

Full Length Article

Laser-induced copper superhydrophobicity to improve heat transfer and reduce limestone deposition in water heating systems

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ABSTRACT

The spectroscopic and electrochemical properties of copper (Cu) superhydrophobic surfaces produced from laser scribing operating in the nanosecond pulsing regime are reported herein. μ -Raman spectroscopy highlighted the synthesis of copper oxide films with the simultaneous sharp increase of the substrates' specific surface area through one single laser processing step. Higher laser power densities resulted in cupric oxide (CuO) with higher crystallinity and more homogeneous surface chemistry, whereas cuprous oxide (Cu₂O) dominates surfaces processed at lower laser power densities. Steady-state contact angles using water of $162^\circ \pm 9^\circ$ were measured for the lowest laser power employed, representing a grounded and meaningful development for substrates of this kind using laser technology. The results show that the combination of surface roughness and the presence of Cu₂O and hydrocarbon chains at the surface contributed to the superhydrophobicity of the copper foils. Additionally, variations in the thermal conductivity of the samples' surface are influenced by changes in the chemical composition. The surfaces were exposed to limestone-rich water and the amount of deposited solute was quantified using atomic absorption spectrometry. A fivefold reduction in calcium carbonate (CaCO₃) was observed, unequivocally demonstrating the impact of laser treatments in reducing CaCO₃ nucleation rates in Cu for water heating applications.

1. Introduction

The full control of the wetting properties of surfaces and coatings has opened new prospects in a wide range of applications, including microfluidics, self-cleaning surfaces, anti-icing coatings, electrochemistry, fluid transportation (e.g. both domestic and seawater), sensing, and more [1–7]. The wettability of a surface depends on its composition and morphology [8]; therefore, superhydrophobicity can be achieved by following two main approaches. Hierarchical micro/nanostructures can be created on low surface energy substrates, thereby increasing surface roughness and achieving the desired superhydrophobicity. Moreover, surfaces with suitable roughness can undergo chemical transformation

to lower the material's surface energy.

Numerous techniques, occasionally combined, have been employed to create superhydrophobicity on the surface of metallic substrates. Superhydrophobicity can be achieved by increasing the surface roughness of Cu via electrodeposition of nickel films. Surface structures can vary from nickel crystals and nickel myristate packed in cauliflower/thorn-like clusters [9] to micro/nano protuberances of pinecone shape [10]. Superhydrophobic films can also be obtained on aluminum alloys through the combination of electrodeposition and chemical etching. These samples exhibited good anti-adhesion, self-cleaning, and corrosion resistance properties [11]. Chemical vapor deposition (CVD) has emerged as a method of interest in this context, with studies

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demonstrating superhydrophobicity in Cu-coated substrates, achieving contact angles above 160° [12,13]. In these studies, polymeric coatings are commonly used to reach lower surface energy. Solution immersion-based processes have led to the formation of various surface structures on Cu, including nanorod arrays and micro-flowers [14], as well as nanogrooved conical Cu hydroxide nanoneedles [5]. Hybrid methods combining laser ablation and chemical treatment have also shown promise, achieving rapid wettability transitions and enhanced corrosion resistance in acidic and alkaline environments [15]. Superhydrophobic and self-cleaning CuO nanoneedle-covered Cu foils have been produced using a controllable anodization process, assisted by fluorosilanization reactions. This resulted in outstanding protection against corrosion, along with a contact angle of 169° [16]. Other chemical routes, such as hydrothermal synthesis followed by modification with stearic acid, were used to produce CuO films on Cu substrates. However, film deterioration was observed after prolonged contact with a saline solution due to changes in the chemical composition on the surface of the film [17].

Indeed, chemical routes often involve complex and multi-step procedures, along with the use of generous amounts of hazardous chemicals. Physical processes offer an interesting alternative to chemical methods, with lasers emerging as an affordable solution for reducing wettability. Chemical and corrosion stability are crucial for superhydrophobic surfaces. Laser-induced fluorinated coatings have demonstrated excellent resistance to alkaline environments, retaining superhydrophobicity and corrosion resistance at pH 13, showcasing their industrial potential [18]. Cai et al. (2018) established a correlation between geometrical models of contact angles and experimentally measured ones on 316L stainless steel surfaces. For this, they utilized a nanosecond pulsed fiber laser emitting at a wavelength of 1064 nm [19]. Nanosecond UV laser processing of aluminum alloys results in outstanding hydrophobic characteristics when exposed to water droplets [20]. Nanosecond pulsing lasers have been reported in the literature as capable of inducing superhydrophobicity in Cu substrates [21]. The transition to superhydrophobicity involves laser-induced surface structures and chemical modifications, and hydrocarbon chemisorption, validated by thermal annealing. This approach enables rapid, durable surface treatments for industrial use. Contact angles of up to 152° were achieved with a laser fluency of 75 J/cm^2 (1064 nm wavelength), particularly in the context of chemical sensing applications [22]. In the work of Emelyanenko et al. (2018), the processing of Cu substrates was followed by vapor deposition of fluorooxysilane molecules, resulting in the attainment of superhydrophobic (contact angle above 170°) and corrosion-resistant samples. Cupric and cuprous oxides were found on the surface, and the chemical composition and corrosion resistance varied depending on the laser processing parameters [23]. A Nd:YAG third-harmonic 355 nm UV laser, operated in the nanosecond regime, has been utilized on Cu substrates to induce contact angles above the superhydrophobicity limit. Following low-temperature annealing processes and several hours of air exposure, contact angles of 159° were achieved in the best-case scenario [24]. In the same work, spectroscopy measurements were used to quickly assess the presence of CuO and Cu₂O species after laser irradiation. The low-temperature annealing process, first introduced by Chang et al. [25], was found to be accelerated when assisted by ethanol, as demonstrated by He et al. [26] after processing Cu substrates with a 1060 nm pulsed laser. This process generated a surface grid of micro-grooves, imparting superhydrophobicity and ultrahigh adhesion to the material. Cu polycrystalline substrates were processed with pulsed lasers operating in the femtosecond regime with a wavelength of 800 nm, to produce sensitive surface-enhanced Raman scattering platforms [27]. After laser ablation, the surfaces became hydrophobic after a week of exposure to open air, with contact angles reaching 139° .

The inherent properties of Cu, such as its high thermal conductivity and mechanical robustness, make it indispensable for a broad range of industrial applications. Despite its widespread use, many existing Cu surface treatment methodologies involve additional, often chemically

based, steps, prompting ongoing endeavors to streamline processes and achieve desired outcomes through an efficient approach free from supplementary coatings.

This study delves into innovative approaches for enhancing system performance through a detailed characterization of laser-modified Cu surfaces. The spectroscopic and morphological aspects that support laser-induced superhydrophobicity in commercially available Cu foils, particularly relevant to components utilized in industrial-scale water heating systems, are investigated. These systems are susceptible to scaling due to the presence of hard water, rich in CaCO₃, resulting in the accumulation of substantial deposits that obstruct pipes and escalate maintenance expenses [28–31].

The most common scale compound found in crystallization fouling is CaCO₃, and its deposition is usually the result of an increase in pH (leading to the loss of dissolved CO₂), an increase in temperature, or an increase in salt concentration. Three polymorphic modifications of calcium carbonate commonly found in these deposits are calcite, aragonite, and vaterite. Andritsos and Karabelas investigated the effect of different calcium carbonate polymorphs suspended in water on the scale formation of CaCO₃ [32]. The results showed that the presence of low-concentration fine particles had a synergistic role in increasing the mass deposited and contributed to the onset of scaling at relatively lower supersaturation levels. This was explained by the authors as being due to an increased mass transfer rate resulting from microroughness caused by deposition and cementation with calcium carbonate of the aragonite clusters.

Different strategies have been employed to address the formation of CaCO₃ [33]. Among these, the most effective methods reported involve chemical treatment of water, including softening by ion exchange, pH control through acid dosing, and the use of chemical inhibitors. From an equipment producer standpoint, achieving water control may not be practical due to logistical, economic, and environmental/health reasons. One possibility is to modify the exposed surface of equipment to prevent scaling formation.

Surface roughness appears to influence scale formation [34], potentially due to increased adhesion resulting from a larger contact area. In boiling systems, roughness peaks may also serve as favorable nucleation sites. Other studies [30,35] have revealed that surfaces with low surface energy exhibit reduced adhesion strength with calcium carbonate crystals. As such, this work presents a practical application of laser-modified Cu surfaces in the manufacture of water heating systems.

2. Experimental details

2.1. Materials

Highly pure (> 99.9 %) commercial rolled Cu foils were sliced into smaller pieces ($40 \times 100 \text{ mm}^2$) (procedure A) and cleaned before laser irradiation. Samples underwent a base cleaning (procedure B) that aimed at removing biological traces from sample handling and involved the following steps in sequence: 1) rinsing in boiling water for 5 min; 2) dipping in a mixture of ethanol for 5 min, ammonium hydroxide (25 %) for 5 min, and distilled water; and 3) drying with compressed air.

For complementary surface modification methods, namely glow discharge optical emission spectroscopy (GDOES), a different chemical cleaning/etching process (procedure C) was used after process B to remove a few microns from the surface of the Cu foils, consisting of two steps: 1) rinsing in a solution of sulfuric acid (95–98 %) of 160 g/l for 4 min; and 2) rinsing in a mixture of acetic acid (99 %), phosphoric acid (85 %), distilled water and hydrogen peroxide (27 %) in parts ratio of 5.2:10:3:2 for 10 s [36]. Alternatively, an electrochemical etching (procedure EC) was performed after procedure B using a two-cell electrode apparatus, with both working and counter electrodes being Cu foils. The procedure involved the application of a potential scan within a voltage window of 0 to 3 V at a sweep rate of 0.1 V/s over 10 cycles in 14 M phosphoric acid [37].

2.2. Laser treatment

A Neodymium-doped yttrium aluminum garnet (Nd:YAG) pulsed laser with emission at 1064 nm (Rofin Starmark SMP 100wII) was used to modify the Cu surfaces after cleaning. The laser is equipped with a scan head coupled to an F-Theta Lens ($f = 100$ mm), enabling single-area patterning of square centimeters without the need to move the sample position (see Fig. 1). The samples were positioned under the laser beam at the focusing point, resulting in a laser spot (crater) diameter of approximately 50 μm . Scanning proceeded from left to right, with the distance between scanning lines set to the minimum allowed by the setup ($d = 100$ μm). The impact of laser power on the Cu surface was evaluated for a fixed laser repetition rate of 33 kHz and a pulse width of 100 ns. The laser average power was set to 6.3, 8.0, 9.7 and 11.4 W, denoted as L1, L2, L3 and L4, respectively, covering a laser energy density range of 9.7–17.6 J/cm². Scanned areas up to 40 $\times$ 40 mm² were irradiated for each selected laser fluence and were studied approximately 2 weeks after production to minimize post-treatment instabilities [22].

2.3. Substrate morphology

To characterize sample morphology and assess the impact of laser operating conditions on surface roughness, a high-resolution VEGA3 TESCAN scanning electron microscope (SEM) operated at 10 kV was used to acquire secondary electron images. SEM micrographs were analyzed using the software Image J (version 1.45 s) [38]. For well-resolved 3D images, a Sensofar S Neox non-contact 3D optical profiler (software version 6.2.0.0) was used under confocal imaging mode. A 50 $\times$ lens was primarily used, allowing the generation of maps with an area of 351 $\times$ 264 μm^2 and 3 nm vertical resolution.

2.4. Surface chemistry

To structurally characterize the surfaces of the processed samples, micro-Raman spectra were measured at room temperature in a Jobin Yvon HR800 (Horiba, Japan) apparatus equipped with a 441.6 nm He-Cd laser line (Kimmon IK Series, Japan). The laser light was focused on the samples using a 50 $\times$ lens (NA = 0.5) objective and a neutral density filter OD = 1 was used to attenuate potential thermally induced modification of the samples during the measurements. A 600 lines/mm grating was selected, and the Raman signal was collected using a

multichannel CCD detector. Exposure time was set to 3 s and 1 s for single spot and mapping measurements, respectively. For the mapping procedure, a scanning XY table with 1 μm spatial resolution was used. Raman spectra were baseline subtracted and fitted to Gaussian-Lorentzian type shape functions using the LabSpec software (version 5.17.17).

A Horiba Jobin Yvon GDOES instrument was used to indirectly measure the Cu, oxygen, and carbon depth profiles. Given that this technique needs a relatively flat and large area for sputtering (< 8 mm), only samples without laser treatment were analyzed. The measurements were performed for 30 s flushing time, 30 s pre-integration time, 30 s total measurement time, at a 650 Pa working pressure and a total power discharge of 30 W. The capacitor module and phase voltage were set to 7 V and 4 V, respectively.

For XPS measurements a Kratos Axis Supra spectrometer with a monochromatic Al K α source was used. The spectra were recorded with an aperture of the hemispherical analyzer measuring 110 μm in diameter, resulting in a measurement spot size of 500 μm in diameter. To study the stability and composition of the topmost layers, a monoatomic Ar⁺ ion beam of 500 eV was used to superficially wear out the laser-treated regions over a total lateral area of 2 $\times$ 2 mm². The erosion process was conducted in five individual steps, each lasting 60 s, for a total erosion time of 300 s. The flowchart in Fig. 2 represents the different steps of the XPS analysis on the laser-treated areas. M0 corresponds to the initial XPS measurement, E1 corresponds to the subsequent etching step, and M5 represents the final XPS measurement to obtain the surface composition.

2.5. Wettability tests

Contact angle measurements, typically used to assess the degree of wettability of surfaces, were conducted using a DataPhysics Instrument OCA20. The sessile drop method was employed for measuring contact angles of Cu substrates. A total of ten distilled water (DI) droplets, each approximately 3.0 μL in volume, were used to determine the wetting angle for samples produced under different laser fluences, with each measurement repeated three times.

2.6. CaCO₃ deposition and quantification

To establish the adequacy of the laser-treated copper elements for application in day-to-day water heating and pumping technologies, we

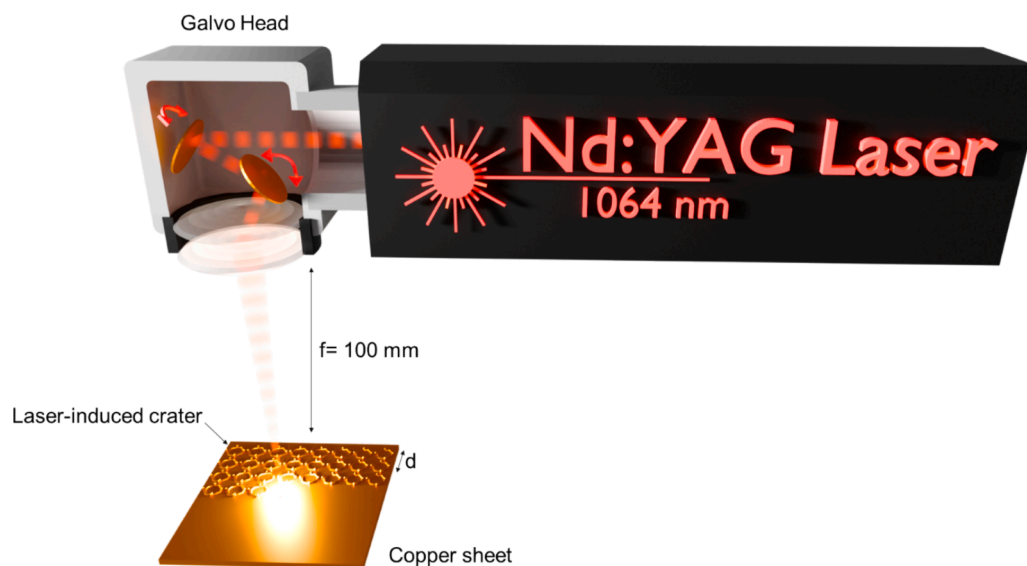


Fig. 1. Schematic of the pulsed laser and scan head coupled to an F-Theta Lens ($f = 100$ mm), enabling single area patterning of the Cu surface while maintaining sample position. “d” corresponds to the distance between scanned lines.

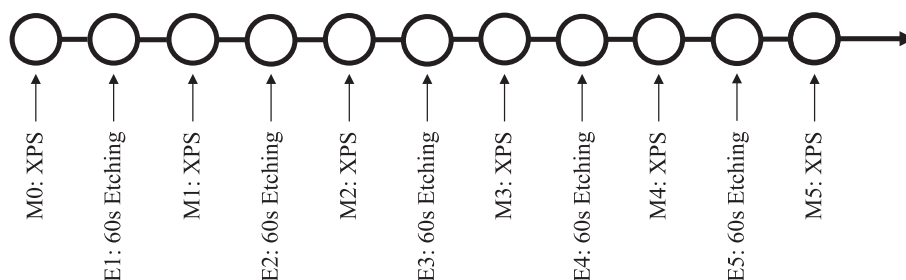


Fig. 2. Step-by-step schematic of performed XPS measurements. M and E stand for the corresponding measurement and etching step, respectively.

devised a setup to conduct CaCO_3 deposition experiments on relatively large copper sample surfaces ($\varnothing 19.5$ mm). In this setup (refer to Fig. A1 in the Supplementary Information), an acrylic reservoir with open extremities is placed in contact with the two twin Cu plates (specimens processed under similar conditions), which will then be exposed to a saturated solution of CaCO_3 . Three repetitions of the deposition tests were performed on reference Cu samples cleaned with procedure B and laser-treated samples (specifically, only L1 and L3). The test samples are electrically insulated with cork and placed in contact with two resistances ($R_1 = 43 \Omega$ and $R_2 = 44 \Omega$). When connected to a 30.5 V power supply, these resistances heat the plates, promoting the nucleation and deposition of CaCO_3 above room temperature. Temperature readings are recorded at three different locations in the cell: the two test specimens and the solution.

CaCO_3 (500p.p.m.) was obtained by the reaction of 65 ml of 0.01 M CaCl_2 with 65 ml of 0.02 M NaHCO_3 . The resulting solution was then kept at 60°C for 7 h in the cell previously described, where Cu plates were exposed to CaCO_3 . Fig. A2 displays the temperature profiles registered for the cell presented in Fig. A1. Temperature readings were taken in solution (TT) as well as in the samples (T1 and T2), showing constant temperature throughout the 7 h of deposition.

After conducting CaCO_3 deposition studies, the Cu specimens were rinsed in DI water and dried in air. To quantify the resulting Ca^{2+} , the samples were immersed in 40 mL of 0.2 M HCl overnight for CaCO_3 dissolution. Subsequently, Ca^{2+} quantification was performed using an atomic absorption flame spectrometer (GBC Scientific Equipment – Avanta) under specific operating conditions: Air-Acetylene flame; 2.00 L/min fuel flow; 10.0 L/min oxidant flow; 3.0 s read time; no time constant; 3 replicates; 5.0 mA lamp current; 422.7 nm wavelength; 0.5 nm slit width and normal slit height.

2.7. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was used to investigate the influence of different surface treatments on the corrosion of Cu samples. The measurements were carried out in a three-electrode cell, using a saturated calomel electrode (SCE) as reference electrode, a platinum wire as counter-electrode, and the Cu sample as working electrode (exposed area ca. $3.37\text{--}3.70\text{ cm}^2$). The electrochemical cell was placed inside a Faraday cage to avoid interference arising from external electromagnetic fields. The measurements were performed using a Gamry FAS2 Femtostat with a PCI4 Controller and carried out from 100 kHz down to 10 mHz frequency range with 7 steps per decade. All spectra were recorded at open circuit voltage with an applied 10 mV root mean square (RMS) sinusoidal perturbation. The measurements were repeated three times. All spectra were fitted using Gamry Echem Analyst (v 5.61), with the quality of fitting assessed by chi-square values (< 0.01).

2.8. Thermal characterization

Scanning thermal microscopy (SThM) measurements were performed with a calibrated probe from Kelvin Nanotechnology under

atmospheric conditions, using an SThM module coupled to a Park Systems XE7 Atomic Force Microscope. The thermal probe consists of a palladium-resistive element lithographically patterned on an atomic force microscopy (AFM) tip apex, which is mounted on a silicon nitride cantilever. The resistive element is part of an electrical circuit through which an electrical current (< 2.5 mA) flows to the probe, heating it by the Joule effect. The radius and height of the probe are 100 nm and 12 μm , respectively. It has a sensitivity of approximately $1 \Omega/^\circ\text{C}$, provides a 50 nm spatial resolution and endures temperatures up to 200°C . The Park Systems XE7 atomic force microscope can acquire topographic data using the thermal probe in the conventional contact mode of atomic force microscopy (AFM), as well as employing a standard AFM probe for the same purpose [39,40]. In the contact mode AFM topography scans, standard AFM probes with a radius less than 10 nm, a force constant of 0.2 N/m, and a resonance frequency of 25 kHz were utilized.

The information gathered on the thermal conductivity of the probed materials is indirectly assessed, as described hereafter. The reduced dimensions of the probe allowed localized thermal analysis inside the craters, where the material was directly impacted by the laser. On that location, two complementary approaches were taken: 1) a reference temperature was chosen (35°C) and the necessary electrical current was provided to the probe so that, while in contact with the material, the probe measured said the reference temperature of 35°C ; 2) an electrical current of reference was chosen (0.910 mA) and the temperature of the probe, while in contact with the material, was measured. The higher the current/power required by the probe to sustain the reference temperature, the higher the local thermal conductivity of the probed material. Furthermore, the higher the local thermal conductivity of the material, the lower the temperature it will reach for the same current/power value. This procedure was performed at various locations within the same crater and for different craters within each sample. Specifically, twelve spots were probed for each sample, both within the crater and on its periphery. This procedure involved conducting measurements at various locations within the same crater and for different craters within each sample. The twelve spots were probed for each sample, both within the crater and on its periphery. The average of the twelve values was computed, with the standard deviation serving as the measurement uncertainty for each sample.

Surface roughness was assessed through atomic force microscopy (AFM) scans conducted on both the craters and the sample before laser treatment. The chosen AFM scan areas were $400 \times 400\text{ nm}^2$, selected to be pertinent to the probe-sample contact. Thirty areas were probed for each sample. RMS values derived from $400 \times 400\text{ nm}^2$ atomic force microscopy (AFM) scans are referred to as 'local roughness' or 'local RMS' to distinguish them from the optical profiler's RMS values, which covered larger areas ($351 \times 264\text{ }\mu\text{m}^2$). The local RMS for each sample was determined by averaging results from 30 areas, with the standard deviation serving as the measurement uncertainty. The XEI software developed by PARK Systems was utilized to calculate the RMS value for each $400 \times 400\text{ nm}^2$ area.

3. Results and discussion

3.1. Laser interaction and surface topography

The surface topography of unirradiated commercial copper foils after cleaning (procedure B), obtained with a high-resolution 3D optical profiler, is depicted in Fig. 3a. The surface of the sample before the laser treatment is homogeneous with low surface roughness, as shown in the inset profile in Fig. 3a, with an RMS height of ca. 0.3 μm . Fig. 3b illustrates the average RMS as a function of laser power for samples L1 (6.3 W), L2 (8.0 W), L3 (9.7 W) and L4 (11.4 W). A significant increase in surface roughness is observed as soon as the laser starts to interact with the sample due to reaching the melting threshold caused by the locally applied power densities on the sample's surface. It is important to note that only a small fraction of the laser energy is absorbed by the material at a wavelength of 1064 nm, as copper has been reported to have an absorptivity below 5 % at this wavelength [41]. Additionally, it is worth noting that the lowest laser power used in this study corresponds to the lower limit of the laser beam's interaction with the copper surface.

Fig. 4 presents detailed surface topography for various samples subjected to different laser treatments. The left side of the figure shows the surface top view of the processed samples, while the right side showcases the corresponding 3D images and the representative line scan profiles. It can be concluded that the heat absorbed by the Cu foils resulted in the formation of molten pools, followed by the spreading of molten Cu droplets throughout the surrounding areas, subsequently quenching under an oxidative atmosphere. This is observed for lower powers as shown in Fig. 4a and b, as well as the RMS values presented in Fig. 3b for L1 and L2. For instance, when the power is as low as 6.3 W, the laser craters exhibit an oval shape with the largest diameter of approximately 63 μm , and they are well visible and marked. At the lowest power, the resulting topography of the surface areas that directly interacted with the laser spot is almost unaffected, while the areas between two consecutive laser-processed lines are easily identified in this sample, showing smaller amounts of re-solidified droplets.

At 9.7 W (L3) and 11.4 W (L4) (Fig. 4c and d, respectively), a more stochastic distribution of topographical features is evident throughout the samples. This is due to the deeper penetration of the laser beam into the substrate, resulting in a larger amount of molten copper being removed from the laser-irradiated spots and subsequently spread into the periphery. Consequently, significant variations in surface morphology are observed under these laser conditions. Moreover, higher energy allows sputtered material to be redeposited at longer distances, resulting in the material from the spot being redeposited in areas that were previously irradiated, leading to most of these regions being covered with material that has re-solidified at potentially higher cooling rates. On the other hand, samples irradiated with lower energy

show limited redeposition of material in previously irradiated spots and in the periphery. For the L1 sample, it is expected that areas between two consecutive laser-processed lines have different characteristics (e.g., microstructure) compared to the irradiated areas. This can be confirmed by the representative roughness line-scan plots presented in Fig. 4. For instance, at higher laser power (L4) craters were dug twice as deep, and material features in the periphery of each spot were built up to twice the height of those in the L2 sample. Additionally, fewer material deposits are found in the interior of the craters and in the periphery between two consecutive lines for L1, as seen at about 50 μm in the corresponding plotted line scan. Fig. B1 shows 3D profiling measurements at specific areas of the samples to illustrate the topology of the surfaces at representative craters and peripheral areas for L1 and L4 samples. It shows that the surfaces are composed of micro/nanostructures, with sizes from hundreds of nanometers to a few micrometers (likely below 4 μm in height) as observed at the peripheral areas of the craters.

SEM micrographs of these copper surfaces after laser treatment for different laser powers are shown in Fig. B2 as complementary imaging results with higher contrast.

3.2. Copper oxide formation

Raman scattering was used for the identification and semi-quantification of copper oxide phases. The topographical results shown in Fig. 4 suggest that the areas between craters are also of interest for the analysis, as they accommodate most of the molten copper released from the areas directly hit by the beam. Since Raman spectroscopy is a local surface analysis technique in which the dimensions of the examined spot are determined by the area of the laser excitation source (here $\sim 1 \mu\text{m}$), the properties of both regions (i.e., inside and outside laser craters) are surveyed, allowing for the assessment of their role on the electrochemical properties, wettability and limestone deposition rate. Raman spectra were fitted and peaks were assigned based on spectra commonly found for copper oxides produced from heat-treated copper substrates in the oxidative atmosphere [42–45] and other methods [46,47].

The red dots in Fig. 5a correspond to the spectrum data obtained at the center of a crater induced with an average laser beam power of 11.4 W. Spectra obtained for samples processed under such conditions show all copper oxide peaks detected for the whole set of samples produced in the present work. Furthermore, the Raman spectrum shown in this figure shows seven peaks related to cuprous oxide (Cu_2O) phase optical vibration modes, which are here centered at 150, 189, 215, 420, 496, 639 and 797 cm^{-1} . Cu_2O is formed at lower temperatures than cupric oxide (CuO), usually below 300 $^\circ\text{C}$ [42,45,48], while it crystallizes in a cubic lattice [49]. According to its representations, 9 of the optical modes are considered Raman active while 21 are IR active [49,50].

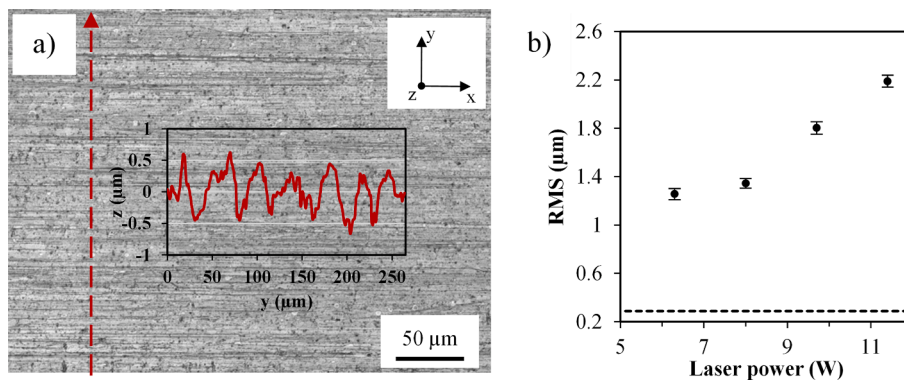


Fig. 3. a) surface image of reference sample, i.e., after procedure B and before laser treatment, obtained from 3D optical profilometry. The inset profile corresponds to the sample topography along the red dashed arrow. b) Average and corresponding standard deviation for the RMS height obtained for three different areas of each laser-treated sample. The dashed line is the average RMS of unirradiated samples.

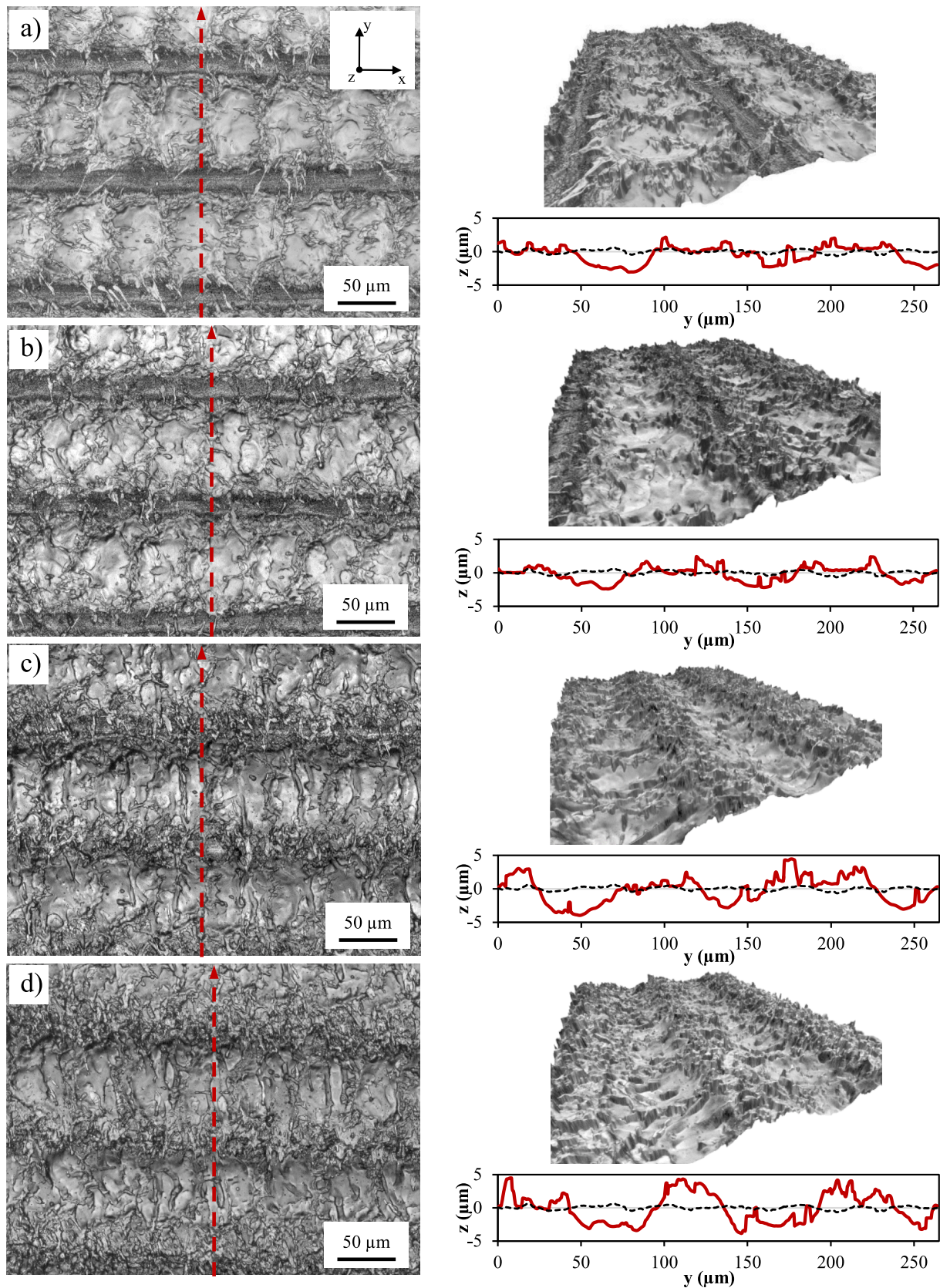


Fig. 4. Surface image of samples processed at laser powers (a) L1, (b) L2, (c) L3 and (d) L4 obtained from 3D optical profilometry. The corresponding 3D reconstructions are shown on the right-hand side of each 2D picture, together with the representative topographical line scan (full red line in the plots) taken along the y-axis of each image (delineated by the red dashed line). The black dashed lines included in each plot correspond to the line scan shown in Fig. 3 for the sake of comparison (reference).

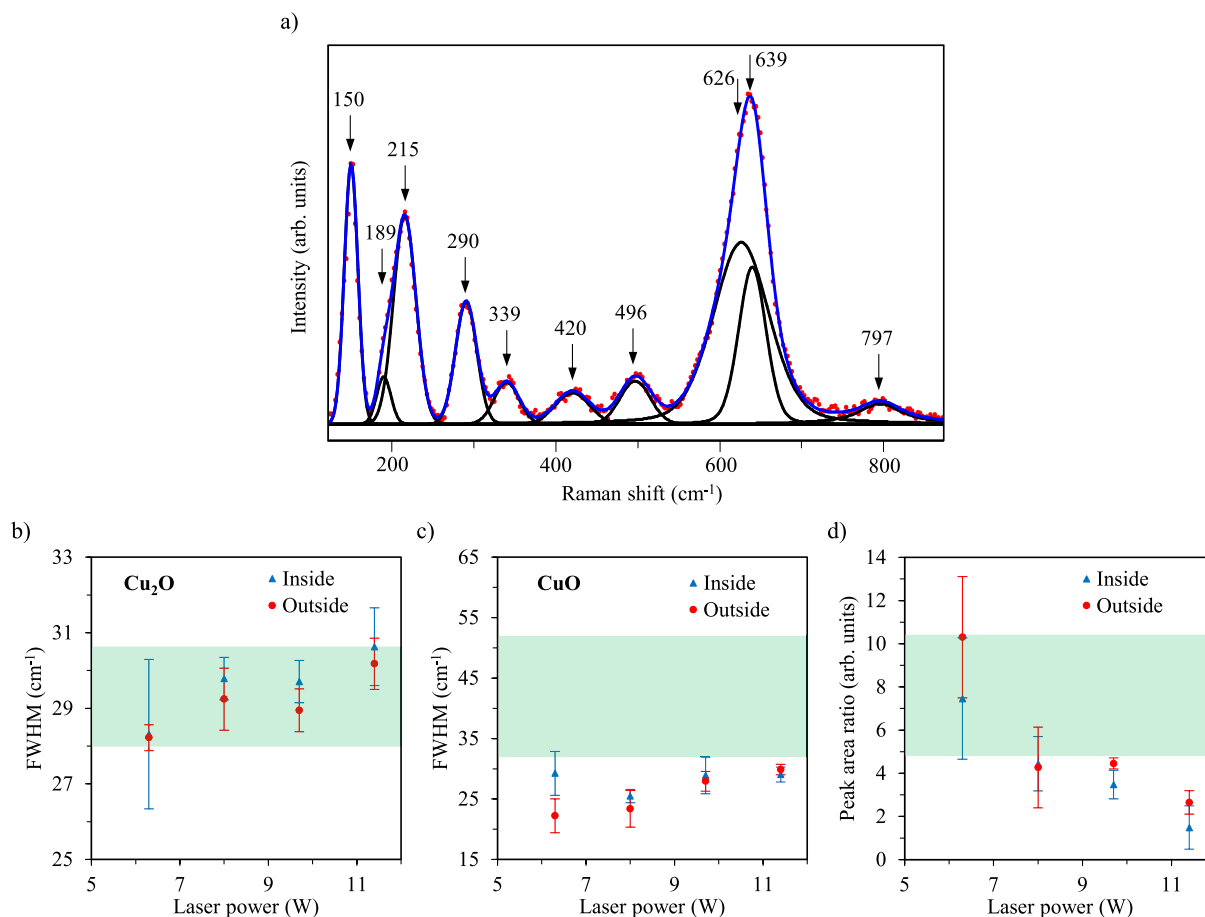


Fig. 5. (a) Representative Raman spectrum (red dots) assigned peaks (black-like) and spectrum resulting from the peaks deconvolution (blue line) obtained at the center of a crater in a L4 sample. The positions of the ten peaks are included in the figure. FWHM as a function of laser power for (b) Cu_2O 2E_u and (c) CuO A_{1g} Raman-active modes measured inside and outside several craters (vertical bars correspond to standard deviations). (d) Peak area ratio between Cu_2O 2E_u and CuO A_{1g} modes is shown as a function of the laser power (c). The green areas are the ranges obtained for the reference sample (B).

Based on that, the peaks identified at 150 cm^{-1} and 639 cm^{-1} correspond to two IR active phonon modes [51]. The intense peak at 215 cm^{-1} is assigned to a second-order Raman-allowed 2E_u mode, while the peak at 420 cm^{-1} results from multi-phonon Raman scattering processes [50]. T_{2g} active mode, here peaking at 496 cm^{-1} , is a Raman-allowed mode [52]. For instance, Niveditha et al (2016) have reported similar Raman active modes but using electrodeposition to obtain Cu_2O films [47]. The additional peak at 189 cm^{-1} may be related to resonant modes of Cu on oxygen sites as reported by Reydellet et al. (1972) [53]. Peaks at 290 , 339 and 626 cm^{-1} are assigned to CuO phase, and correspond to A_{1g} , B_{1g} and B_{2g} modes, respectively, which are three optical Raman-active modes assigned to this species [45,52]. CuO is considered the other stable phase in the Cu–O system, and is formed with a monoclinic symmetry at higher temperatures when compared to Cu_2O [48]. For instance, the position of the three CuO -related peaks obtained in the present work are similar to the ones found in a 2-step process flow involving sputtered copper thin films and subsequent heat treatment ($200\text{--}400\text{ }^\circ\text{C}$ for 1 h) in air [42].

The intensity of the most intense Cu_2O -related peaks in the reference sample decreases when the laser treatment is applied as shown in Fig. B3 (see Supplementary Information). The spectrum of sample L1 in Fig. B3b shows relatively sharper Cu_2O -related peaks than that of its counterpart in Fig. B3a, namely the one peaking at 797 cm^{-1} . This is an indication that such laser conditions promote the formation of such phase in between two consecutive laser-treated lines. Moreover, the peaks related to CuO start to increase in intensity with laser fluence. Although the two phases co-exist in samples processed at higher laser

fluences (i.e. L3 and L4), spectra are still dominated by Cu_2O -related peaks. The peak position of the A_{1g} mode shifts towards lower wavenumbers as the laser power increases and may change according to the growth technique and resulting CuO microstructure [46,49,52,54,55].

2E_u vibration mode has been used to ensure the Cu_2O films quality [43,44], as it is one of the most intense Raman peaks. After peak fitting, its average full width at the half maximum (FWHM), and corresponding standard deviation, were calculated and shown as a function of laser processing power in Fig. 5b. To account for the heterogeneity of phase distribution and crystalline quality, several spectra were collected within the same laser-induced crater (named as “Inside”) and in the periphery between two laser-processed lines (named as “Outside”). The transparent green areas included in the figures are delimitations associated to the reference sample. The FWHM values of Cu_2O appear to increase in both sample regions with laser power, suggesting the possible formation of more defective Cu_2O as the power increases. Additionally, it appears that the Cu_2O crystalline quality is higher in the samples processed at lower laser powers compared to the reference sample. The relatively intense and large FWHM associated with the 2E_u mode of Cu_2O upon laser processing may be attributed to the predicted nanocrystalline morphology of the films formed on the surfaces. While Cu_2O films of higher structural quality can result in sharper Raman peaks, achieving this often requires longer annealing periods (tens of hours) at temperatures above $1000\text{ }^\circ\text{C}$ [56].

Fig. 5c shows the FWHM of peak associated to A_{1g} Raman-active mode, which can be seen as representative of the CuO distribution. No apparent relationship is found between the peak width and the laser

power for the craters. However, an increase in FWHM with laser power is observed outside laser lines. This is predicted to result from the contribution of ablated and damaged metallic copper, leading to a defective oxide. Interestingly, the average FWHM values are similar for both regions under investigation and for the sample processed at highest power used. However, the quality of the oxide is consistently higher than that of the reference sample. The crystalline quality of CuO appears to be lower for this laser-assisted method compared to relatively long heat treatments in an oxidative atmosphere for several hours [42,57]. Furthermore, the FWHM of CuO peak is significantly lower than that of Cu₂O, suggesting that processing samples for longer periods (e.g., increasing pulse dwell time) could promote the formation of CuO with higher crystalline quality.

The peak areas for both the Cu₂O 2E_u and CuO A_{1g} modes were calculated after fitting each individual spectrum, and their average ratio values (i.e. Cu₂O/CuO) are plotted as a function of laser power in Fig. 5d. In this figure, the green area represents values for the reference sample. The results demonstrate that altering the laser power can indeed change the composition of the copper surface. In the sample processed at 6.3 W, there appears to be a divergence in composition between the inside and outside laser craters, with the latter region being richer in Cu₂O. Moreover, the composition of the L4 sample differs significantly from that processed at the lowest power, primarily due to the increased intensity of the CuO peak. The short irradiation periods and high heat diffusion in Cu result in short times of residency to temperatures that promote the formation of CuO. As the temperature of the craters sharply decreases after the laser beam moves to the next spot, the Cu₂O phase will eventually begin to grow, as its formation kinetics are faster than those of CuO [47].

Raman mapping results, showing relative peak intensities of the Cu₂O 2E_u (top row, in red) and CuO A_{1g} (bottom row, in green) Raman

vibrational modes, are presented in Fig. 6, where darker areas correspond to lower signal intensities. The maps were collected to encompass a single laser crater and a significant area surrounding it. The first column in the figure corresponds to an unprocessed reference sample, while the second and third columns correspond to L1 and L3 samples, respectively. The dashed lines represent the beam spot, which has an elliptical shape due to the original maps not being symmetrical (205 × 55 μm² scan areas). Upon comparing the two maps assigned to the reference sample, an apparent correlation is observed between the two copper oxides distribution, where no clear patterns are identified. In L1, two clear and intense vertical red lines surrounding the laser crater, indicating a high-level copper oxidation into Cu₂O of the space between lines. This observation is supported by the results presented in Fig. 5d, where a difference in composition was also detected between the two sample regions. Conversely, CuO exhibits a clear distribution pattern in L3, with higher intensity observed in the region surrounding the laser beam spot.

3.3. Surface chemistry

XPS enables the gathering of information about elements and oxidation states within 5–10 nm from the surface. When combined with the *in-situ* removal of material using a rasterized Ar⁺ ion beam, it becomes possible to access deeper-lying regions. However, as a destructive method, changes to the material, mainly reduction, can also occur during the process. Fig. 7a-e show the Cu 2p_{3/2} core level of all samples before and after successive etching steps (from bottom to top) according to the steps outlined in Fig. 2. The strong satellite emission at 940–945 eV prior to etching indicates the predominance of the Cu²⁺ oxidation state [58], corroborating the Raman analysis where CuO is detected in all processed samples with higher signal intensities measured for L3 and

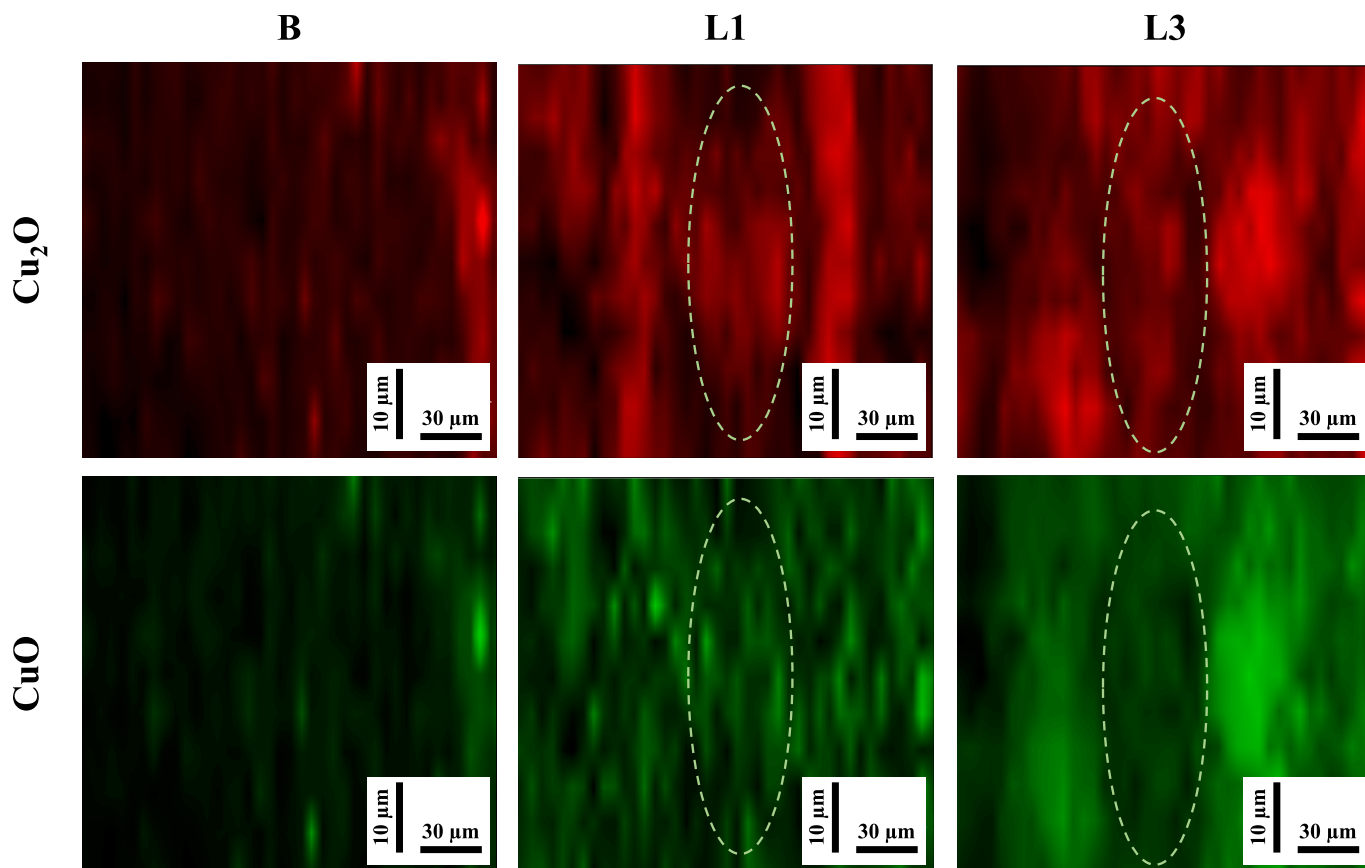


Fig. 6. Cu₂O (red) and CuO (green) relative peak intensity distribution for the reference (first column), L1 (second column) and L3 (third column) samples. Dashed lines are used to represent the corresponding laser spot position and size, while the area of analysis is 205 × 55 μm².

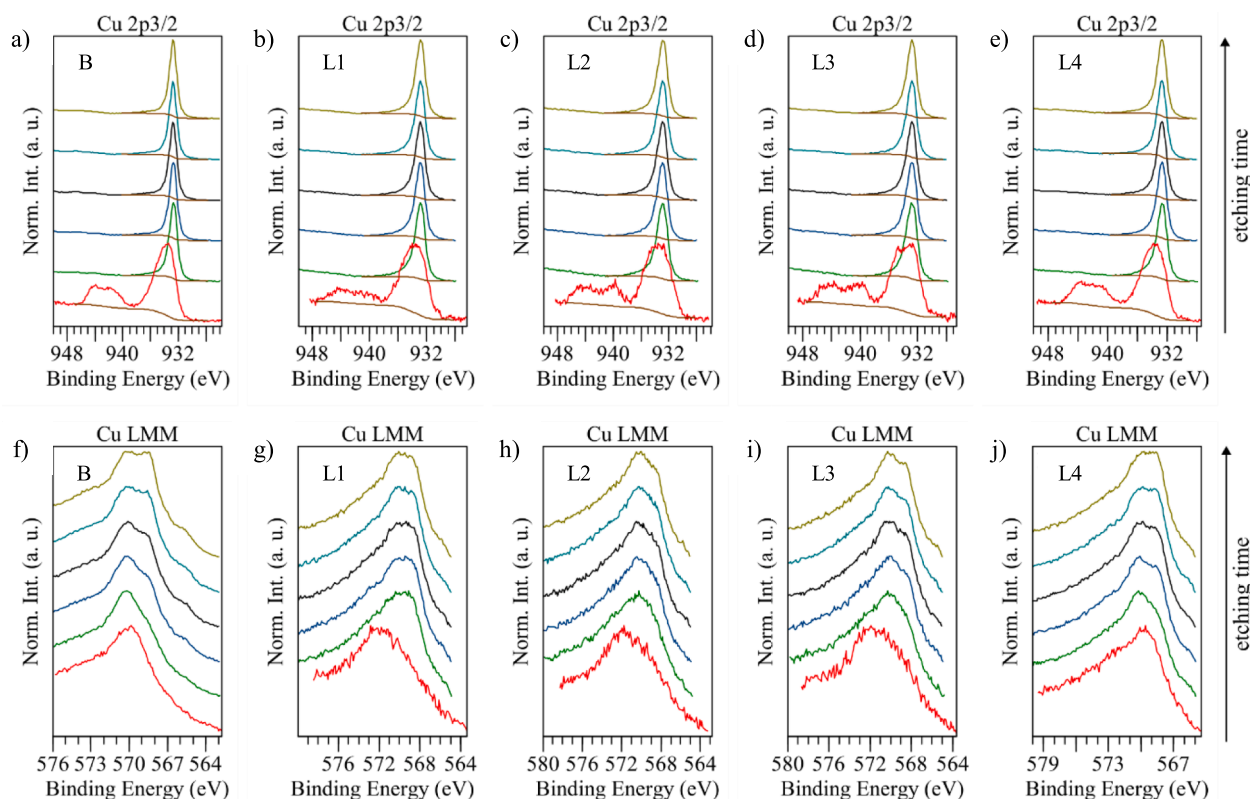


Fig. 7. (a-e) Cu 2p_{3/2} and (f-j) Cu LMM emissions of all samples prior to etching and with increasing Ar⁺ ion beam bombardment (from bottom to top).

L4 samples. It is well-documented that Cu₂O can gradually oxidize into CuO under ambient conditions, particularly in the presence of elevated temperatures or prolonged air exposure. Gong et al. (1995) [42] demonstrated that Cu₂O forms at temperatures below 300 °C but converts to CuO at higher temperatures or under oxidative conditions due to the greater thermodynamic stability of CuO. This transformation can influence surface properties, potentially reducing hydrophobicity due to the higher surface energy of CuO. While the laser-treated samples in this study were characterized within two weeks of processing to minimize such effects, further studies focusing on the long-term stability of Cu₂O under practical conditions are essential to optimize these surfaces for real-world applications. Additionally, Tran et al. (2014) [55] highlighted that the environmental stability of copper oxides is closely linked to their morphology and surface structure, which further modulates their chemical and physical behavior in practical applications. Following etching, the Cu 2p_{3/2} level shows no satellite emission, indicating the absence of Cu²⁺. This suggests that CuO predominantly exists at the surface of the samples under investigation. Since the Cu 2p_{3/2} core level does not allow to distinguish between Cu⁺ and metallic Cu, the Cu LMM Auger emission was recorded and is shown in Fig. 7f-j. After the

first etching step, the peak at 570.3 eV originates from Cu⁺, whereas the peak at 568.6 eV is associated with metallic Cu [58]. Hence, besides the disappearance of Cu²⁺, a gradual transition from Cu⁺ to Cu⁰ occurs with successive etching steps. The Supplementary Information includes the O 1 s and C 1 s emissions of all samples before and after undergoing the sequential etching steps.

The equivalent homogeneous atomic concentrations of all present elements (i.e. copper, carbon, and oxygen) are depicted in Fig. 8a-e with respect to etching time. The most significant observation is the persistence of C 1 s signal even after several runs of etching in all samples. This clearly indicates the high carbon content in the initial copper sheets, which remains in large concentrations even after laser rastering. Fig. B4 (Supplementary Information) shows a predominant peak at 248.8 eV in C 1 s spectra corresponding to (C-C(H)) functional groups [59,60], which was measured for all samples under investigation. The reference sample (B) shows the least carbon content both before and after etching. When lower laser fluences (L1-L3) are employed, higher amounts of carbon are measured, both at the surface and in depth. The highest carbon content is found for L2. Conversely, the highest laser power (L4) shows a decrease in carbon content, with the results approaching those

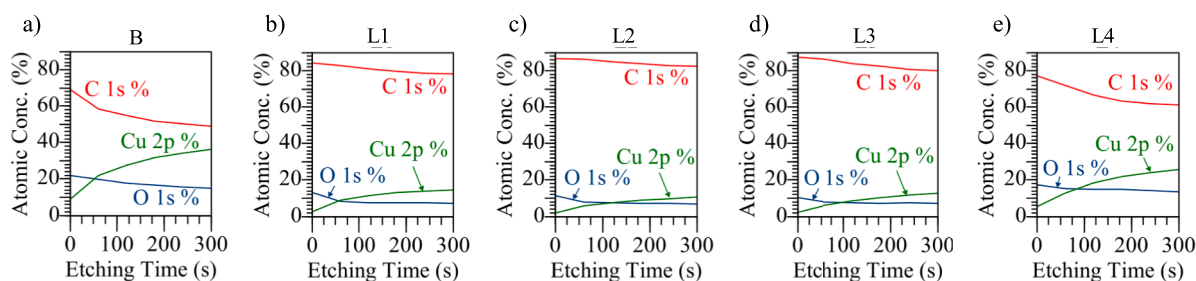


Fig. 8. Atomic concentration of carbon (C 1 s), copper (Cu 2p) and oxygen (O 1 s) as a function of etching time for different laser powers.

measured for sample B. A possible explanation is the amount of carbon that is present in depth, which is then ablated together with Cu and redeposited over the areas between the laser craters. Additionally, due to the topographic characteristics of the samples after laser processing, the major contribution to the measured XPS signals likely originates from the topmost layer of this material. GDOES was used to measure the carbon depth profile over $\sim 2 \mu\text{m}$ for a sample that was solely cleaned using base treatment B and after chemical etching (C). The results are presented in Fig. B5 in the Supplementary Information. It was observed that the carbon content is reduced to 10 % of its initial concentration after sputtering of $\sim 500 \text{ nm}$ from the surface, while the concentration diminishes to a negligible value after 40 nm if a chemical etching is employed prior to measurement. As the laser fluence increases, larger quantities of material are locally removed and vaporized into the surrounding atmosphere, thus avoiding deposition in the surrounding areas. This could explain the lower carbon content measured for L4 compared to other samples processed at lower fluences.

3.4. Water hydrophobicity

The static contact angles were measured using DI water droplets for all Cu sample surface conditions. As shown in Fig. 9a, contact angles are higher for the laser treated surfaces compared to those without laser treatment. While non-laser treated samples have an average angle of $113^\circ \pm 4^\circ$ (black dashed horizontal line in Fig. 9a), the highest angle is found for samples processed at 6.3 W (L1), corresponding to $162^\circ \pm 9^\circ$. With an increase in the laser fluence, the average contact angle decreases to $144^\circ \pm 13^\circ$ (sample L4). This indicates that the laser-treated surfaces may lead to reduced wettability, with most of them having lower contact angles than a so-called superhydrophobic surface (contact angle higher than 150° [57]). Surface roughness was analyzed in this study due to its critical role in influencing surface properties, including wettability, hydrophobicity, and CaCO_3 adhesion. Roughness enhances hydrophobicity by trapping air pockets beneath water droplets, following the Cassie-Baxter model, which reduces wettability and inhibits CaCO_3 adhesion by altering the available interaction sites. This interplay highlights the importance of roughness as a parameter for evaluating the combined effects of surface chemistry and topography on functional performance.

Therefore, laser surface treatment results in a significant increase in the contact angle upon application. Fig. 9b compares the average of all laser-treated samples (L) with other approaches used to modify the surface of commercial Cu substrates for water piping at an industrial scale, including electrochemical (EC) and chemical (C) routes. As shown, laser-treated samples outperform other methods without the use of considerable amounts of chemical reagents, while also saving

processing time.

According to Figs. 3 and 4, the surface roughness increases with laser power, with a significant change observed from sample B to L1. Hydrophobicity also experiences a notable increase from B to L1; however, it decreases as the laser power increases. The observed increase in surface roughness leading to an increase in contact angle with water has also been noted in several studies, where hierarchical micro/nano-structures appear to play an important role [22,61–63]. This can be explained by the Cassie-Baxter model, which is applied when the surface roughness leads to poor wetting of the droplets with the surface. In this case, the droplets are in contact only with the surface lumps while the air fills the pockets, mainly in the crater areas, thus preventing water penetration [6,64]. However, the observed decrease in hydrophobicity with laser power shows that the surface roughness and valley height are insufficient to explain the observed hydrophobic properties. Additionally, the roughness of both C and EP samples is, as expected, 25 % lower when compared to the reference samples. Therefore, the results demonstrate that surface chemistry also plays an important role in the surface hydrophobicity of the laser-processed samples. The hydrophobicity observed in laser-processed surfaces is influenced not only by their topographical features but also by their chemical composition, particularly the presence of Cu_2O and CuO . Cu_2O generally enhances hydrophobicity due to its lower surface energy, while CuO , with its higher surface energy, tends to exhibit hydrophilic behavior [17]. Previous studies have demonstrated that surfaces rich in Cu_2O are more effective in reducing calcium carbonate deposition due to their lower interaction with dissolved ions [16]. Additionally, the Cassie-Baxter model explains how rough surfaces, such as those produced via laser processing, can amplify hydrophobic properties by trapping air pockets beneath water droplets [64]. In our study, the untreated smooth copper baseline (process B) inherently includes a natural oxide layer, composed primarily of Cu_2O with minor CuO contributions. While this layer contributes to the baseline hydrophobicity, the combination of Cu_2O -dominated chemistry and increased roughness in laser-processed surfaces explains the significant difference in wetting angles observed, particularly under lower fluence conditions.

Fig. 5 presented earlier shows an increase in Cu_2O when subjected to laser irradiation under L1 conditions, particularly in regions adjacent to the craters, which are in closer proximity to water droplets. As laser power increases, CuO becomes predominant due to Cu_2O oxidation. While CuO is reported to possess hydrophilic properties, Cu_2O tends to contribute to surface hydrophobicity [22,25,61]. Hence, the heightened presence of CuO encircling the craters may potentially outweigh the effects of increased surface area, resulting in decreased surface hydrophobicity with increasing laser fluence. On the contrary, the size and density of the copper oxide nanocrystallites can change according to the

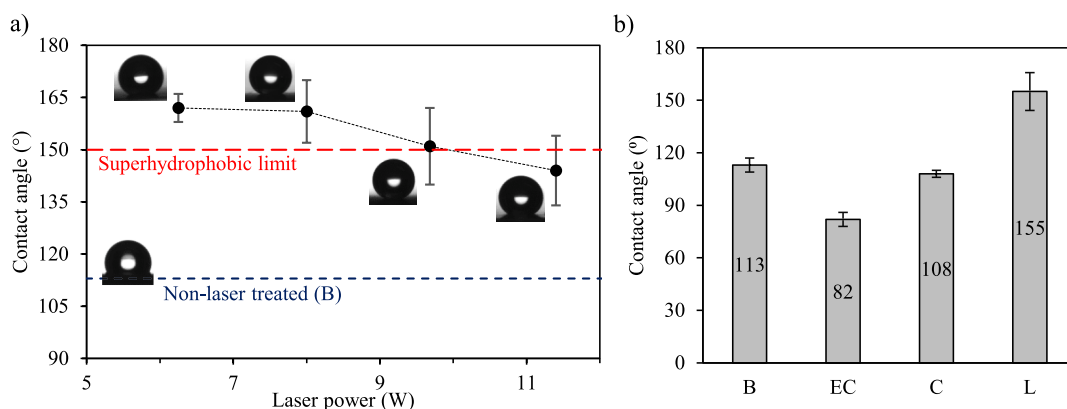


Fig. 9. (a) Water contact angles as a function of laser power, accompanied by images of corresponding representative water droplets. The horizontal dashed lines represent the average angle for non-treated sample B (dark blue) and the threshold for a superhydrophobic surface (red). (b) Contact angles comparison between reference, only cleaned with base treatment B, electrochemically (EC) and chemically (C) polished samples with the average for laser-treated ones (L).

laser fluence. Lower fluences correspond to higher densities and smaller sizes, enhancing the aptitude to adsorb organic compounds from the surrounding atmosphere [59,65].

Sample L1, treated at a relatively low fluence of 9.7 J/cm^2 , is expected to harbor a higher density of smaller crystallites, thereby exhibiting an increased tendency for adsorption of surrounding atmospheric compounds. Indeed, XPS and GDOES results have shown the presence of large amounts of carbon and related functional groups at the surface of the samples, likely originating from the rolling process of the commercial Cu foils. Apart from the rough surfaces and Cu_2O presence, functional groups of non-polar nature could contribute to enhancing surface hydrophobicity. Hydrocarbon chains and graphitic groups (C–C (H)) may contribute to this effect, given their presence in lubricants, which are commonly found in pristine Cu foils, and their formation during Cu exposure to air post-laser processing [59]. Therefore, we hypothesize that the produced substrates outperformed due to the combination of surface roughness and chemical composition.

3.5. Role of surface properties in CaCO_3 deposition

To evaluate the influence of the Cu surface modification on the CaCO_3 deposition rate, samples with and without different laser treatments underwent CaCO_3 deposition studies using the setup shown in Fig. A1. After conducting experiments for 7 h at 60°C , several magnified optical images were captured from the surface of the samples. Selected examples are presented in Fig. 10a. Following the deposition experiments, the surface of the reference samples (base process B) appeared fully covered with white products, whereas laser-treated samples exhibited only small amounts of deposits, which were heterogeneously distributed across their surfaces. Experiments performed on the electrochemically polished substrates also show a small number of deposits while the chemical polishing route results in substrates with observed large agglomerates at the surface. Gentle washing of the surface was

performed with DI water to remove poorly adhered deposits. Observations from Fig. 10a indicate that some of the deposits were easily removed. Furthermore, the larger agglomerates on both sample L1 and C were mostly eliminated after washing, consistent with the anticipated modest interaction between the treated surfaces and the CaCO_3 dissolved in the water. Therefore, laser treatment appears to be a viable technology to reduce CaCO_3 deposition in water pipes. The quantification of Ca^{+} after washing with water and air drying was performed with atomic absorption spectrometry. The results are plotted in Fig. 10b. Comparing these results with those in Fig. 9, the decrease in water contact angle leads to a decrease in the amount of deposited CaCO_3 . This suggests that the increase in contact angles, coupled with the corresponding surface topography (mainly between laser craters) and changes in surface chemistry can have a positive effect, for instance, in potentially reducing the deposition of insoluble salts and particles within Cu tube walls. Notably, the number of deposits observed is even lower than that found on substrates subjected to chemical etching (C). While the lowest CaCO_3 concentrations are observed for electrochemical polishing (EC), this method involves the use of significant quantities of phosphoric acid. Although not a strong acid, its handling, disposal, and associated environmental impact become increasingly problematic when scaled for industrial applications, adding to its operational costs. In contrast, laser processing provides a more sustainable alternative, offering both environmental and economic advantages through its reagent-free and waste-free approach.

3.6. Corrosion during NaCl immersion

The immersion of the substrates in NaCl for 1 h resulted in the alteration of the visual appearance of the substrates when compared to samples prior to immersion, particularly linked to the pattern of the copper oxide corrosion products. However, no significant differences are verified among samples B, L1 and L3 for the same period of immersion as

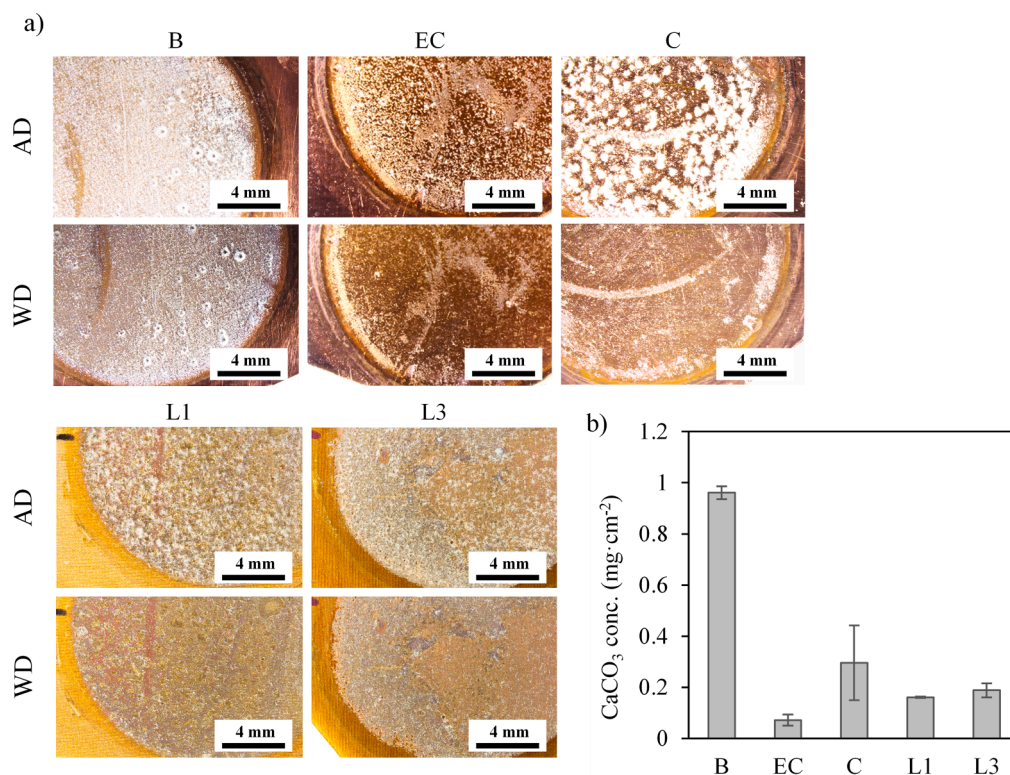


Fig. 10. (a) Representative optical images of samples after CaCO_3 deposition (AD) and subsequent water washing and drying (WD). (b) Average deposited CaCO_3 after 7 h of immersion at 60°C for reference sample (B) and laser-treated samples (L1 and L3) as well as for electrochemically (EC) and chemically polished (C) Cu samples.

shown in Fig. 11a. Moreover, after four weeks of immersion, the substrates are fully covered by corrosion products. The most significant difference is found for sample L1, which displays regions with thinner copper oxide layers as already shown in the spectroscopy results.

The EIS data obtained shows that after 1 h of immersion in NaCl solution (Fig. 11b) all the systems show very similar behaviors and the degradation of all the samples continues to occur during the remaining monitored time (4 weeks of immersion). After 1 h of immersion, a time constant is detected at intermediate frequencies (1–10 Hz) for all the systems, which may arise from ongoing electrochemical processes associated with corrosion. One additional time constant at low frequencies ($< 10^{-2}$ Hz) can also be seen (samples B and L1) and may be attributed to diffusion-controlled processes at the interface (mass transport) [66,67]. While not showing a remarkable difference compared to their counterparts, it is noteworthy that sample L3 exhibited the highest impedance modulus at low frequencies (Fig. B6). For longer immersion times (Fig. 11c), a new time constant can be detected at high frequencies ($\sim 10^5$ Hz) for all samples, which can be due to the buildup of the corrosion products layer over time [67,68]. This layer may also contribute to the minor increase in impedance associated with corrosion processes, observed at low frequencies (Fig. B6). All samples revealed similar behavior, with L1 presenting the highest impedance modulus at low frequencies.

Fig. B7 and Fig. B7B8 show the equivalent circuits for 1 h and 4 weeks, respectively. The results for the fittings of EIS spectra are summarized in Table B1, provided in the Supplementary Information. The fittings confirmed that charge transfer resistance (R_{ct}) and other parameters evolved similarly across all samples, supporting the observed trends in impedance magnitude.

Overall, these results show that the laser treatment does not considerably improve the anticorrosion properties of the substrates, unlike methods involving the application of polymeric coatings, which create hydrophobic surfaces and improve corrosion resistance [6,69]. Despite achieving superhydrophobic levels, characterized by surface grooves and altered chemistry that reduce direct contact with the surface, this treatment does not notably reduce substrate corrosion upon immersion in water. This lack of effectiveness is likely attributed to the defective and rough copper structures produced during laser-induced crater formation. These areas remain in continuous contact with water, facilitating ion penetration across the surface at micro and nano scales. Moreover, the presence of chlorides may also affect the chemical stability of the copper oxides formed, as well described in the literature [70].

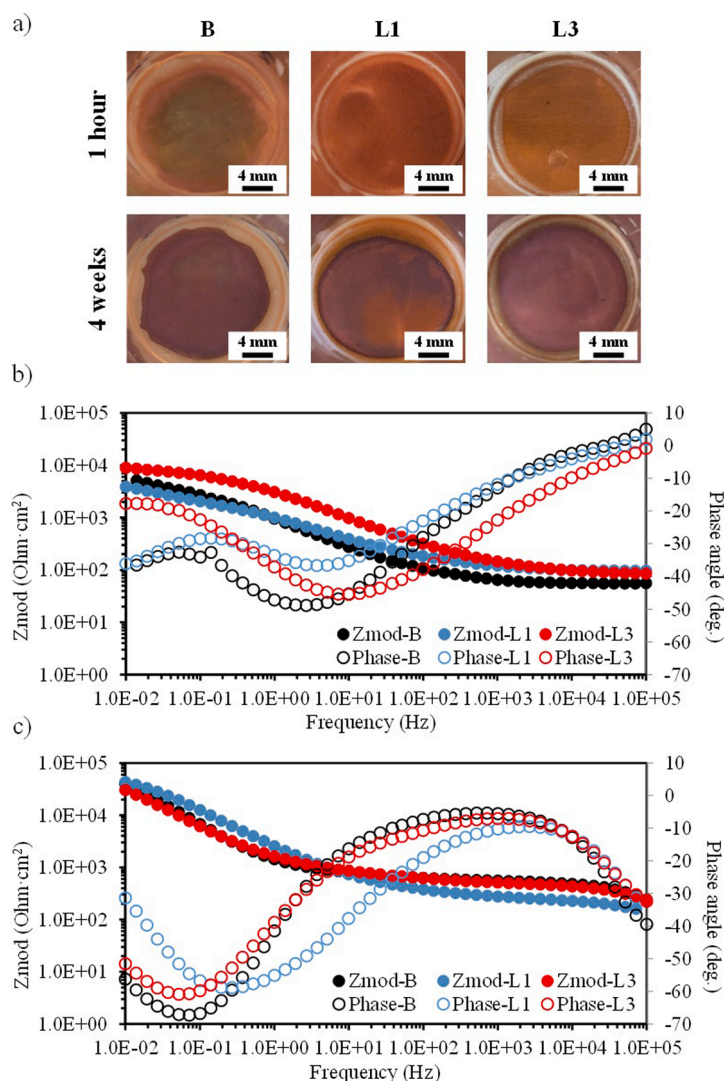


Fig. 11. A) top view optical images of samples (b, l1 and l3) after immersion in nacl for 1 h and 4 weeks (affected areas are inside the circular tubes). Bode spectra of untreated and laser treated Cu samples after b) 1 h and c) 4 weeks of immersion in NaCl.

3.7. Thermal analysis

Different areas of reference sample B and the laser-processed ones L1 to L4 were analyzed with the SThM probe, as described in section 2.8. For each laser processing condition, the sample was probed in different locations and average values for the electrical current fed to the probe (probe current) and temperature measured by the probe (probe temperature) were determined. The dependence of the average values for the probe current and probe temperature on laser processing power, both inside and on the periphery of the craters, and the corresponding standard deviation from the average are shown in Fig. 12a and b. It can be observed that the values obtained inside and on the periphery of the laser-treated area agree within the standard deviation. Local RMS values (Fig. 13) were obtained from AFM scans performed inside craters and on the unirradiated sample (B) (Fig. 14) as described in section 2.8.

As an indirect indicator of the sample's thermal conductivity, the probe current plot (Fig. 12a) illustrates that the sample requiring a higher probe current to reach 35 °C (L2) exhibits the highest thermal conductivity. Compared to the sample before treatment, the thermal conductivity of all treated samples, both inside the craters and in their periphery, is higher. It is observed that the thermal conductivity increases as the laser processing power changes from 6.3 W to 8.0 W and decreases as the power increases to 11.4 W, with the latter registering the lowest thermal conductivity. As expected, the probe temperature vs. laser processing power (Fig. 12b) manifests inversely to the probe current, confirming the previous assessment of the material's thermal conductivity behavior. These are complementary measurements that provide information on the possible existing inhomogeneities in local thermal conductivity. In this context, heat diffusion is confined to a very shallow depth, approximately ten times the probe diameter, which amounts to a couple of micrometers. Consequently, surface composition significantly affects the measurements. The thermal conductivities of Cu and CuO at room temperature are 401 [71] and 76.5 [72] W/mK, respectively, while Cu₂O's thermal conductivities are 6.3 and 7.1 W/mK at 0 and 100 °C [73], respectively. One would expect an initial decrease in this parameter due to the increased presence of Cu₂O on B sample, followed by an increase resulting from the transformation of Cu₂O and Cu into CuO of relatively high crystalline quality (see Fig. 5). However, this expectation is not observed, and the unirradiated sample (B) exhibits the lowest thermal conductivity. One could argue that the abundance of amorphous carbon on the surface might significantly influence the thermal results, especially considering the shallow depth of the measurements. The potential transformation of carbon to graphite-like carbon due to the increase in laser power to 8.0 W [74] could lead to higher local thermal conductivity in the samples [75]. As shown in

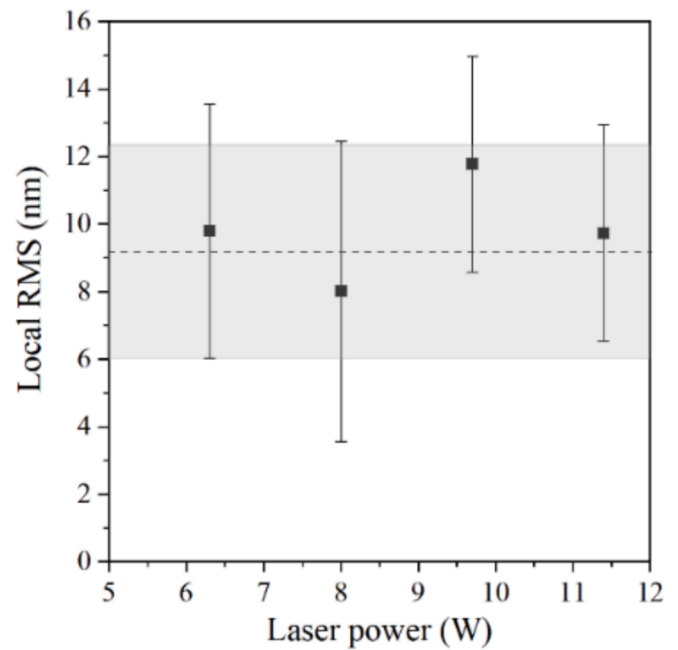


Fig. 13. The dependence of the average local RMS (areas of 400x400 nm²) on laser processing power inside the laser treated area. The dashed line represents the average value for the sample before laser treatment, while the grey band denotes the corresponding standard deviation.

Fig. 8, a subsequent increase in laser power results in a decrease in the total carbon content on the sample surface. This reduction may contribute to the observed gradual decline in thermal conductivity up to the highest fluence utilized in this study.

It is noteworthy that the atomic concentrations of C 1 s and Cu 2p exhibit non-monotonic behavior across various laser power values, as exemplified in Fig. 15 for an etching time of 300 s. These trends align with the variation in probe current observed at $T_{\text{probe}} = 35$ °C (Fig. 12a) and probe temperature observed at $i_{\text{probe}} = 0.910$ mA (Fig. 12b), respectively.

These findings suggest that variations in the thermal conductivity of the samples are influenced by changes in the chemical composition induced by irradiation with different laser power values.

Artifacts in measurements performed with SThM arise from fluctuations in the probe's contact area, impacted by local sample geometry and the available volume for heat transfer. Variations in the probe-

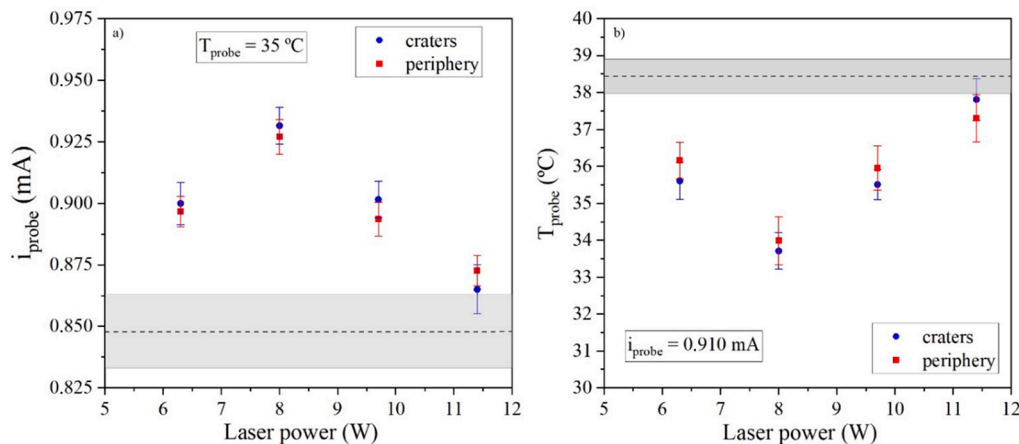


Fig. 12. Average results for the dependence of (a) probe current and (b) probe temperature on laser processing power, inside and on the periphery of the laser-treated area. The dashed lines represent the average value for the reference sample (B) before laser treatment and the grey band indicates the corresponding standard deviation.

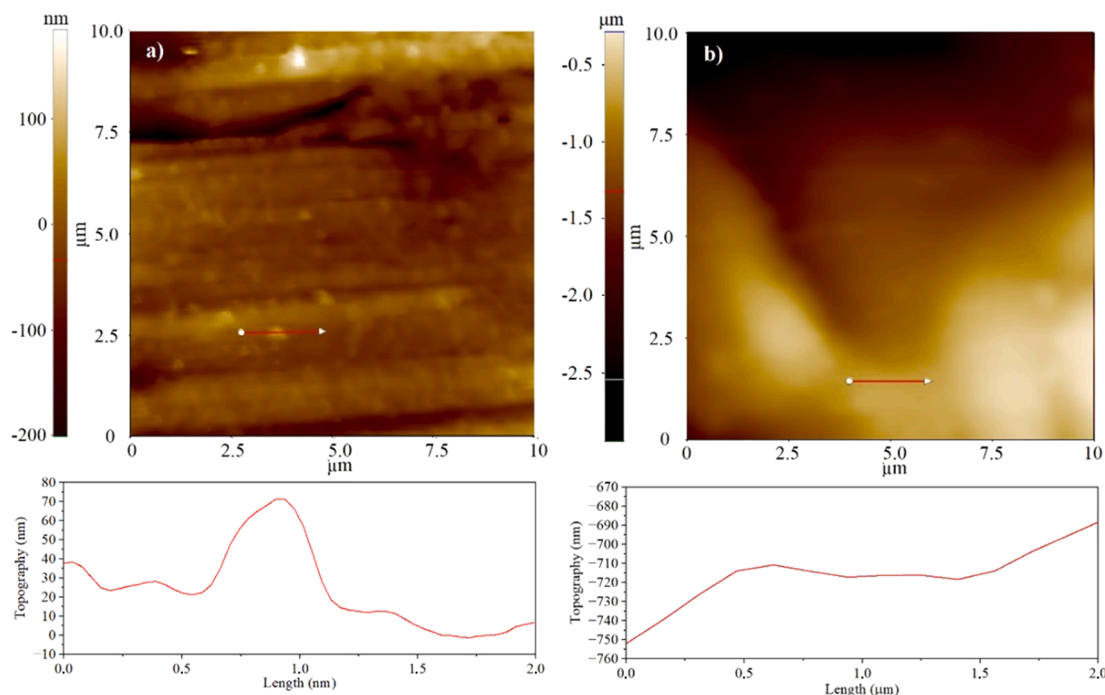


Fig. 14. AFM scans of $10 \times 10 \mu\text{m}^2$ areas of (a) sample B and (b) sample L1 inside a crater. Below each scan, a corresponding representative line profile corresponding to a $2 \mu\text{m}$ length is presented with equivalent vertical and horizontal scales.

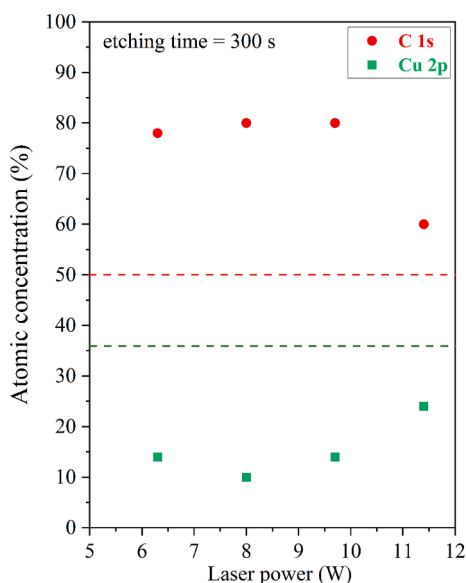


Fig. 15. Atomic concentration for C 1s and Cu2p at an etching time of 300 s (same data as shown in Fig. 8) for the irradiated samples. The dashed lines represent the corresponding values for the unirradiated sample B.

sample area may occur due to changes in roughness, contributing to topography-related effects in the indirect measurement of thermal conductivity [76,77]. To address this, we investigated the samples' topography and assessed the roughness in the relevant study areas.

Fig. 14a and b display $10 \times 10 \mu\text{m}^2$ AFM scans for samples B and L1, respectively. The RMS values for the entire scanned areas in Fig. 14a and b are 37 and 664 nm, respectively, as determined by the XEI software. Beneath each scan, representative line profiles corresponding to a $2 \mu\text{m}$ length are presented a scale deemed more relevant given the dimensions of the thermal probe. At the $10 \times 10 \mu\text{m}^2$ scale, the RMS results align with those in Fig. 8, showing that sample L1 has significantly higher

roughness compared to sample B. The line profiles and the plot in Fig. 13 indicate that at the $400 \times 400 \text{ nm}^2$ scale, local RMS values are notably similar for samples B and L1, whose AFM scan and line profile are representative of all irradiated samples.

By consistently placing the probe on surfaces without crevices or other abnormal features, confirmed by the optical microscope camera integrated into the PARK XE7 system, uniform roughness levels for all samples are guaranteed, implying similar contact areas for the thermal probe in each measurement. Although this correlation lacks explicit confirmation in the literature, it serves as a reasonable assumption. Our efforts to maintain uniform topography in the studied areas aim to ensure that thermal results primarily reflect variations in thermal conductivity rather than differences in contact area between the probe and the sample. Notably, quantifying the contact area is unfeasible for this experiment.

4. Conclusions

Cu substrates were processed using a Nd:YAG pulsed laser with different powers, from 6.3 to 11.4 W, where an increase in the RMS height of ca. 1.3 to $2.2 \mu\text{m}$ was, respectively, achieved. Topographical analysis revealed that regions directly hit by the laser beam lead to the formation of molten Cu pools, with some of the material being spread due to the high energy fluences employed. Laser-induced craters are initially left to cool, allowing molten copper to recrystallize while the surface is exposed to air. This process leads to a significant increase in surface roughness and the formation of copper oxides (CuO and Cu_2O). Changes in laser processing parameters affected both the chemical composition and wettability properties of the copper surface. Raman measurements revealed that Cu_2O , more abundant at lower temperatures (i.e., lower laser fluences), co-existed at higher processing fluences with a form of CuO characterized by increased crystallinity. Nonetheless, XPS analysis indicated the presence of CuO on the surface of all samples investigated, increasing the thickness as the laser fluence increases. SThM measurements showed that variations in the thermal conductivity of the samples' surface are influenced by changes in the chemical composition induced by irradiation with different laser

fluences. The observed changes in thermal conductivity are likely influenced not only by the chemical composition but also by the distribution and thickness of the oxide layers. While determining the exact thicknesses of CuO and Cu₂O would further clarify their contributions to thermal behavior, measuring these layers presents significant challenges. Techniques like XPS depth profiling and SThM probe measurements are constrained by the thinness of the oxide layers and the overlapping signals from the substrate and oxides. Future studies using advanced methods, such as cross-sectional TEM, may offer more precise thickness measurements, enabling a deeper understanding of the interplay between oxide layers and heat transfer.

It is possible to conclude that the superior hydrophobicity of the samples at lower fluences was enhanced by the presence of species at the surface, namely Cu₂O and hydrocarbon chains.

All samples showed reduced wettability, as reflected in water contact angles ranging from 110° to 135°, which successfully deterred CaCO₃ deposition under the conditions investigated. Despite this hydrophobic behavior, this long-term corrosion performance of the laser-treated Cu surfaces resembled that of untreated copper.

Overall, the fast laser processing method employed has proven to be appropriate for application in Cu for water heating systems with the possibility of being integrated in a manufacturing line.

CRediT authorship contribution statement

Guilherme Gaspar: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Maria A. Salvador:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Maria J. Pereira:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Alexandre F. Carvalho:** Methodology, Investigation, Formal analysis, Data curation. **Vitor S. Amaral:** Writing – review & editing, Methodology, Investigation, Formal analysis, Conceptualization. **João Tedim:** Writing – review & editing, Investigation, Formal analysis, Conceptualization. **Jonas Deuermeier:** Investigation, Formal analysis, Data curation. **António J.S. Fernandes:** Methodology, Investigation, Formal analysis, Conceptualization. **Rui F. Silva:** Writing – review & editing, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Florinda M. Costa:** Writing – review & editing, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apsusc.2025.162614>.

Data availability

Data will be made available on request.

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