Applied Surface Science 270 (2013) 49–57

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Effect of dry and wet ambient environment on the pulsed laser ablation of titanium

Nisar Ali*, Shazia Bashir, Umm-i-Kalsoom, Mahreen Akram, Khaliq Mahmood

Centre for Advanced Studies in Physics, GC University Lahore, Pakistan

ARTICLE INFO

Article history:
Received 13 August 2012
Received in revised form
10 November 2012
Accepted 8 December 2012
Available online 11 January 2013

Keywords:
Titanium
Laser ablation
Ambient environment
Surface morphology

ABSTRACT

Surface and structural properties of the laser irradiated titanium targets have been investigated under dry and wet ambient environments. For this purpose KrF Excimer laser of wavelength 248 nm, pulse duration of 20 ns and repetition rate of 20 Hz has been employed. The targets were exposed for various number of laser pulses ranging from 500 to 2000 in the ambient environment of air, de-ionized water and propanol at a fluence of 3.6 J/cm^2. The surface morphology, chemical composition and crystallographical analysis were performed by using Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Diffraction (XRD), respectively. For both central and peripheral ablated areas, significant difference in surface morphology has been observed in case of dry and wet ambient conditions. Large sized and diffused grains are observed in case of dry ablation. Whereas, in case of wet ablation, small sized, and well defined grains with distinct grain boundaries and significantly enhanced density are revealed. This difference is ascribed to the confinement effects of the liquid. The peripheral ablated area shows redeposition in case of dry ablation whereas small sized grain like structures are formed in case of wet ablation. EDS analysis exhibits variation in chemical composition under both ambient conditions. When the targets are treated in air environment, enhancement of the oxygen as well as nitrogen content is observed while in case of de-ionized water and propanol only increase in content of oxygen is observed. X-ray diffraction analysis exhibits formation of oxides and nitrides in case of air, whereas, in case of de-ionized water and propanol only oxides along with hydrides are formed. For various number of laser pulses the variation in the peak intensity, crystallinity and d-spacing is observed under both ambient conditions.

1. Introduction

Pulsed laser ablation is a successful and rapidly progressing technique for material processing and device fabrication [1]. In recent times, material surface processing in liquid confined environment is becoming popular and emerging area of research [2,3]. The main advantages of liquid assisted ablation includes effective cooling, useful chemical reactions, highly confined plasma pressure, debris and pollution free modified surface [2,3]. Bussoli et al. [4] investigated laser induced morphological changes on titanium surface in the air ambient and reported applications of nanosecond and picosecond pulsed laser ablation of titanium as an implant in medical industry. Schwickert et al. [5] studied the process of laser hydriding of titanium that leads to the development of TiH_2. The aim of the study was to compare the behavior of titanium after irradiation in hydrogen atmosphere with previous studied process of laser nitriding. Mahmood et al. [6] investigated the effects of laser treatment on the microstructure, yield stress (YS), ultimate tensile stress (UTS) and microhardness polycrystalline titanium target. They found an increase in microhardness with increasing number of laser pulses but changes in YS and UTS with laser shots were found to be anomalous. The growth of nanostructures on the tungsten surface after ablation in liquid environment, improves its thermionic properties [7] due to reduction in its work function.

The motivation of the present work is to explore the effect of ambient environment (air, de-ionized water and propanol) on surface and structural modification of the titanium targets after laser ablation. For this purpose titanium targets are ablated with KrF Excimer laser for various number of laser pulses in ambient environments of air, de-ionized water and propanol. Scanning Electron Microscope (SEM) is used to investigate the surface morphology of ablated targets. Energy Dispersive X-ray Spectroscope (EDS) and X-ray Diffractometer are employed to correlate the surface features with the change in chemical composition, and crystallinity.

2. Experimental details

Pulsed laser ablation of titanium target was performed by using KrF Excimer laser (EX 200/125-157 GAM Laser, USA) with the central wavelength of 248 nm, pulse duration of 20 ns, repetition rate

* Corresponding author. Tel.: +92 3344039791.
E-mail address: chnisarali@gmail.com (N. Ali).

0169-4332/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2012.12.049

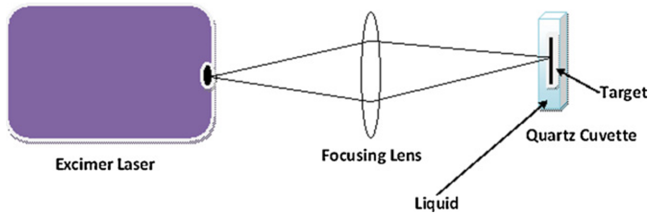

Fig. 1. The schematic diagram of experimental setup.

of 20 Hz and pulse energy of 70 mJ. The unfocused rectangular beam having size 11 mm × 7 mm is focused on the targets by using 50 cm focal length lens.

Rectangular shaped titanium targets with length of 15 mm, width of 10 mm and thickness of 2 mm were grinded, polished and ultrasonically cleaned with acetone for 30 min. The prepared targets were placed in quartz cuvette of height of 45 mm and width of 10 mm. The schematic of the experimental setup is shown in Fig. 1.

All samples were irradiated with laser 5 cm away from the focus, for a fixed laser fluence of 3.6 J/cm^2. The numbers of overlapping laser pulses used for the exposure of targets were 500, 1000, 1500 and 2000. Three set of experiments were performed for the ambient environment of (a) air, (b) de-ionized and (c) propanol under the same laser parameters. For each exposure quartz cuvette was filled with fresh liquid in case of de-ionized water and propanol. For 248 nm wavelength, the percentage laser energy absorption is measured by measuring laser pulsed energy before and after transmission from both liquids. It comes out to be 6% for propanol and 2% for de-ionized water. By using following equation of Beer–Lambert Law [8] we calculated the values of absorption co-efficient for both liquids i.e. de-ionized water and propanol:

$$I(x) = Io e^{-\alpha x} \tag{1}$$

where Io is the intensity of incident beam (W/m^2), α is the absorption co-efficient (m^{-1}) and x is the thickness of liquid film.

By substituting values of $I(x)$ = 0.98 for de-ionized water and 0.94 for propanol; x = 4 mm for both liquids (fixed) in above equation we get the values of absorption coefficients that are 5.05×10^{-2}/mm for de-ionized water and 1.5×10^{-2}/mm for propanol.

The surface morphology of ablated targets was investigated using Scanning Electron Microscope (SEM-JEOL JSM-6480 LV). Energy Dispersive X-ray Spectroscopy (EDS-S3700N) was used for chemical analysis. X-ray diffractometer (X'Pert PRO (MPD)) was employed to determine the crystallographic structure and phase analysis.

3. Results and discussion

Fig. 2(a) shows the SEM image of un-irradiated titanium surface. Significantly modified surface of titanium is observed after irradiation with 500 accumulative laser pulses at 3.6 J/cm^2 as shown in Fig. 2(b). The width of ablated area is measured from SEM image for 500 pulses is 1.062 mm which increases with increase in number of pulses. For 2000 number of pulses its value is 1.187 mm. Accumulation of resolidified material can be clearly seen at the peripheral ablated area. The shock-wave propagation and the recoil momentum offered by the vapor plume expulsion causes the surface depression in the central ablated area and generate the shoulder at the periphery.

Fig. 3(a)–(d) reveals SEM images of the central ablated area of titanium in an ambient environment of air for various number of pulses of (a) 500, (b) 1000, (c) 1500 and (d) 2000. It demonstrates the appearance of grains with diffused boundaries. Heat generated during laser irradiation is responsible for this grain growth [6]. The formation of grain-like surface structures involves two mechanisms: (i) melting and recrystallization of metal resided in the irradiated zone and (ii) cooling and crystallization of metal transferred by hydrodynamic forces owing to intense boiling [9]. The molten metal is ejected from the central irradiated area and cools on a relatively colder target area. Thus, the surface and undersurface layers exhibit residual thermal tension and compression stresses, respectively. The high rates of heating and cooling result into the tremendous temperature gradients. This is related to the local heating, and the plasma-dynamic flows. This is responsible for the generation of residual stresses in the surface layer e.g. the deformation owing to the action of the shock waves. The localized heating also generates thermal and structural stresses related to the changes in volume accompanying the phase transformations. The localized heating and cooling results in preferential crystallization, grain growth process and texture development [9]. The number

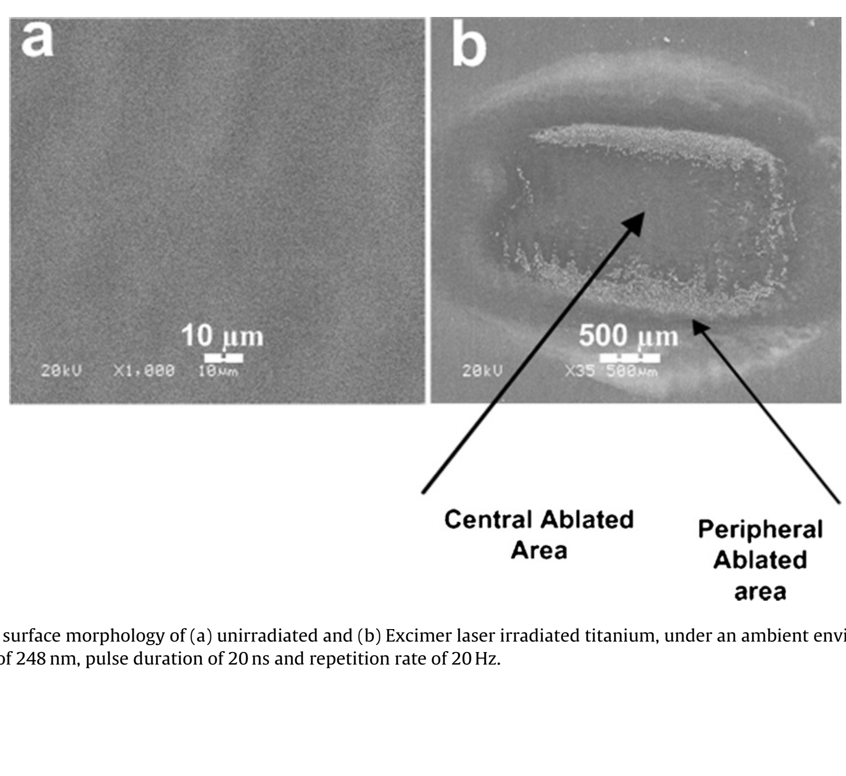

Fig. 2. SEM images revealing the surface morphology of (a) unirradiated and (b) Excimer laser irradiated titanium, under an ambient environment of air, by 500 pulses at a fluence of 3.6 J/cm^2, wavelength of 248 nm, pulse duration of 20 ns and repetition rate of 20 Hz.