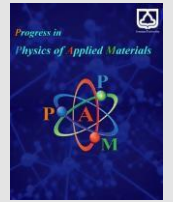




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Near the Ablation Threshold of Copper Surface Which Irradiated by 10.6 μm CO_2 Laser Beam

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ABSTRACT

In this paper, the ablation threshold of several metals has been considered by analogize the characteristics such as: fluence, specific heat of vaporization, and deposited energy. Analytically, the results showed that the threshold ablation happens when copper surface is radiated by CO_2 laser pulses. Experimental observations showed the evaporation for Al and Zn and ablation threshold on Cu as expectation. Thereby, the analytical results have been confirmed by the experimental observation, completely. Oxidation has been observed on Cu surface in phase of Cu_2O , particle sizes are around 200nm. The scanning electron microscope (SEM) image from the radiated surface clearly showed the starting point of the ablation, while the separation not happened, yet. Thus, observation could be interpreted as the ablation threshold. Notably, it could be concluded as such: first, the ablation threshold happens on the interaction of pulsed CO_2 laser with copper surface. Second, observation on mentioned threshold approves the possibility of Cu_2O nanoparticles synthesis by nanosecond CO_2 laser in free space without a reactor.

1. Introduction

Laser ablation is a method which uses a laser source to ablate the targets. In this process, a laser beam with high energy is concentrated at a certain point on the target surface and causes ablation and evaporation [1-5]. Laser ablation has been widely applied to cutting, thin film deposition, metal surface cleaning, marking, drilling, and nanoparticles synthesis [2-5]. Some of the advantages lead to more attraction such as: being a dry process, convenient to collect the removed substances, and its process operation depends on laser beam parameters such as: laser pulse duration [6], shots [7], fluence [8], and wavelength [9]. Industrially, the laser ablation process on metallic surfaces almost concentrated on the cutting and cleaning, especially, in applying the nanosecond pulse lasers. Metallic surfaces cleaning and cutting have been reported based on applying the excimer laser [10] and CO_2 lasers [11]. Notably, the excimer lasers are proper for the thin layers due to their low penetration depth [12]. However, for some layers such as rust and paint on metal surfaces that have higher deposited layers, CO_2 lasers have more efficiency than excimer lasers [3,4]. Therefore, CO_2 laser ablation threshold is a crucial parameter to access the optimum metal surface cleaning without scorching and oxidation on the main considered metal.

The ablation threshold depends on the deposited energy closely. Specific heat of evaporation and the threshold

fluence are the parameters to adapt the laser and the metal properties to access the ablation threshold. Notably, the absorption and reaching the fluence to calculated energy are complementary [13,14]. Furthermore, according to Girad et al the laser ablation threshold is the lowest level of laser fluence that can be observed as surface modifications by scanning electron microscope (SEM) [16]. Therefore, in this paper, our headlines are studying the ablation threshold of several metals to access the most probable metal, confirms the analytic study by experimental observation, and determining the phase and morphology of appeared particle in exploded plume on the surface. Thus, the ablation has been analytically investigated for some metals based on crucial parameters. The interaction between the laser and Cu, Zn, and Al surfaces has been observed. The results showed the threshold ablation on Cu surface, while, the plasma plume is formed, but. the absorption energy is not sufficient to separate the formed particles. The X-Ray Diffraction (XRD) analysis revealed the oxidation on the Cu surface in the phase of Cu_2O and gives the particle size by using Deby Scherrer equation. The observation of exploded plume is possible by SEM figures to see the modification on the surface. The Cu_2O particle size has also been calculated by Dynamic Light Scattering (DLS) test. It is also desired, that results showed the possibility of laser ablation in free space by CO_2 laser without a complicated reactor and equipment.

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2. Results and discussion

Under nanosecond pulses, the absorbed energy heats the target to the melting point up to the evaporation temperature [17]. Furthermore, vapor temperature may be defined as a point in which the small particle of surface convert from the melting state to the vapor state and will separate from surface. Also, the high pressure created in a plasma plume before separation. When, the deposited energy through the target per unit mass (E_m) is higher than the specific heat of evaporation (Ω), a significant vaporization is happened in a special moment and this moment is when, laser ablation has been started. It should be mentioned that specific heat of evaporation is a thermodynamic property of the materials and has a specific value for each material. However, the strong evaporation conditions lied under $E_m \gg \Omega$ and threshold happens when they are adjacent [17].

Depending on the properties of the metal and the features of the laser, an analytical value of fluence is obtained for each metal, and they are experienced the ablation threshold on this fluence. The fluence (F_{th}) and deposited energy (E_m) are calculated using equations (1) and (2) respectively.

$$F_{th} = \rho(\Omega\sqrt{D}) \times \sqrt{\tau_l} \tag{1}$$

$$E_m = \frac{I_a \sqrt{\tau_l}}{\rho D} \tag{2}$$

Where, ρ , Ω , D , τ , and I_a , are density, specific heat of evaporation, heat diffusion coefficient, duration of the laser pulse, and absorption intensity, respectively [17]. It should be mentioned that the reflectivity (R) of metals tend to zero due to applying the high intensity laser, consequently, we consider $I_a ; I_0$ with a good approximation [17-19].

Where, I_0 is the laser intensity.

A comparison of Maximum fluence of the laser and analytical values of metal fluences may give good information to start.

Fig. 1 shows copper fluence is adjacent to maximum laser fluence (used in experiment), but The sentence is not complete. Therefore, in figure 2, specific heat of evaporation and deposited energy are illustrated for several metals. Result shows that the curves overlap on the point which shows copper. This result approves the derived result from Figure 1. It is obvious that ablation threshold might be seen on irradiated copper and vaporization may happen on zinc and aluminum. Experiment on these three metals could validate our estimation. Although gold and silver could be options component but both of them have high heat diffusion coefficient (D), and this means that deposited energy spread quickly on the surface of metal and does not concentrate in a point, so, the possibility of plasma formation and metal evaporation is very low.

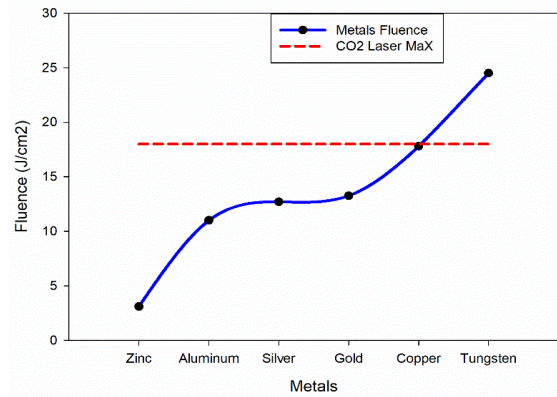


Fig. 1. metals fluence when radiated by CO₂ laser.

The applied laser properties are shown in table 1.

Table 1. Laser properties.

Laser Type	Pulse Width (ns)	Wavelength (μm)	Power (w)	fluence (J/cm ²)	Beam Spot (μm)
CO ₂ laser	150	10.6	up to 100	up to 19	10

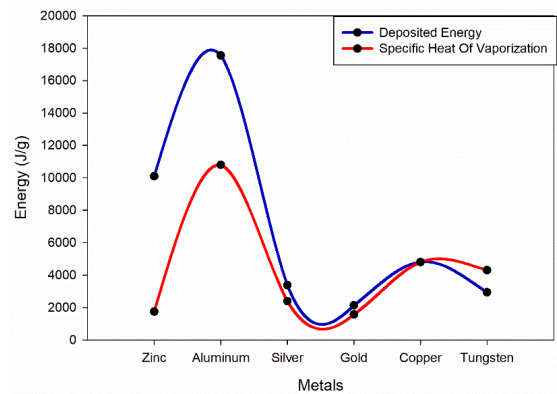


Fig. 2. Specific Heat of vaporization [19] and deposited energy for several metals.

In our experiments 5 cm*5cm*0.2cm plate of Copper, Zinc, and Aluminum with 99% purity have been prepared. They have been Polished by using a soft sandpaper. Finally, to remove any surface contamination, they have been cleaned with ethanol and acetone solutions and distilled water, respectively.

The applied laser source is CO₂ laser fabricated by Coherent Company. It provides laser pulses at 10.6μm wavelength and fluence up to 19 J/cm² with 150 ns pulse width (characterized in Table 1). The laser beam is focused on the targets after passing through a ZnSe lens with focal length of 25 mm. The beam spot diameter on the surface is about 10 μm. The target stage moved at a specified pattern by 2mm/s speed. The pattern illustrated in figure 3. The experiment setup is shown in the figure 4. When the laser light is radiated on the metal surface, some of pulse energy is absorbed by the surface. This action causes the temperature to increases sharply. Therefore, ablation or evaporation process happens soon.

By experiment on the Al and Zn surfaces, the evaporations have been observed, whereas, substance

oxidation is also seen on edge of burnt lines. However, on Cu surface, just a thin oxidation layer on the top adhesion has been created, as such as, created plumes are opened. In the following, we analyze the irradiated Cu surface.

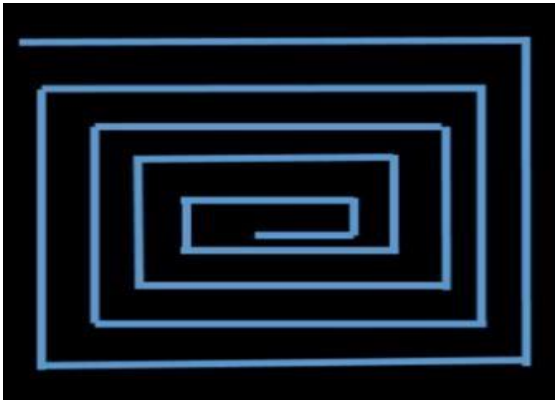


Fig. 3. Pattern of the laser movement on metal surface.

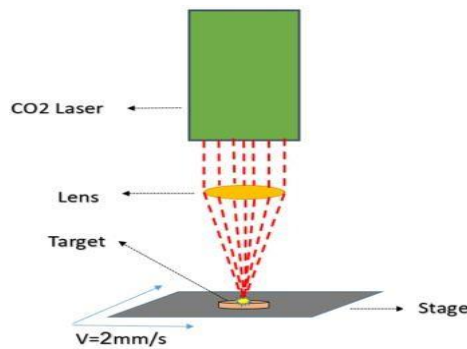


Fig. 4. the schematic structure of experimental setup.

Scanning electron microscopy FESEM (Quanta 200, United States), was used to analyze the morphology and structure of the Cu surface along with observation the ablation threshold. The XRD pattern was recorded by X-ray diffraction device (D8 Advance, Germany) to reveal the created substance phase and size. DLS test was applied to measure particle size, using a DLS device (Nano Ds, France). To prepare sample for DLS, some of the powder formed on the copper surface is mixed with deionized water by ultrasonic machine.

The XRD diagram of the irradiated copper surface has been shown in figure 5. This analysis is performed to identify the phase of the formed layer on the Cu surface. XRD peaks indicate that the thin layer formed on the surface of copper is Cu_2O . Their structures are cubic and corresponds to the standard card JCPDS-PDF 05-0667. This experiment has been performed in free space that oxygen molecules around the surface combine with the ablated copper and perform the copper oxide. Notably, the formed Cu_2O has a cubic structure with lattice constants of $a=b=c=4.26\text{\AA}$.

Also, the mean crystallite size calculated by XRD pattern is 200 nm.

Fig. 6, shows the hydrodynamic size distribution graph of nanoparticles that flew out together with the laser plasma torch/plume. The results show calculated hydrodynamic mean size is 263 nm. It should mentioned

that, the particles were on threshold of separation because they did not receive the vaporization level and remained on the exploded plume, it is normal that particles stick together, and this size can be justified.

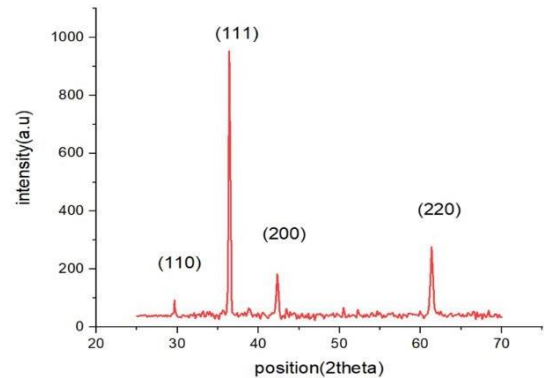


Fig. 5. X-ray diffraction diagram of radiated copper surface.

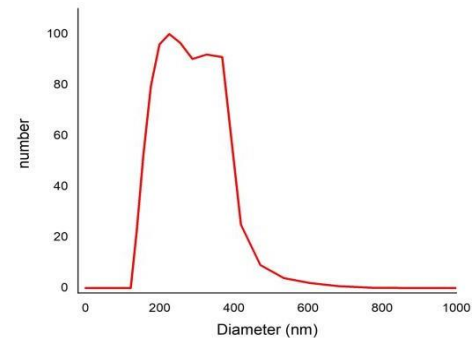


Fig. 6. Hydrodynamic size distribution graph of tested nanoparticles by DLS.

SEM images from irradiated copper surface by different magnifications are illustrated in figure 7 and 8. In these images, the modification of copper surface have clearly been observed. It has been observed that, laser ablation process caused a slight disruption and deformation of the copper surface, such as seen exploded plume, but no evaporation or explosion occurred.

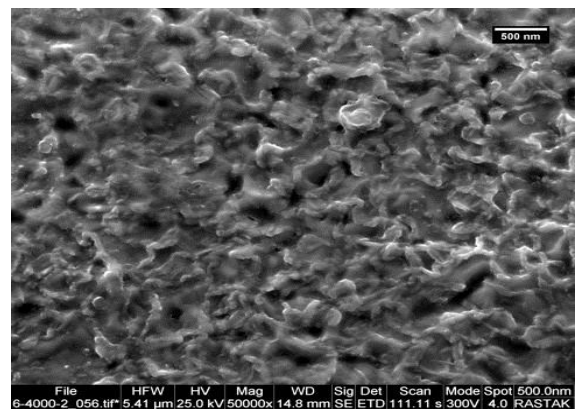


Fig. 7. FE SEM image of the irradiated copper surface with 5000x magnification.

Copper has a bit high heat diffusion coefficient (D). When, surface is radiated by laser and causes heat transfer among the surface, a large amount of heat is dissipated

rapidly on the surface. In fact, deposited energy inside the target at the point of irradiation is less than the energy required to evaporate the metal, thus, we observed the copper metal did not reach the evaporation temperature during the experiment as already demonstrated in obtained results from figure 1 and 2. Meanwhile, the applied intensity by mentioned laser reaches the copper to ablation threshold, which is clearly visible on SEM images.

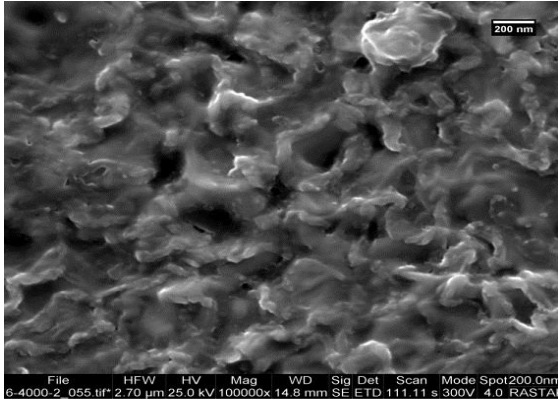


Fig. 8. FE SEM image of the irradiated copper surface with 10000x magnification.

3. Conclusions

The present study demonstrates demonstrate the laser ablation threshold on irradiated copper surface by a 10.6 μm CO₂ laser. Oxidation has been happened and 200nm nano Cu₂O is produced on exploded plume. Whereas, zinc and aluminum surfaces are evaporated. Therefore, the experimental observations have validated the analytical study. The results have also shown the possibility of nano Cu₂O production using nano second laser in free space without any complicated setups.

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