Laser Ablation of Metal Substrates for Super-hydrophobic Effect

M. Tang[1, 2], V. Shim[3], Z. Y. Pan[4], Y. S. Choo[2] and M. H. Hong[1, 4, *]

1- Department of Electrical and Computer Engineering, National University of Singapore, Singapore 117576
2- Department of Civil Engineering, National University of Singapore, Singapore 117576
3- Department of Mechanical Engineering, National University of Singapore, Singapore 117576
4- Data Storage Institute, Agency for Science, Technology and Research, Singapore 117608

*Corresponding Author: elehmh@nus.edu.sg

Pulsed UV laser ablation is applied to fabricate super-hydrophobic surfaces on metal substrates. The spike shape micro-structure arrays achieved by the laser ablation on the brass substrates increase the surface roughness (R_a) from ~ 400 nm to ~ 5 μm. Meanwhile, plenty of nano-structures (200 ~ 600 nm) are also formed and scattered on the surface of the micro-structures. It is found that the water contact angle of the brass substrate increases from 110° to 161°. Super-hydrophobic property of the metal surfaces with both the micro- & nano-roughness is explained by water repellent model for double roughness structures. High speed camera imaging is used to analyze water droplet dynamics during its rolling down along the slanted super-hydrophobic brass surface. It shows that the pulsed laser ablation is a versatile approach to create large area super-hydrophobic surfaces for industrial applications.

DOI:10.2961/jlmn.2011.01.0002

Keywords: Laser ablation, super-hydrophobic surface, contact angle and high speed camera imaging

1. Introduction

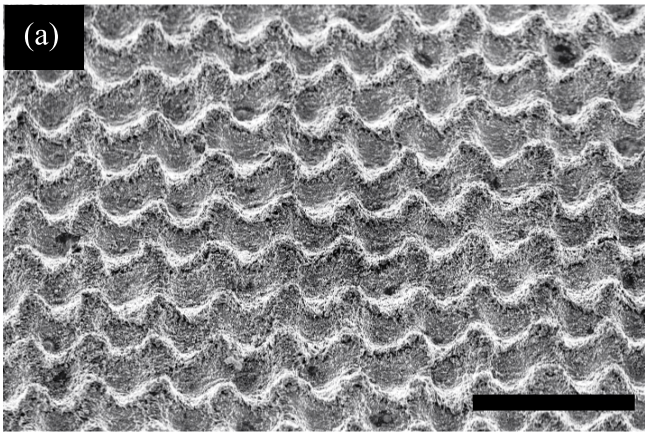
Metals, like copper and copper alloys, are important materials used in modern industries. They have good electrical and thermal conductivity, mechanical workability and their relatively noble properties. They are widely used in many applications for maritime and offshore industries as valves and pipelines for sea water transportation and heat exchangers. The main problem in these metal facilities is metal corrosion, which has attracted many research interest.[1] One of the potential solutions to reduce the metal corrosion is to make the metal interfaces with water super-hydrophobic. Super-hydrophobicity describes strong water repelling property on material surfaces.[2] This phenomenon is first observed in nature, as being prominently demonstrated on the lotus leaf and other organic surfaces. Water droplets standing on these organic surfaces have been found to appear in a near-spherical shape while these surfaces can possess self-cleaning effect. The near-spherical water droplets roll off the surfaces easily and thus remove the contaminates in their paths.[3] It is observed that the lotus leaf is covered with numerous micro-/nano-structures, which motivates researchers to create artificial super-hydrophobic surfaces by mimicking the lotus leaf.[4] Many super-hydrophobic surfaces are fabricated by the self-assembly of micro-/nano-structures and other complicated chemical methods.[5] However, one of the drawbacks of these super-hydrophobic surfaces is that they are fragile and easily peeled off, although they can achieve contact angles above 160° for super-hydrophobic property.[6] In this paper, the super-hydrophobic surfaces are directly fabricated on the metal surfaces using a high power pulsed UV laser. Laser is a flexible micro-fabrication tool which allows the precise control over the required dimensions of micro-structures and fabricates the super-hydrophobic surfaces over a large area without further chemical wet process. Especially, the UV laser at a shorter laser wavelength allows to achieve smaller focused spot size than other pulsed lasers, which is more appropriate to be applied for the micro-fabrication.[7] Hence, the laser fabricated metal super-hydrophobic surfaces have more stable physical and chemical properties for the durable super-hydrophobility.

2. Experimental

A third harmonic diode-pumped solid-state (DPSS) UV laser (model: AVIA 355-23, Coherent) with the wavelength of 355 nm was employed to micro-machine brass samples. The pulse repetition rate was fixed at 30 kHz with the pulse duration (FWHM) of 20 ns. The spot size is focused to ~ 40 μm and the calculated laser fluence is estimated to be ~10.5 J/cm^2. The laser beam was coupled into a galvanometer after passing through a 10 × beam expander and focused by an f-theta lens with a focal length of 100 mm and then focused on the brass sample surface. UV laser beam directly writes designed patterns on the brass substrates by the software programming through a PC graphic interface. The scanning field is 60 × 60 mm. The scanning speed is 200 mm/s during the laser ablation process.[8] The brass samples are in a cubic shape. Before laser ablation, the brass surfaces were initially polished by silicon carbide papers and the surface roughness (R_a) was reduced down to ~ 400 nm. The brass samples were then washed in acetone and isopropanol (IPA) for 5 minutes to clean the sample surfaces. The morphology of the brass surface after the laser ablation was examined with a field emission scanning electron microscope (SEM, Hitachi S4100) equipped with energy-dispersive X-ray spectroscopy (EDX) function. Surface roughness was measured by a 3D topography device from MicroPhase working with Zeiss microscopy.

3. Results and Discussion

Spike shape micro-structures are formed on the brass substrates by controlling the laser beam moving along a quadrilateral grid, as shown in Figs. 1 (a) - (d). The brass sample is first heated up due to the absorption of the laser energy by the materials under the laser irradiation. The heating of the brass then causes the surface brass to melt and eventually evaporation takes place. The total amount of metals ablated away is dependent on laser fluence and pulse number. The area of removed materials by laser ablation depends on focused laser spot size. The pitch of the quadrilateral grid equates to the spot size of laser focused beam at ~ 40 µm. Therefore, it can achieve the dense distribution of spike shape micro-structure arrays with the height of ~ 20 µm. These spike shape micro-structures have been proved to have better hydrophobicity than the cylinder shape micro-structures.[9] The surface roughness (R_a) was measured by the 3D microscopy to be ~ 5 µm. It is also observed that plenty of nano-structures are also formed and scattered on the surface of the micro-structures, as shown in magnified Figs. 1 (c) & (d). The phenomenon is due to Gaussian distribution of the laser beam at the focus points so that the energy density at the border of the laser beam is lower than that of the centre. The surrounding area of laser ablation absorbs less laser energy, therefore only central part of metal is melted and formed liquid pools where the heating temperature is not high enough to vaporize the metal. During this process, the ripples are generated on the surfaces of metal liquid pools, which create plenty of nano-structures since the metal liquid is splashed and shrunk into nano-particles during the re-solidation.[10] When the laser irradiation ends, the metal surface layer is cooled down rapidly by heat conduction into the metal substrate and nano-structures are remained on the surfaces of the micro-structure, as shown in Fig. 1 (d). These nano-structures are in the size of 200 ~ 600 nm.



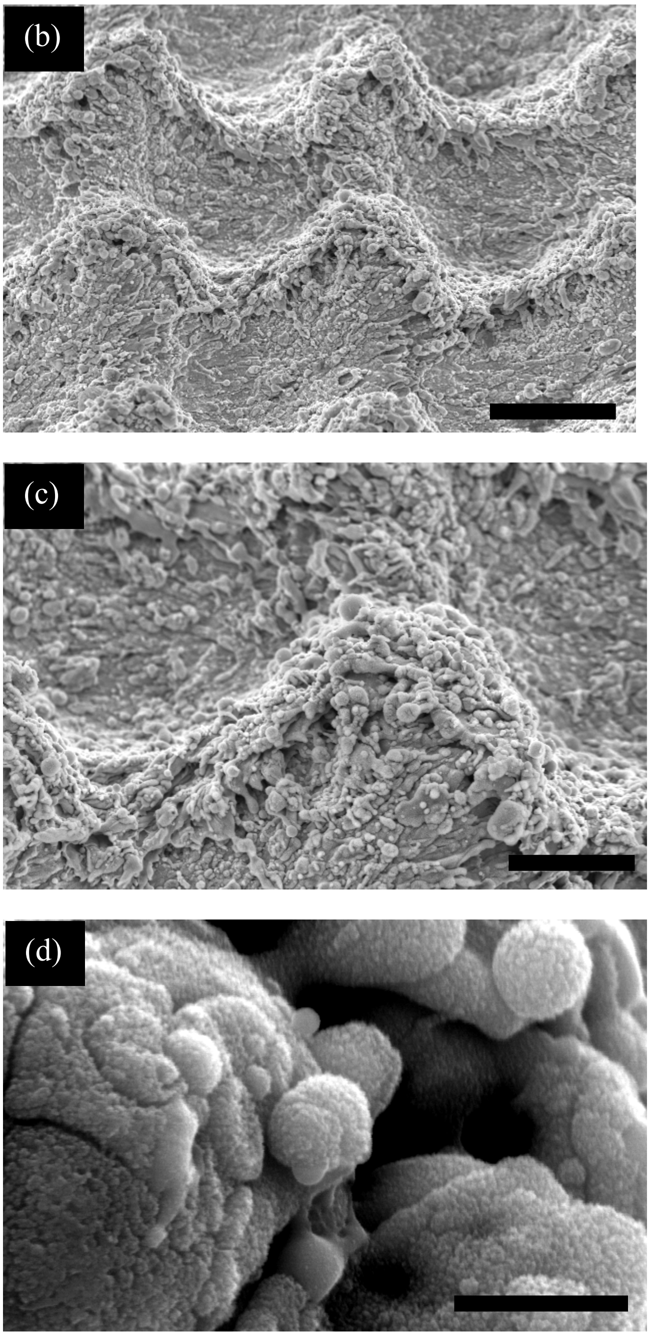


Fig. 1 SEM images of spike shape micro-/nano-structures formed on the brass substrate by 355 nm UV laser ablation at different magnification scales. Scale bars in (a) - (d) are 100, 20, 10 and 1 µm, respectively.

A high resolution camera is employed to measure the static contact angles of water droplet on metal samples and analyze the hydrophobicity property of metallic surface.[11] The volume of water droplet for the testing is 1 µl. After the laser treatment, the water contact angle of the laser textured brass surface was ~ 10°. It is very interesting to find out that the contact angle of the laser textured brass surface increases when exposing to air. After two weeks, the contact angle of the laser textured brass sample reaches a plateau and the surface become super-hydrophobic surface with a contact angle of ~ 161°, as shown in Fig. 2 (a). For comparison, the contact angle of the original flat brass

Rev2 Q1

Rev2 Q3

substrate is only ~ 110°, as shown in Fig. 2 (b). The similar phenomenon was also reported by Kietzig et al.[12] The main compositions of the brass substrates are copper and zinc with less lead and carbon. Figure 3 (a) shows EDX analyses of the brass sample just after the sand paper polishing and further cleaning, while Fig. 3 (b) shows that of the brass sample with super-hydrophobic surface after the laser ablation and then exposed to air for two weeks. It is noticed that the distinct oxygen peak appears besides the peaks of copper and zinc. This is because the copper and zinc in the surface layer are oxidized when the brass substrate exposed to air for two weeks. The atomic percentage of oxygen is approximated to the total atomic percentage of copper and zinc atomic percentages after EDX analyses on the surface layer. It implies that materials of the outer layer on the brass surface are converted into stoichiometric ZnO and CuO, which are hydrophobic materials.[13, 14]

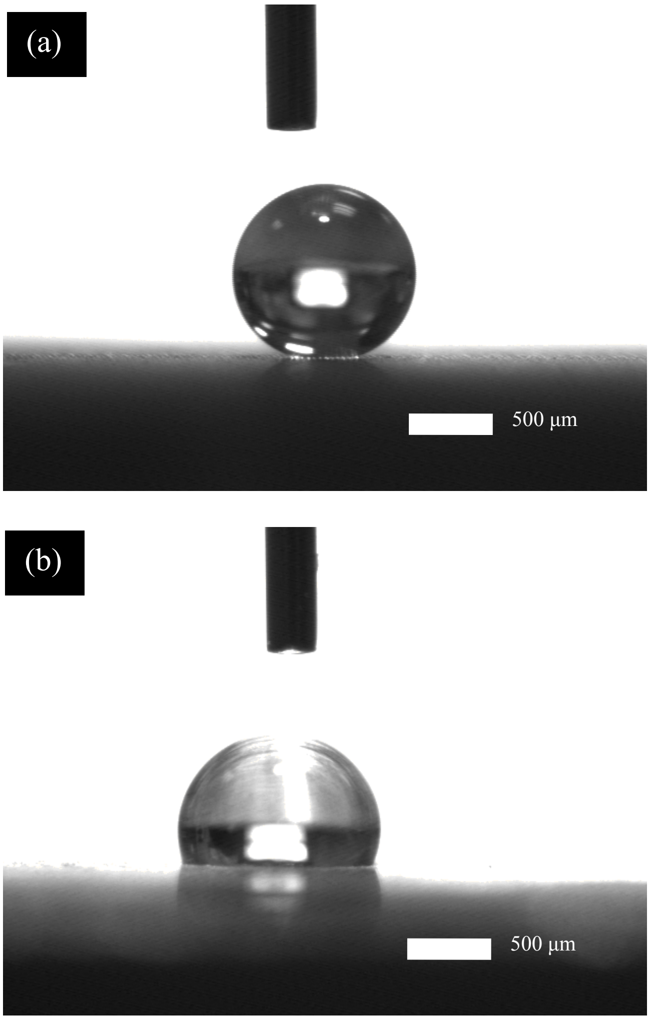


Fig. 2 Microscope images of water droplets on (a) laser textured surface after two weeks exposed to air and (b) the original flat brass surface.

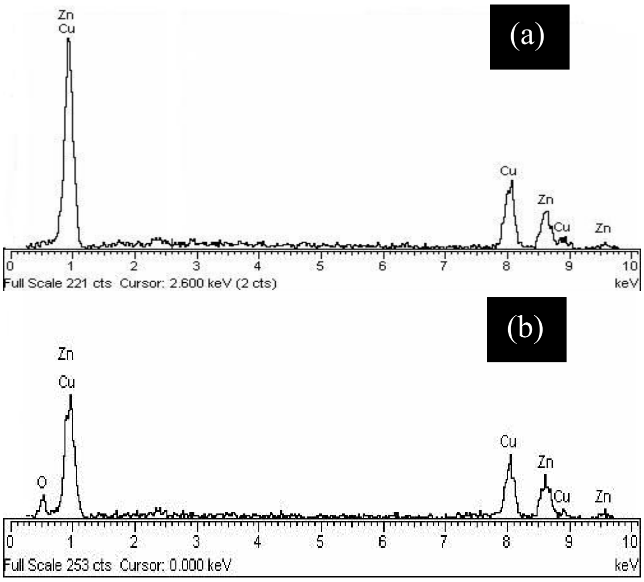


Fig. 3 EDX analyses of the surface (a) before and (b) after the laser ablation and exposed to air for two weeks.

To explain why the laser textured brass surface shows super-hydrophobic property, the lotus leaf surface is compared to the laser textured surface. The surface of the lotus leaf is covered with micro-bumps in the size of ~ 15 μm. Furthermore, these bumps on the lotus leaf are decorated with randomly oriented nano-pillars in the diameter of ~ 100 nm. Similar double roughness structures are also formed on the laser textured surface on the brass. The spike shape micro-structures formed on the brass surface are covered with small nano-structures. Hence, according to the work done by Cha et al., the water repellent model for double roughness structures can be applied to explain the physical behaviors. At the water dewetting state, water droplet rests on the top of both micro- and nano-structures with air gaps between the micro- and nano-structures, respectively, as shown in Fig. 4. Analogous to the lotus leaf, this laser textured surface on brass substrate presents strong water repellent property.[15]

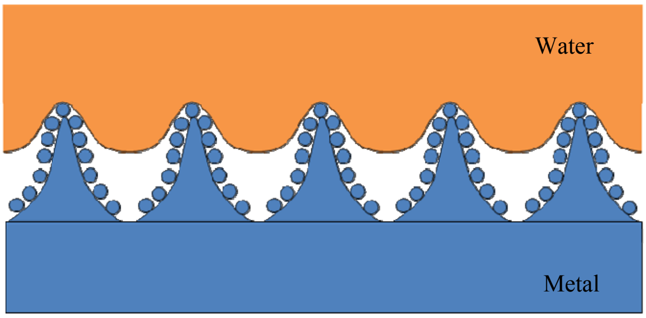


Fig. 4 Schematic drawing of the interface between water and double roughness surfaces.

This super-hydrophobic brass surface has a very small sticking force with the water droplet. The water droplet easily rolls down this super-hydrophobic surface. This phenomenon was observed using a high speed camera. The resolution used for the image recording is 768 × 768 pixels at a frame rate of 1000 frames per second with a shutter speed of 100 µs.[16] Figure 5 shows time-sequence snapshots of a water droplet with a volume of 2.48 µl free-falling on the super-hydrophobic brass surface. The droplet has a radius of 0.84 mm and is released from a height of 2 mm at the first impacting velocity of 0.063 m/s. The slanted angle at which the brass sample made with the stage is ~ 4º. Several rebounds can be observed during the water droplet is rolling down. When the water droplet interacts with the super-hydrophobic brass surface, its shape becomes oblate spheroid by the compressing force of its own gravity. In contrast, when water droplet jumps up and leaves the surface, its shape becomes ellipsoid. The rolling speed of the water droplet increases continuously along the slanted surface. It shows that this super-hydrophobic surface has a very small slide angle.[17]

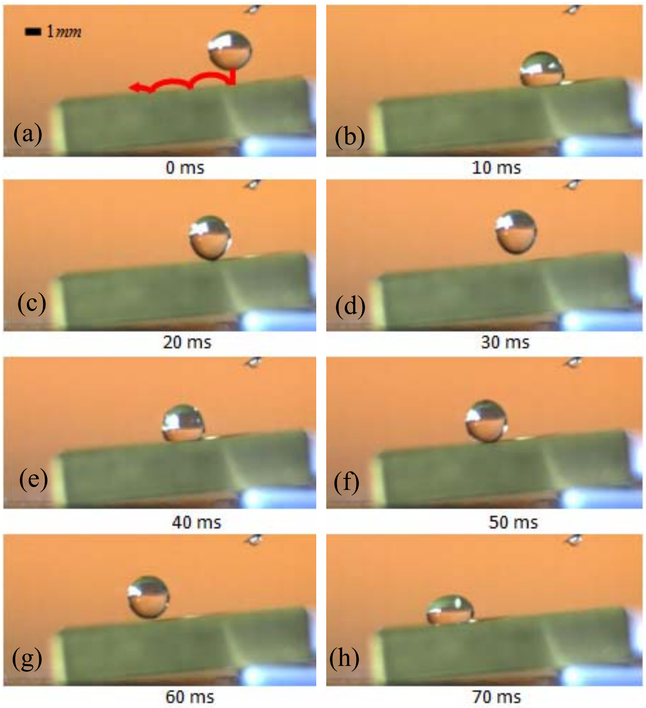


Fig. 5 Snapshots of a water droplet impacting on the slanted super-hydrophobic surface with double roughness structures fabricated by the laser ablation.

It has been found that the super-hydrophobic surface could improve the anti-corrosion of metals in the water successfully. As the water fluid is contacting to the super-hydrophobic surface, air gaps exist between the water and super-hydrophobic metal surfaces. The contact area of water with super-hydrophobic metal surface is much smaller than that with the metal surface without the laser treatment, which can reduce chemical reaction and improve the anti-corrosion property.[18-19]

4. Conclusions

Super-hydrophobic metal substrate surfaces are fabricated by a high power pulsed UV laser. Spike shape micro-structures are formed by controlling laser beam moving along a quadrilateral grid. The surface roughness (R_a) is increased from ~ 400 nm to ~ 5 µm. Nano-structures in size of 200 ~ 600 nm are scattered on the surface of the micro-structures. The laser textured brass surface after two weeks exposed to air becomes super-hydrophobic at a contact angle of 161°. Super-hydrophobic property of the metal surface with both the micro- and nano-structures is explained by water repellent model for double roughness structures. Very small slide angle (less than 4º) of the metal super-hydrophobic surface is illustrated by high speed imaging of water droplet rolling down along a slightly slanted super-hydrophobic metal surface. Pulsed laser ablation is proved to be a versatile approach to fabricate super-hydrophobic surfaces with enhanced anti-corrosion performance of metal structures over a large area at a low processing cost which is important for potential industrial applications.

Acknowledgements

This work was funded by Lloyd's Register Professorship (WBS: R264002006720) at the Centre for Offshore Research & Engineering in National University of Singapore.

References

[1] L. N´u´nez, E. Reguera, F. Corvo, E. Gonzalez and C. Vazquez: Corros. Sci. 47, (2005) 461.
[2] L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang and D. Zhu: Adv. Mater. 14, (2002) 1857.
[3] V. Zorba, E. Stratakis, M. Barberoglou, E. Spanakis, P. Tzanetakis, S. H. Anastasiadis and C. Fotakis: Adv. Mater. 20, (2008) 4049.
[4] C. Yang, U. Tartaglino and B. N. J. Persson: Phys. Rev. Lett. 97, (2006) 116103.
[5] L. Jiang, Y. Zhao and J. Zhai: Angew. Chem. Int. Ed. 43, (2004) 4338.
[6] E. Hosono, S. Fujihara, I. Honma and H. Zhou: J. Am. Chem. Soc 127, 13458 (2005)
[7] S. Preuss, A. Demchuk and M. Stuke: Appl. Phys. A 61, (1995) 33.
[8] M. Tang, M. H. Hong and Y. S. Choo: PhotonicsGlobal@Singapore. Singapore, (2008)
[9] R. D. Narhe and D. A. Beysens: Europhys. Letts. 75, (2006) 98.
[10] T. Götz and M. Stuke: Appl. Phys. A 64, (1997) 539.
[11] A.Lafuma and D. Quéré: Nat. Mater. 2, (2003) 457.
[12] A. M. Kietzig, S. G. Hatzikiriakos and P. Englezos: Langmuir. 25, (2009) 4821.
[13] B. Liu and H. C. Zeng: J. Am. Chem. Soc. 126, (2004) 8124.
[14] M. Li, J. Zhai, H. Liu, Y. Song, L. Jiang and D. Zhu: J. Phys. Chem. B 107, (2003) 9954.
[15] T. G. Cha, J. W. Yi, M. W. Moon, K. R. Lee and H. Y. Kim: Langmuir 26, (2010) 8319.
[16] M. Barberoglou, V. Zorba, E. Stratakis, E. Spanakis, P. Tzanetakis, S. H. Anastasiadis, and C. Fotakis: Appl. Surf. Sci. 255, (2009) 5425.
[17] Z. Wang, C. Lopez, A. Hirsa, and N. Koratkar: Appl. Phys. Lett. 91, (2007) 023105.
[18] T. Liu, Y. Yin, S. Chen, X. Chang and S. Cheng: Electrochim. Acta. 52, (2007) 3709.
[19] T. Liu, S. Chen, S. Cheng, J. Tian, X. Chang and Y. Yin: Electrochim. Acta. 52, (2007) 8003.

(Received: June 07, 2010, Accepted: December 01, 2010)