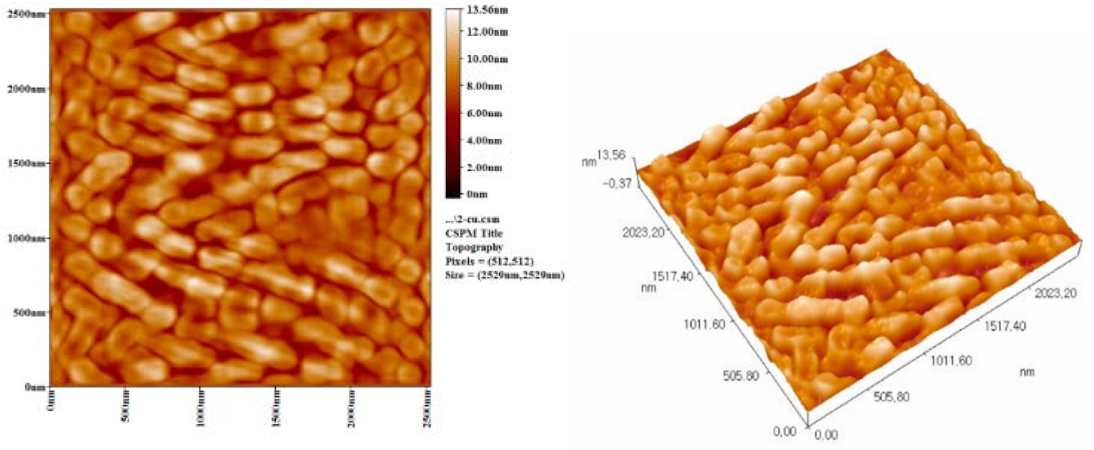


*Fig.4: AFM Surface scans of copper surface after LST, a. (3D) View. b. (2D) View section analysis showing roughness parameter.*

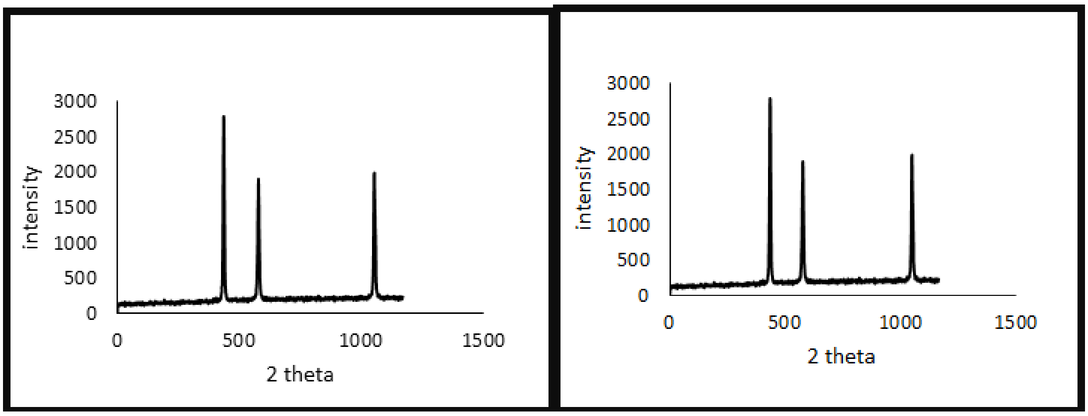
## Hardness test

The macro-hardness of copper notches was done at three different points. For the objective of comparison, the Table 3 listed the mean hardness between two samples of copper before and after surface treatment by Nd: YAG laser. The results offer that sample treaded owing to increase the surface hardness which leads to reducing in corrosion rate on the surface [13].

*Table 3: Average micro-hardness, before LST and after LST.*

| Test No. | HV before | HV after |
|---|---|---|
| 1 | 57 | 91 |
| 2 | 53 | 99 |
| 3 | 51 | 99 |
| Ave. | 53 | 96 |

Figs.5 shows the XRD of the same copper sample before and after laser surface treatment. It was observed that the crystal structure does not change for copper where FCC remains, and this corresponds to fact that the crystal structure of copper remains unchanged with any heat treatment.



(a) (b)

*Fig.5: XRD spectrum for copper sample (a) before and (b) after LST.*

## Conclusion

Due to the laser surface treatment with energy 1Joul to melting surface, there are many changes had been happened on the surface of the spaceman of the copper metal, as lower roughness, where the grain refinement of the top surface layer, and higher hardness due to the fast melting and recrystallization of the copper metal surface, in addition of creation very thin oxide layer as a passive layer which was created through laser surface melting process in the air, all of these changes were contributed of increasing the corrosion resistance of the copper metal in aggressive environment.

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