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One-step fabrication of near superhydrophobic aluminum surface by nanosecond laser ablation

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ABSTRACT

Inspired by the micro and nano structures of biological surface such as lotus leaf, rice leaves, etc. a functional near superhydrophobic surface of pure aluminum has been fabricated using one-step nanosecond laser processing. Thin aluminum sheets are micro-patterned with ultraviolet laser pulses to create near superhydrophobic surface in one-step direct laser writing technique. The impact of number of pulses/microhole with respect to the geometry and static contact angle measurements has been investigated. The microstructure shows the formation of blind microholes along with the micro-wall by laser processing, which improves the composite interface between the three phases such as water, air and solid, thus enhance the wetting property of the surface. The geometrical changes are supported by the chemical changes induced on the surface for improving the degree of hydrophobicity. Laser processed microholes exhibited near superhydrophobic surface with SCA measurement of $148 \pm 3^{\circ}$. The static contact angle values are very consistent for repeated measurement at same area and across the laser patterned surface.

1. Introduction

Nature has variety of functional surfaces to meet the harsh environments on the day to day life. In recent years, natural functional surface has gained considerable interest due to the potential applications in industries as well as in home appliances. Among the functional properties, the high degree of water repellency or superhydrophobic property of the lotus leaf has been gained attention among the researcher due to the anti corrosion and low hydrodynamic friction [1,2]. Inspired by the water repellency and self cleaning property of the lotus leaf, successful attempts have been made to change the surface's wettability in three ways; (a) by modifying the surface chemistry with chemical coatings (e.g., fluoroalkyl silane) to reduce the surface free energy; (b) by micro manipulating [3] fabricating dual scale surface roughness (micro-nano); (c) by both of these technique [4].

Different kind of techniques like photolithography, nanocasting, extruding of polymers, block copolymers, vertically aligned carbon nanotubes, and electron-beam lithography, have been adopted to improve the wetting properties by creating large-scale roughness on variety of materials. However, these techniques suffer from the weakness such as expensive masks and time consuming due to the multiple steps involved in creating the periodical roughness. Ultrafast laser sources can be used to create a variety of micro and nano structures in open environment and in robust time. In general, the superhydrophobic surface is realized by micromachining the metal surface and applying chemical coatings on the machined area to decrease the high surface energy of the machined surface. This has been termed as "two step process". Whereas, the wetting properties are improved just by introducing the micropatterns on the metal surface without any chemical coatings has been termed as single step processing.

The recent studies on laser micromachining demonstrated their ability for fabricating micron/nano scale features with very limited distortion to peripheral area [5–7]. Material is removed from a substrate by ablating the surface, using one or more laser pulses. The ablation process, and thus the micron scale features created, depends on the laser properties such as laser pulse width, energy of the pulse, repetition rate and the properties of the material used. The wettability of a solid surface is normally addressed by measuring the static contact angle measured between the water droplet and the solid surface. In general, a hydrophilic surface has contact angle less than 90° and a hydrophobic surface has more than 90°. Superhydrophobic surfaces have more than 150° contact angle [8]. Baldacchini et al. successfully demonstrated the ability of converting a hydrophilic silicon surface to hydrophobic by applying a fluorosilane coating on laser textured structures [9]. Superhydrophobic effects were reported by Jagdheesh et al. on metals by adopting two step process [4] and on ceramics by single step laser process [3] with picosecond sources. In recent past,

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superhydrophobic surfaces have been produced by various types of coatings on laser patterned surface [4]. However, applying a coating of foreign material onto the laser structured surface is undesirable as it manipulates the surface chemistry and cannot provide durable hydrophobic surface. Therefore, surface manipulation by transforming the base material is preferable method.

The quality of the micromachining can be improved by the appropriate choice of wavelength and pulse repetition rate. Most metals have high reflectivity at infrared wavelength and it decreases at shorter wavelengths. Although, laser pulses in nanosecond regime can produce defects in micromachining like, relatively large heat-affected zones, dross and recast, these laser sources are widely preferred in industry due to its well proven industrial robustness, large pulse energies and high pulse repetition rates, which provides accelerated machining process. The nanosecond laser processed structure/pattern of metals at ultra violet (UV) wavelength is one of less explored aspect with respect to improvement of wetting properties. Pure aluminium is the material which is widely used in the industries for the manufacturing of domestic appliances and automobile spare parts. The improvement of the wetting properties may increase the life time of components by providing better corrosion and wear resistance.

In this study, nanosecond laser pulses of 500 mW were applied on flat substrates of aluminum (Al) to fabricate blind microholes. Two sets of blind microhole patterns with 40 and 80 pulses/microhole have been investigated with respect to the static contact angle measurement (SCA). The resulted micropatterns were analyzed by scanning electron microscope (SEM) and confocal laser scanning microscope (CLSM) to evaluate the geometrical parameters of the structures. The influence of applied laser power and laser pulses/unit area has been studied with respect to the evaluation of SCA.

2. Experimental

Flat aluminum, sheets of thickness less than 100 μm were machined by ultraviolet laser pulses. A Spectra-Physics laser source with nanosecond (ns) laser pulses, which has central wavelength of 1064 nm, was used. The fundamental frequency is 1064 nm was frequency-tripled (wavelength of 355 nm) by the process of non-linear optical conversion. The laser source has average maximum power of 20 W at 100 kHz. The experiments were performed at fixed pulse duration of about 30 ns. The laser beam was guided over the samples surface by an optical system that includes six mirrors, a beam expander, and a lens with 250 mm focal length. The maximum scanning speed is up to 200 mm/s for the fix optic scanner.

The laser beam has Gaussian power density profile and the machining was performed in atmospheric conditions with an apparent spot size of 15 μm. Two sets of samples were produced at a power of 500 mW, with 40 and 80 pulses/blind microhole by carefully varying the translation speed in proportion to the repetition rate. Successive rows of blind microholes were fabricated with separation distance ranging from 15 to 35 μm. This distance is hereafter termed as pitch "*P*" for future reference in the text. The detailed laser processing conditions are listed in Table 1.

The laser machined blind microholes were analyzed with scanning electron microscope (SEM) attached with Energy dispersive X-ray spectroscope (HITACHI, Model S-3000N) and confocal laser scanning microscope (CLSM) to evaluate the geometry of the microholes. Energy dispersive X-ray spectroscopy (EDX) measurements were made to evaluate the chemical changes on the laser micro manipulated surface. The hydrophobicity/water repellence of the samples was studied by measuring the static contact angle using the sessile drop technique, with a video-based optical contact angle measuring device (OCA 15 plus from Data Physics Instruments). An 8 μL droplet of distilled deionized water was dispensed on the laser-machined surface structures under atmospheric conditions, and the static contact angle was calculated by analyzing droplet images recorded just after the deposition.

3. Results

3.1. Morphology

The blind microholes patterns are produced with the laser power of 500 mW with 40 and 80 pulses/microhole. Fig. 1 represents the blind microholes generated by 500 mW power with 40 pulses/microhole. Five different pitches (*P*) such as 15, 20, 25, 30 and 35 μm have been fabricated. For case of *P*: 15 μm, there is an overlap of about 10% between the successive blind microholes in the machining direction. This has been caused by small stretch in the shape of the laser spot along one direction. As the pitch increases, the holes are well separated as seen in Fig. 1C.

The signature of the ablation suggests that the material has been removed layer by layer, which is very similar to the ablation of the Al2O3 by picosecond laser [3]. The negative factor of the micromachining with the (ns) laser sources is large amount of melt formation compare to picosecond (ps) or femtosecond (fs) laser sources. Irrespective of the pitch and the number of pulses/microhole, the recast layer has been formed on the circumference of the blind microholes. The laser machined blind microholes also have condensed metal vapor (bright white spots) on the top surface of the recast layer. At some points on the recast layer, the condensed metal vapor has formed micro clusters (Fig. 2B). The melt effect has been highly pronounced at the area of overlap between the successive holes. It appears that, the recast has been repeatedly melted by train of laser pulses striking the same spot.

Fig. 2 shows the blind microholes generated with 80 pulses/microhole. Five different *P* such as 15, 20, 25, 30 and 35 μm has been fabricated to study the effect of geometry with respect to the laser pulses per microhole. For the *P*: 15 μm, there is high overlap between the successive holes in the machining direction similar to 40 pulses/microhole. The increase and the relatively larger amount of recast material on the rim of the blind microholes have resulted in reduction of the microhole radius in one direction. Moreover, the width of the recast layer has been widened due to the increased number of the pulses/microhole which leads to relatively large amount of melting. The possibility of melt flows along the walls of the microholes cannot be denied. As the *P* increases, the holes are well separated as seen in Fig. 2C. The same kind of material removal as noticed for 40 pulses/microhole has been observed.

Fig. 3 clearly shows the formation micro-wall like structure resulted from recast material around the rim of the blind microholes. Further, there is an inward flow of the molten material due

Table 1
Laser processing parameters.

Pitch, *P* (μm)	15	20	25	30	35	15	20	25	30	35
Laser power (mW)			500 mW					500 mW		
Number of pulses/microhole			40					80		
Repetition rate, (RR) kHz			100					100		

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