Journal of Alloys and Compounds 625 (2015) 208–215

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Laser treatment of zirconia surface for improved surface hydrophobicity

B.S. Yilbas

Mechanical Engineering Dept., King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia

ARTICLE INFO

Article history:
Received 19 May 2014
Received in revised form 5 November 2014
Accepted 11 November 2014
Available online 27 November 2014

Keywords:
Zirconia
Laser treatment
Hydrophobicity
Fracture toughness
Residual stress

ABSTRACT

Laser surface texturing of yttria stabilized zirconia is carried out under the high pressure nitrogen assisting gas ambient to enhance the surface hydrophobicity. Morphological and metallurgical changes in the treated layer are examined by using electron scanning and atomic force microscopes, energy dispersive spectroscopy, and X-ray diffraction. The microhardness and fracture toughness of the surface are measured incorporating the indentation tests. The residual stress formed at the treated surface is determined from the X-ray diffraction data. The wetting state of the laser treated surface is assessed through the contact angle measurements. It is found that laser treated surface composes of micro/nano grooves, which improves the surface hydrophobicity. The roughness across the treated surface varies, which in turn result in Cassie and Wenzel states; provided that Cassie state dominates over Wenzel state at the treated surface. Laser treatment improves the microhardness and lowers the fracture toughness of the treated surface and the residual stress determined from the X-ray data is in the order of -1.6 ± 0.05 GPa, which is compressive.

1. Introduction

Stabilized zirconia is widely used in industry due its superior properties such as high wear and temperature resistances, and low thermal conductivity. Some of the applications include thermal barrier coating in jet and diesel engines to allow operation at higher temperatures [1], sensor technologies for oxygen sensing [2], and fuel cell membranes operating at high temperatures [3]. The surface characteristics of stabilized zirconia, including hardness and hydrophobicity, can be improved further through various surface treatment methods. Since biomimetic characteristics of surfaces received great attention in industry, various methods have been developed in this regard. Some of these methods include phase separation [4], electrochemical deposition [5], template method [6], emulsion [7], plasma method [8], crystallization control [9], chemical vapor deposition [10], sol–gel processing [11], lithography [12], electrospinning [13], and solution immersion [14]. However, transforming low-surface-energy materials into textured surfaces is one of the techniques, which can be used to enhance hydrophobicity of the surfaces. Laser surface texturing through a controlled ablation offers considerable advantages over the conventional texturing methods. Some of these advantages include high speed operation, high precision, local treatment, and low cost. However, the presence of the mixed regime of melting and ablation at the surface modifies the surface texture, which alters the wetting state of the surface. In addition, high stress levels are developed in laser treated region because of the high temperature gradients, which are formed in the irradiated region due to high heating and cooling rates. The fraction toughness of the surface also reduces due to microhardness enhancement at the surface after the treatment process. Consequently, investigation of laser treatment of zirconia surface for improved hydrophobicity and assessment of the residual stress and the fracture toughness in the treated region becomes essential.

Considerable research studies have been carried out to examine laser treatment of zirconia surfaces. Laser surface treatment of partially stabilized zirconia for biomedical applications was presented by Hao and Lawrence [15]. They observed that the thickness of the adsorbed human serum albumin decreased as the polar surface energy of the magnesia partially stabilized zirconia increased. Laser treatment of zirconia surfaces was examined by Chwa and Ohmori [16]. They indicated that the surface roughness of zirconia prior to the laser treatment was important, since the melt depth of the polished coatings was approximately half of the rough coatings when treated at the same power density. Laser surface treatment of plasma-sprayed yttria-stabilized zirconia coatings was investigated by Pinto et al. [17]. They showed that the microstructure of the treated layer presented a cellular structure which has grown perpendicular to the surface and the micrographs depicted small cracks and absence of porosity. Laser surface nitriding of yttria stabilized tetragonal zirconia was studied by Kathuria [18]. The findings revealed that the transformation of the t-ZrO_2 exhibited the

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E-mail address: bsyilbas@kfupm.edu.sa

http://dx.doi.org/10.1016/j.jallcom.2014.11.069

typical yellow–gold color of ZrN with high hardness at the surface. Laser surface modification of plasma sprayed yttria stabilized zirconia coatings was examined by Shankar and Mudali [19]. They observed that distinct interface separating fine and coarse grains took place at all scan speeds and the microhardness of the glazed surface improved considerably. Laser treatment of zirconia surface and morphological and microstructural changes in the treated layer was investigated by Daniel et al. [20]. They showed that the surface morphology closely followed the microperiodic heat treatment provided by the interfering laser beams and the pore size distribution within the periodic surface morphology ranged from a few nanometers to a maximum of half of the periodic line distances. Laser ablation characteristics of yttria-doped zirconia in nanosecond and femtosecond regimes were studied by Heiroth et al. [21]. They showed that femtosecond pulses prevented the exfoliation of micron-sized fragments, but result invariably in a pronounced ejection of submicron particles. Thermal fatigue properties of laser treated surfaces were investigated by Aqida et al. [22]. They observed that carbides and oxides compounds were formed on the laser treated surface after the thermal fatigue test. Thermal stability of laser treated die material for semi-solid metal forming was examined by Aqida et al. [23]. The findings revealed that crystallization in glazed zone increased as the annealing temperature increased and the micro-hardness decreased due to local crystallization at the surface.

Hydrophobicity of the substrate surfaces can be improved through forming fine poles at the surface during laser texturing [24]. Modification of wetting properties of laser-textured surfaces was studied by Bayer et al. [25]. They showed that superhydrophobic surfaces could achieved through Teflon deposition at the laser textured surface. Bacterial retention on superhydrophobic laser ablated titanium surfaces was investigated by Fadeeva et al. [26]. They indicated that the untreated surface hydrophobic, whereas the laser-treated surface became superhydrophobic; in which case, attached bacterial cells were found to be below the estimated lower limit. Laser patterning of steel surfaces for improved hydrophobicity was examined by Luo et al. [27]. They showed that when the laser produced pattern was set at 25 μm spacing, the contact angle of the surface could be increased to about 130°, compared to the 68.5° corresponding to a plain smooth steel surface with Ra $\leqslant$ 0.01 μm.

The surface energy of zirconia can be modified by a laser heating at the surface [28], which may further improve surface hydrophobicity. Although laser treatment of zirconia surfaces were examined previously [29,30], the morphological and metallurgical changes at the treated surface were the main focus and the surface hydrophobicity was left obscure. Consequently, in the present study, laser controlled ablation of zirconia surface under high pressure nitrogen assisting gas was considered and the surface characteristics including texture and hydrophobicity were investigated. The morphological and metallurgical changes in the treated region are examined by using electron scanning and atomic force microscopies, energy dispersive spectroscopy, and X-ray diffraction. The microhardness and fracture toughness of the treated surface were evaluated incorporating the indentation tests. The residual stress developed in the surface region of the treated layer was determined from the X-ray diffraction data. The surface hydrophobicity was assessed through the contact angle measurements.

2. Experimental

A 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 0.2 mm. Nitrogen assisting gas emerging from the conical nozzle and co-axially with the laser beam was used. The laser melting parameters are given in Table 1.

Table 1
Laser processing parameters.

Feed rate (m/s)	Power (W)	Frequency (Hz)	Nozzle gap (mm)	Nozzle diameter (mm)	Focus diameter (mm)	N_2 pressure (kPa)
0.1	2000	1500	1.5	1.5	0.3	600

The zirconia tiles 25 mm × 15 mm × 3 mm were used in the experiments. JEOL JDX-3530 scanning electron microscope (SEM) was used to obtain photomicrographs of the cross-section and surface of the workpieces after the tests. The Bruker D8 Advance having Cu Kα radiation was used for XRD analysis. A typical setting of XRD was 40 kV and 30 mA. It should be noted that the residual stress measured using the XRD technique provided the data in the surface region of the specimens, which was because of the penetration depth of Cu Kα radiation into the treated layer, i.e. the penetration depth was in the order of 5 μm. The measurement relied on the stresses in fine grained polycrystalline structure. The position of the diffraction peak exhibited a shift as the specimen was rotated by an angle ψ. The magnitude of the shift was related to the magnitude of the residual stress. The relationship between the peak shift and the residual stress (σ) could be written as [31]:

$$\sigma = \frac{E}{(1+v)\sin^2\psi}\frac{(d_n - d_o)}{d_o} \tag{1}$$

where E is Young's modulus, v is Poisson's ratio, ψ is the tilt angle, d_n are the d spacing measured at each tilt angle, and d_o is the stress-free lattice spacing. If there are no shear strains present in the specimen, the d spacing changes linearly with $\sin^2\psi$. Fig. 1 shows the linear dependence of $d(113)$, in nanometer unit, on $\sin^2\psi$ in the region of laser treated surface. The Zr_3O peak takes place at 63.106°, which corresponds to (113) plane with the inter-planer spacing of 0.1472 nm. The slope of the curve indicates that the in-phase residual stress is compressive. The XRD experiment for the residual stress measurement was repeated five times at four locations at the laser treated workpiece surface to secure the repeatability of the results. The error related to the measurements is estimated as 3%.

The fracture toughness of the surface was measured using the indenter test data for microhardness (Vickers) and crack inhibiting. In this case, the crack length generated due to indentation at the surface was measured. The length (l) measured corresponded to the distance from the crack tip to the indent. The crack lengths were individually summed to obtain l as described in the previous study [32]. The crack length "c" from the center of the indent was the sum of individual crack lengths (l) and half the indent diagonal length "$2a$". Therefore, $c = a + l$. However, depending

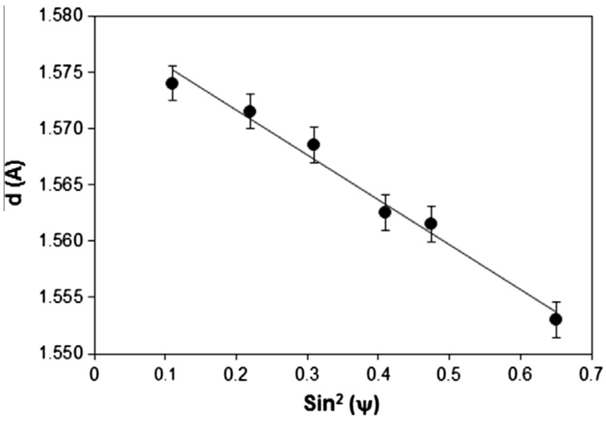

Fig. 1. Linear dependence of $d(113)$ on $\sin^2\psi$.

Table 2
Microhardness and fracture toughness and data used for fracture toughness calculations.

	Hardness HV (GPa)	Fracture toughness (MPa $\sqrt{m}$)	P (N)	a (μm)	c (μm)
As-received surface	15.7 ± 0.06	9.5 ± 0.4	5	20	50
Laser treated surface	19.2 ± 0.06	7.2 ± 0.4	5	25	50