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Copper surface wettability modification by microsecond laser surface texturing

Suleiman Elhamali [1*], Lubna Zawi [2], Hussein Elmasrub [3]
[1,2] Libyan Center for Plasma Research, Tripoli, Libya
[3] Libyan Advanced Center of Technology, Tripoli, Libya

تعديل خواص التبلل لسطح النحاس باستخدام النسج بالليزر النبضي

سليمان موسى الهمالي [1*]، لبنى محمد الزاوي [2]، حسين احمد المصروب [3]
[2،1] المركز الليبي لأبحاث البلازما، طرابلس، ليبيا
[3] المركز الليبي المتقدم للتقنية، طرابلس، ليبيا

[*]Corresponding author: suleiman_hamali@yahoo.co.uk.

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Abstract:
Copper and its alloys are susceptible to deterioration in moist environments. Creating a hydrophobic surface can provide protection against these problems. Low power Nd: YAG laser marking machine with microsecond pulse durations was used in this study. It offers a more cost-effective option compared to common ultrafast laser systems. This study investigated the effects of multiple laser processing parameters on copper surface wettability to optimize the fabrication process. Contact angle measurements revealed that laser texturing significantly increased the contact angle of copper surfaces, shifting them from hydrophilic to hydrophobic. Hydrophobic copper can be valuable in applications requiring moisture resistance or water repellency.

Keywords: Microsecond laser, Contact angle, Hydrophobic surface.

الملخص
النحاس وسبائكه عرضة للتدهور في البيئات الرطبة. يمكن أن يوفر إنشاء سطح كاره للماء الحماية ضد هذه المشاكل. في هذه الدراسة تم استخدام آلة وسم الليزر Nd: YAG منخفضة الطاقة بمدة نبضة ميكروثانية. إنها توفر خيارًا أكثر فعالية من حيث التكلفة مقارنة بأنظمة الليزر فائقة السرعة الشائعة. بحثت هذه الدراسة في تأثيرات معلمات معالجة الليزر المتعددة على قابلية سطح النحاس للبلل لتحسين عملية التصنيع. كشفت قياسات زاوية التلامس أن النسج بالليزر زاد بشكل كبير من زاوية تلامس الأسطح النحاسية، مما يحولها من محبة للماء إلى كارهة للماء. يمكن أن يكون النحاس الكاره للماء قيماً في التطبيقات التي تتطلب مقاومة الرطوبة أو طرد الماء.

الكلمات المفتاحية: ليزر، زاوية الالتصاق، أسطح كارهة للماء.

Introduction

Surface texturing is a technique employed to modify the surface topography of materials, thereby enhancing their performance characteristics. Surface texturing plays a crucial role in creating hydrophobic metal surfaces. Several surface texturing methods have been developed in research and industry, including mechanical and chemical methods [1-10]. Alternatively, laser surface texturing (LST) has gained considerable interest for producing micro-patterns due to its better accuracy, fast, good controllability, high efficiency, repeatability, and machining rate compared to traditional methods[11-14]. Micro-texturing produced by laser beam manipulates surface energy and contact angle, resulting in enhanced hydrophobicity and improved tribological characteristics [15]. Laser texturing enables precise control over surface wettability through the creation of micro-scale, nano-scale, or a mix of both. In this process, a laser beam is directed at the metal surface, melting and removing material to create the desired texture.

Wettability is a quantitative measure of a liquids tendency to spread on a solid surface. In the specific context of metal surfaces, wettability describes the interaction between water and the metal. Hydrophobicity is a term used to describe a materials tendency to repel water. A hydrophobic surface minimizes contact with water, causing droplets to bead up rather than spreading out. The contact angle, an angle formed between the tangent to the liquid surface at the contact point and the solid surface, is a common measure of hydrophobicity. It gives us insights into how a liquid interacts with a solid surface, which is affected by the surface texture, composition, and the liquid characteristics. Hydrophobicity is characterized by a contact angle greater than 90 degrees, while hydrophilicity is associated with a contact angle less than 90 degrees (figure 1) [16]. The wetting behavior of a liquid on a textured surface can deviate from the idealized Cassie-Baxter [17] and Wenzel [18] models, involving intermediate states such as mixed and hemi-wicking [15, 19].

Both hydrophobic and hydrophilic surfaces are utilized in a wide range of applications[20, 21]. This paper is concerned with controlling the wettability of a copper surface, shifting it from hydrophilic to hydrophobic. Hydrophobic copper is a valuable material for various electronic applications due to its corrosion resistance, self-cleaning properties, and dust protection [22]. Nd-YAG laser marking machine with low power will be used for laser texturing process. Using a laser marking machine for laser texturing is a quick, clean, and precise way to achieve a good texturing process. By adjusting laser parameters such as laser power, pulse duration, pulse frequency and scan speed, it's possible to create structures that trap air within the surface. This air pocket repels water, making the surface hydrophobic. The commercial pulse lasers can be classified based on their pulse duration as millisecond, microsecond, nanosecond, picosecond, and femtosecond lasers. In the laser surface texturing (LST) processes, the duration of the laser pulse significantly influences the process efficiency [14].
The roughness of the textured surface is crucial. A balance between roughness and structure is necessary to optimize hydrophobicity[23, 24]. Additionally, surface roughness influences the wettability of metal surfaces[25]. A model reported by Kubiak et al. successfully correlated surface roughness with water contact angle for a wide range of metals, such as aluminum, iron, and copper[26]. Their study showed that a higher contact angle can be reached for smoot surfaces. Yang et al. reported that laser treatment and subsequent chemical modification can modify the surface wettability to exhibit hydrophobic or super hydrophobic properties [22]. Overall, laser texturing is a promising technique for creating hydrophobic or superhydrophobic metal surfaces. The study aimed to optimize the laser texturing process to transform a hydrophilic copper surface (low contact angle) into a hydrophobic surface (high contact angle). Few scientific reports have studied the surface wettability of materials using microsecond pulse laser texturing.

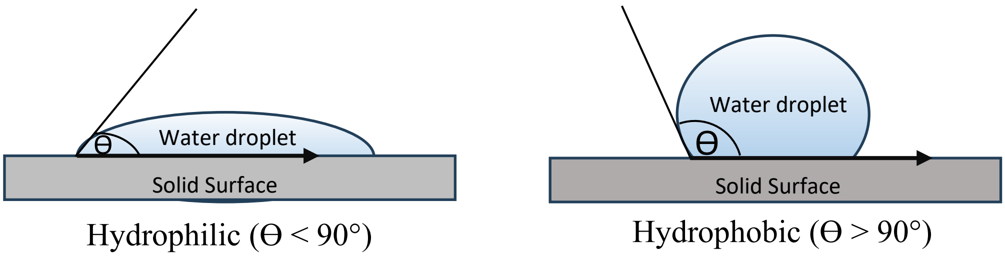

Figure 1: Classification of surfaces based on contact angle between water droplet and solid surface**.**

Material and methods
copper alloy sheet used in a commercial electronic board was used in this study. It was used as-received prior to laser texturing process. All samples were cut into a square shape of 27 mm with a thickness of 0.1 mm. The sample surface was subjected to consecutive cleaning steps: ultrasonication in water for ten minutes, acetone for two minutes and distilled water for five minutes, sequentially, and then dried at 100 degrees. The cleaning process was conducted to remove impurities and any oil remaining on the copper surface. Chemical analysis was conducted utilizing a high-performance optical emission spectrometer (OES), specifically the Foundry Master Pro instrument. The results of the chemical analysis test performed on the as-received copper are depicted in Table 1.

The copper samples were textured using a 75W Nd:YAG laser (Model EVCOMPACT 75 D-EVLASER, Italy) operating at 1064 nm with a pulse repetition rate of 30 kHz and a pulse duration of 9 µsec. The laser beam moves in a spiral rectangular pattern starting from the edge and gradually moving towards the sample center. Figure 2 shows a schematic image of the laser marking machine and the created pattern on the surface. The scan line separation was kept constant at 10 µm as indicated in the figure 2.

The wettability of the copper surface was evaluated by measuring apparent contact angle (APCA) with an automatic contact-angle measuring instrument (Rame-Hart Model 200 Goniometer – United State). The resistivity of distilled water used to measure the wettability, is typically around 18.2 MΩ·cm at 25°C.The values of APCA on the surface of each sample were measured four times at random locations. To achieve good measurements, the droplet of 5µL settled gently and carefully onto the copper surface, growing and shrinking until it reached a stable state. Contact angles were measured by taking images of water droplets on the surfaces with U1 Series camera (CCD, 100fps, Progressive Scan, Sony Sensor, 659 x 494 pixels) and then using DROPimage Standard v 2.4 software to analyze the images.

Table 1 Chemical composition of copper alloy samples.

Elements Wt. (%)	Cu 98.6	Zn 0.098	Pb 0.165	Sn 0.115	P 0.0189	Mn 0.0155	Fe 0.190	Ni 0.179
Elements Wt. (%)	Si 0.0122	Cr 0.0087	Al 0.0241	S 0.0048	As 0.0157	Ag 0.0081	Co 0.0581	Sb 0.0875
Elements Wt. (%)	B 0.0348	Nb 0.0838	C 0.0500	Mg 0.0003	Zr 0.0090	Se 0.0123	Te 0.0859	Bi 0.0441

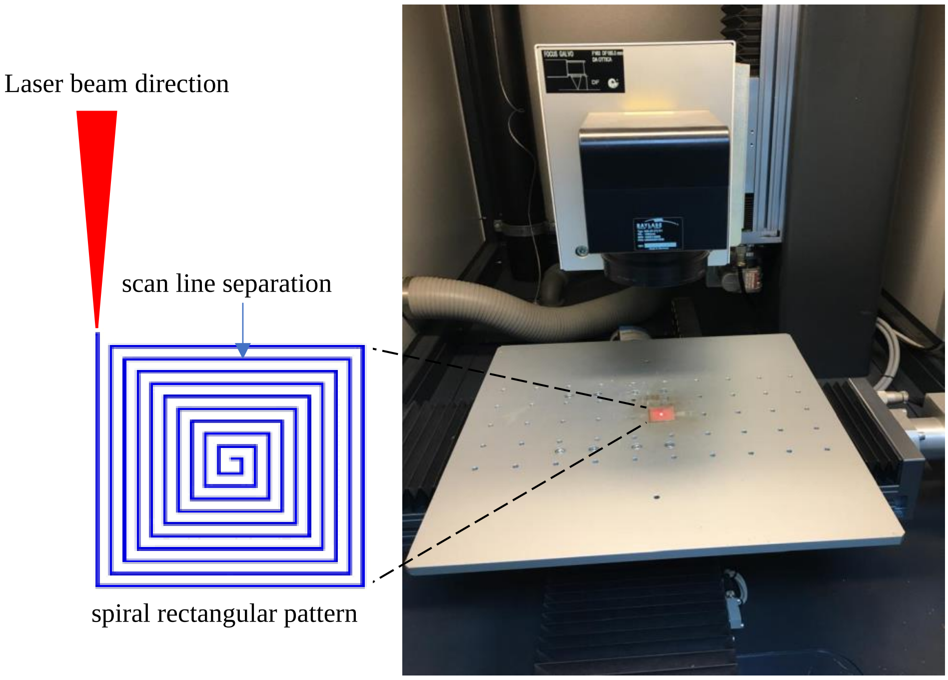

Figure 2: Schematic image of the laser marking machine and the pattern design.

Results and discussion

The copper samples were textured using a microsecond pulsed laser with a Gaussian beam profile and a maximum power of 75 W. Microstructures on the surface were created by scanning the laser beam with a different speed, power, and frequency in both x and y directions. The process parameters of the laser marking machine are summarized in Table 2.

Figure 3 shows the appearance contact angle (APCA) measurements of the samples with different laser power as a function of scanning speed. A clear trend of increasing contact angle with adjusting scan speed and power was observed during laser texturing. It is increased from 82.40° for an untextured surface (as-received) to 110.73° for textured one. It demonstrates that the laser-textured surfaces exhibit a marked improvement in copper hydrophobicity (ϴ > 90°). This phenomenon could be attributed to the formation of a rougher surface texture with more micro-, nano-scale features, or its combination as the scan rate increases. These features can trap air pockets, reducing the contact area between the water droplet and the copper surface, leading to a higher contact angle. Laser powers exceeding 30 W failed to induce hydrophobic properties on the surface. This indicates that the surface retained a high surface energy and exhibited hydrophilic characteristics. Contact angle data measured on both untextured and laser textured copper surfaces are shown in Table 3.

Allahyari et al. [27] studied the effect of laser surface texturing on copper targets using femtosecond laser pulses, observing an increase in surface hydrophobicity with increasing laser energy. Kietzing et al. [13] observed hydrophobic wetting behavior on copper surfaces irradiated with a femtosecond laser beam after a few days of air exposure. Ta et al. [28] found that copper surfaces textured with nanosecond laser pulses initially exhibit hydrophilicity, but gradually become superhydrophobic over time. This change is attributed to surface deoxidation, transitioning from CuO to Cu_2O. Ma et al. [29] also successfully created a hydrophobic copper surface by using a nanosecond pulsed laser followed by a simple heat treatment. Previous studies [20, 30-32] have demonstrated that metal surfaces become initially hydrophilic following laser micro-structuring. The formation of metal oxides, combined with high surface energy, is responsible for the observed phenomenon [15, 33]. Yang et al. [22] reported that initial superhydrophilicity of the laser-treated surfaces can be attributed to their highly nonequilibrium state, abundant surface defects, and high surface energy. However, exposure to ambient air can induce a transition to hydrophobic properties. Overall, understanding how laser processing parameters affect the surface morphology and feature sizes is crucial for optimizing LST process in order to achieve desired surface properties.

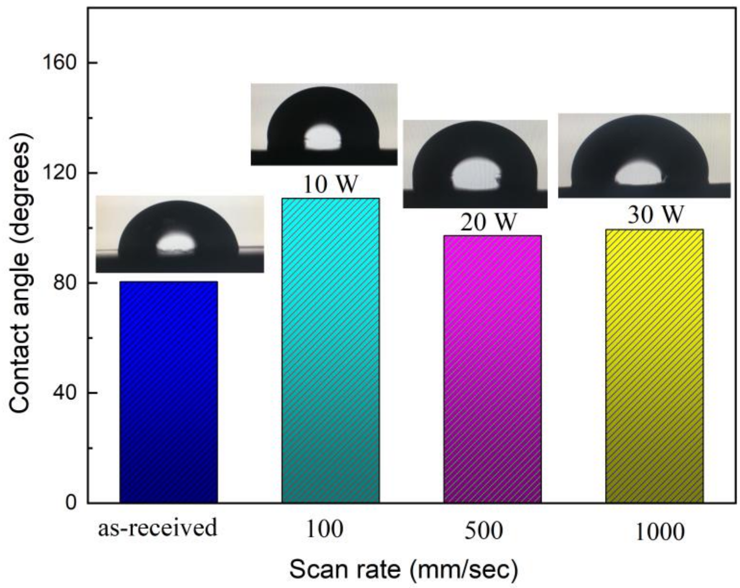

Figure 3: Relationship between contact angle and scanning speed at different laser power.

Table 2 Laser processing parameters of laser marking machine

Laser parameters	Value
Power (W)	10,20, …... 75
Pulse frequency (KHz)	10,20, …….100
Pulse duration (μsec)	9
Scanning speed (mm/sec)	100, 200, ……2000
Scan line separation ((μm)	10

Table 3 Contact angle data measured on both as-received and laser textured copper surfaces.

	Contact angle (°) ± 0.02	**Surface energy (mJ/m²) ±0.01**	**Work of adhesion (mJ/m²) ±0.01**
Untextured (as-received)	82.40	33.98	82.43
Textured 100 mm/sec	110.73	16.67	47.03
500 mm/sec	97.13	24.00	65.06
1000 mm/sec	99.40	23.41	60.91

Conclusion

The hydrophobic surface was fabricated on copper using a microsecond Nd: YAG laser marking machine without the need for additional heat treatment. Microsecond lasers offer precise control over material removal, making them ideal for creating intricate surface textures. Adjusting the scan rate and laser power during laser texturing significantly increases the contact angle, making the surface more hydrophobic. The maximum contact angle is indeed achieved at 100 mm/sec and 10 W. This work introduces a direct-write, cost-effective, and environmentally friendly laser texturing method for modifying the wettability of copper and its alloys, enabling multifunctional applications. Further investigations are needed to clarify the role of surface roughness and morphology in the wettability of copper surfaces.

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