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Laser texturing of alumina surface for improved hydrophobicity

B.S. Yilbas[a,*], M. Khaled[b], N. Abu-Dheir[a], N. Aqeeli[a], S.Z. Furquan[a]

[a] ME Department, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia
[b] CHEM Department, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia

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ABSTRACT

Laser texturing of alumina surface is carried out to enhance the surface hydrophobicity. Laser controlled ablation of the surface is achieved under high pressure nitrogen assisting gas. The morphological and metallurgical changes at the surface are characterized using optical, electron scanning, and atomic force microscopes. The microhardness and the residual of the treated surfaces are measured using the X-ray diffraction technique. The contact angles at the surface are measured and the hydrophobic states are assessed. It is found that laser controlled ablation results in micro/nano texturing of the surface. Although the surface texture does not exactly follow a regular pattern, it consists of pillars and dimples like structures and the surface roughness is within the sub-micro scale. High pressure nitrogen assisting gas causes formation of AlN and AlON species at the surface while modifying the surface energy after the treatment process. The presence of AlN contributes to hydrophobicity enhancement at the surface. Wenzel and Cassie and Baxter states are present at the treated surface due to the variation in the surface texture. In general, laser texturing improves the surface hydrophobicity.

1. Introduction

Alumina is widely used in industry due to its superior properties, which provide resistance to harsh environments such as high temperatures, large wearing, and highly corrosive environments. Aluminum is highly ionic ceramic and shows some hydrophobic characteristics at the surface. The hydrophobic surfaces receive special interest in industry due to anti-sticking, anti-contamination, and self-cleaning characteristics. One of the methods to improve the hydrophobic characteristics of the surface is to nano/micro texture the surface mimicking some natural plants. Nano/micro structures on variety of surfaces are observed in nature exhibiting hydrophobicity, such as lotus leaves, rice leaves, red rose petals, fish scales, etc. [1–5]. In general, for a known material, the surface free energy and surface roughness are two important factors governing the surface hydrophobicity. In the case of surface roughness, the hydrophobicity of the surfaces can be enhanced significantly by the combination of different scales including micro–nano binary structures [6]. The surface free energy can be modified through altering chemical composition at the surface via nitriding reactions and new alloying elements. Many techniques were proposed and strategies were introduced to enhance the hydrophobicity of the surfaces [7–15]; however, some of these techniques involve with multi-step procedures and harsh conditions or required specialized reagents and equipment. Some of these techniques, which were reported, include phase separation [7], electrochemical deposition [8], plasma treatment [12], sol-gel processing [13], electrospinning [14], and solution immersion [15]. The micro/nano texturing of surfaces faces many challenges; however, laser controlled surface ablation may offer less challenges with cost effective texturing. Lasers can be used one of the effective tools to achieve a controlled ablation at the surface for nano/micro texturing. Since the laser surface ablation involves with non-mechanical contact, the mechanical properties of the ceramic, such as hardness and fracture toughness, do not influence the end product quality. Although laser ablation of ceramic tiles, such as alumina, has many advantages, high stress fields are developed during the process due to the high temperature gradients, which may cause thermally induced cracks at the ablated surface. Despite the fact that the laser controlled ablation can reduce the defect sites such as micro-cracks, large size cavities, further investigation into laser ablation of alumina surfaces becomes essential, particularly for achievement of the geometric texture pertinent to the surface hydrophobicity.

Considerable research studies were carried out to examine laser treatment of ceramic surfaces. Modification of sol–gel-derived amorphous Al_2O_3 thin films by a laser irradiation was studied by Takeda et al. [16]. They showed that the surface morphology and density of the film were significantly altered after laser irradiation and the surface properties of the film were also changed

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* Corresponding author. Tel.: +966 3 860 5223; fax: +966 3 860 2949.
E-mail addresses: bsyilbas@kfupm.edu.sa (B.S. Yilbas), mkhaled@kfupm.edu.sa (M. Khaled), abudheir@kfupm.edu.sa (N. Abu-Dheir), naqeeli@kfupm.edu.sa (N. Aqeeli), sfurquan@kfupm.edu.sa (S.Z. Furquan).

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from hydrophilic to hydrophobic. The osteoblast behavior of laser deposited coatings due to ultra-short pulses was investigated by Qu et al. [17]. They indicated that the average roughness and hydrophobicity were the highest on titania-deposited surfaces, while carbon nitride was the most hydrophilic one. In addition, the osteoblasts on all surfaces showed a flattened and spread-out morphology. Laser ablation of alumina ceramic in sodium hydroxide solution was examined by Zhu and Yuan [18]. The results revealed that the mass loss from the irradiated surface increased with increased processing voltage; however, the mass loss of alumina sample decreased with increasing laser scanning speed. The aerosol formation during laser ablation of ceramics was studied by Alloncle et al. [19]. They showed that most of the particles leaving the ablation cell were nanoparticle aggregates generated from vapor condensation and the condensation converge on the formation of a spinel structure with large coherence domains. The laser ablation of alumina in water was investigated by Musaev et al. [20]. They indicated that the submicron and all of the micron-sized particles had sharp edges and did not have spherical shapes, which showed that the dominant ablation mechanism was due to crack propagation. The thermal stress analysis in relation to laser scribing of ceramics was carried out by Modest and Mallison [21]. They showed that substantially high tensile stresses developed over a thick layer below and parallel to the surface, which might be the cause of experimentally observed subsurface cracks.

Although laser gas assisted treatment of pre-prepared aluminum surfaces were investigated previously [22–25], the main focus was the controlled melting at the surface rather than forming the micro/nano texturing through controlled ablation. Therefore, in the present study, laser gas assisted ablation of alumina surfaces is carried out to enhance the surface hydrophobicity through micro/nano texturing of the surface. Nitrogen at high pressures is used during the ablation process to modify the surface chemistry. The morphological and microstructural changes at the surface are examined by using optical, electron scanning, and atomic force microscopes, energy dispersive spectroscopy, and X-ray diffraction technique. The contact angles of the water droplets are measured at different locations on the resulting surface. The residual stress formed at the surface is obtained from the X-ray diffraction technique and microhardness of the treated surfaces is evaluated using the indentation tests.

2. Surface hydrophobicity

One of the parameters for the wettability of solid surfaces by liquids is the contact angle. The contact angle of a liquid on a perfectly smooth and chemically homogenous solid surface is formulated by Young's Eq. [26]:

$$\cos\theta = \frac{(\gamma_{\mathrm{sv}} - \gamma_{\mathrm{sl}})}{\gamma_{\mathrm{lv}}} \tag{1}$$

where θ is the contact angle, γ_{sv} is the interfacial tensions of solid–vapor, γ_{sl} is the interfacial tensions of solid–liquid, γ_{lv} is the interfacial tensions of liquid–vapor. However, the surfaces are rough and chemically heterogeneous in practice and the applicability of Young's equation becomes limited with extremely smooth and homogenous surfaces. The formulation of the contact angle including surface roughness is proposed by Wenzel [27] and Cassie and Baxter [28]. In the case of Wenzel formulation, liquid penetrates into the rough grooves and the contact angle formulation becomes [27]:

$$\cos\theta_{\mathrm{W}} = \frac{r(\gamma_{\mathrm{sv}} - \gamma_{\mathrm{sl}})}{\gamma_{\mathrm{lv}}} \tag{2}$$

where θ_{W} is the rough surface contact angle, r is the surface roughness factor, which is defined as the ratio between the actual and projected surface areas, i.e. $r = 1$ is the perfectly smooth surface and $r > 1$ represents the rough surface. In general, Wenzel equation predicts that wetting lessens by roughness for $\theta_{\mathrm{W}} > 90^{\mathrm{o}}$; however, air bubbles may be trapped in some rough grooves and the liquid droplet is situated on the composite or heterogeneous surface rather than the solid surface. In this case, the wetting behavior can be described by Cassie and Baxter equation. The liquid surface interface consists of a liquid–solid and liquid–vapor interfaces; therefore, the contact angle should include contributions of two-interfaces. The equation for the contact angle yields [28]:

$$\cos\theta_{\mathrm{c}} = f_1 \ \cos\theta_1 + f_2 \cos\theta_2 \tag{3}$$

where θ_{c} is the apparent contact angle, f_1 is the surface fraction of liquid–solid interface, f_2 is the surface fraction of liquid–vapor interface, θ_1 is the contact angle for liquid-solid interface, and θ_1 is the contact angle for liquid–vapor interface. However, for the air–liquid interface, f_1 can be represented as f, which is the solid fraction, and air fraction (f_2) becomes $(1 - f)$. The parameter f ranges from 0 to 1; in which case, $f = 0$ is the case where the liquid droplet is not in contact with the surface and $f = 1$ is case where the surface is completely wetted. It was reported that in the Cassie–Baxter state, the small contact area between the liquid droplet and solid surface allowed the droplet to roll easily at the surface [29].

In practice, the contact mode changes from Cassie–Baxter state to Wenzel state when the surface texture changes or when the droplets impact at the surface [30] and two states can co-exist on a nano-pillared surfaces [31]. However, when a liquid–air interface can remain pinned at the pillars tops, transition to the Wenzel state is possible, if the sag in the curved liquid–air interface is such that it touches the bottom of the groove [32,33].

3. Experimental

The CO_2 laser (LC-ALPHAIII) delivering nominal output power of 2 kW was used to irradiate the workpiece surface. The nominal focal length of the focusing lens was 127 mm. The laser beam diameter focused at the workpiece surface was ~0.25 mm. Nitrogen assisting gas emerging from the conical nozzle and co-axially with the laser beam was be used. Laser treatment tests were repeated several times by incorporating different laser parameters and laser parameters resulting in the minimum surface defects, such as very small cavities with no cracks or crack networks, are selected. Laser treatment conditions are given in Table 1.

Alumina (Al_2O_3) tiles (Ceram Tec-ETEC, 2010) with 3 mm thickness were used as workpieces. Material characterization of the laser

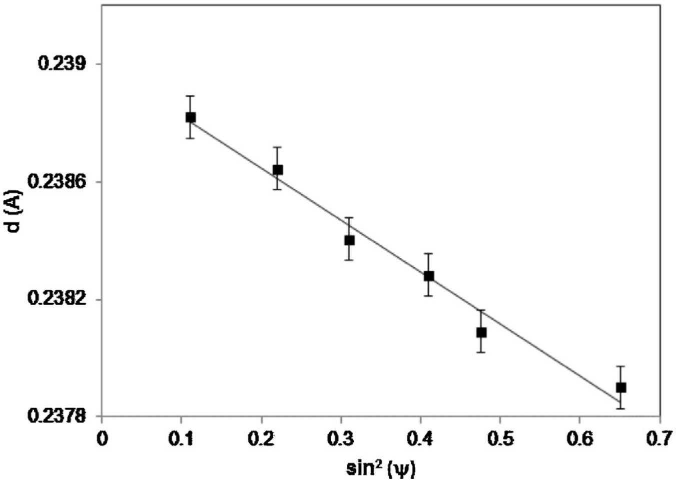

Fig. 1. Linear dependence of d(3 1 1) on $\sin^2\psi$.

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