Ultraviolet laser treatment of titanium surface

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Abstract. Interaction of a third harmonic of DPSS laser, wavelength 355 nm and pulse duration of 30 ns with titanium wafers was studied. It was investigated the structure of laser ablated titanium surface, depending on the laser beam scanning speed, and laser pulse frequency. The titanium surface modification was studied by scanning electron microscopy (SEM) and XPS (X-ray Photoelectron Spectroscopy). Nanosecond irradiation with ultraviolet light of Ti plate led to the formation of high porous granular structures consisting of agglomerated micro- and submicro-particles.

1. Introduction
Titanium oxide coatings exhibit a wide variety of physical properties that allow using them in many fields such as photocatalysis, gas sensors, medical implants and optical coatings. Anatase and rutile are used as catalysts, water splitting systems, as well as gas and humidity sensors. The adsorption and desorption characteristics of TiO₂ sensing films can be improved by maximizing the pore sizes on the surface. Titanium is also a widely used biomaterial, especially for bone-tissue implants. The good biocompatibility of titanium is to a large extent depends on its chemical surface properties and surface topography at mesoscopic level [1].

Surface oxidation by laser treatment of metals and semiconductors in air or in chemically active atmospheres promise approach for producing of metal oxide structures with large active surface area and open pore structure. In this work we explored the possibility to obtain titanium oxide coatings by laser irradiation of titanium wafers in air.

SEM and XPS methods were used to investigate the surface morphology, composition and chemical state of Titanium surface before and after laser ablation with ultraviolet light.

2. Experiment
The third harmonic of a Nd:YAG laser (DPSS MATRIX 355; λ= 355nm, pulse duration ~ 30ns, Average power − 5W, beam divergence − 2mrad) operating at a repetition rate of 50kHz was focused by 100mm lens on the Titanium plate. Movement of laser beam in parallel lines with pitch 80μm was achieved by Scanlab scanner head. The treatment was done at fluence 25J/cm² (focal spot d = 20μm) and flowing
scanning beam velocities: 5mm/s, 40mm/s, 160mm/s, 320mm/s, 640mm/s, 1280 mm/s. The experiments were performed at room temperature in the air.

During laser interaction with metals, including titanium, the laser energy is absorbed primarily by free electrons [4, 5]. The absorbed radiation energy in the skin layer involves thermalization within the electron sub-system.

Due to the electron thermal diffusion, energy transfers to the lattice and heat is transported into metal. For the laser pulses with laser fluence higher than the damages threshold the thermal diffusivity cannot be neglected. Generally say, a series of effects such as melting, vaporization of the molten materials, dissociation and ionization of the vaporized material, etc., can be generated on the target.

For this laser source with relatively short pulses ($t_p=30$ns) the heat affected zone is small. It can be estimate after one laser pulse using the relation:

$$L_t = 2\sqrt{D \cdot t_p},$$

where D is thermal diffusivity coefficient, $0.86 \cdot 10^{-5}$m$^2$.s$^{-1}$ for titanium. In this case the length for significant effect on heat wave is $L_t=1$µm which is very small compare to the focal laser spot of 20µm.

The composition and the chemical properties of the films were analyzed by X-ray photoelectron spectroscopy (XPS). The measurements were carried out on AXIS Supra electron- spectrometer (Kratos Analytical Ltd.) using monochromatic AlK$_\alpha$ radiation with photon energy of 1486.6eV. The energy calibration was performing by normalizing the C1s line of adsorbed adventitious hydrocarbons to 285.0eV. The binding energies (BE) were determined with an accuracy of ±0.1eV. The chemical compositions of the films were determined monitoring the areas and binding energies of C1s, O1s, Ti2p and N1s photoelectron peaks. Using the commercial data-processing software of Kratos Analytical Ltd. the concentrations of the different chemical elements (in atomic %) were calculated by normalizing the areas of the photoelectron peaks to their relative sensitivity factors.

The morphology of the titanium surface irradiated by the third harmonic of Nd:YAG laser was observed by scanning electron microscopy (SEM) using a Philips SEM-515 electron microscope.

3. Results

3.1. SEM results

Figure 1 shows SEM images of the surface of the irradiated Ti targets with the nanosecond laser pulses under atmospheric pressure in air. The laser irradiation causes a change in the surface morphology due to the processes of melting and subsequent solidification. SEM studies showed that laser beam velocity determine the Ti morphology evolution under pulsed laser irradiation. In air, the vaporized titanium particles from the plume react with O$_2$ and water vapor, this resulting in formation of oxide nanoclusters. These clusters then are deposited on the surface, which becomes less flat at a submicron level.
Morphology of the ablated surface depends strongly on number of pulses over focal spot. This can be calculated by \( N = \frac{d.f}{V} \) and varied from 3 for 320 mm/s to 200 for 5 mm/s. It is visible on micrographs that the laser ablation increases when \( N \) is increasing, that means for slower scanning velocity (see figure 1d). In air, the vaporized titanium particles from the plume react with \( O_2 \) and water vapor, this resulting in formation of oxide micro and submicro clusters. But main part of microclusters are formed by solidification of melted titanium. The result of this process is visible mainly on figure 1a, b achieved at higher scanning velocity.

### 3.2. XPS studies

The surface composition and chemical state of the titanium wafers exposed to laser irradiation have been investigated by XPS. The analysis shows a presence of C, O, Ti and less amount of N on the surface of plates. The XPS spectra of titanium is well known in literature. Typical peaks and the values for binding energy are available in table 1.

| Core level | Binding energy (eV) |
|------------|---------------------|
| Ti2s       | 561.4               |
| Ti2p1/2    | 460.8               |
| Ti2p3/2    | 454.7               |
| Ti3s       | 59.1                |
| Ti3p       | 34.0                |
| O1s        | 531.4               |
| O2s        | 23.5                |

**Table 1.** XPS binding energies of untreated titanium.
One typical spectra for treated Ti surface and the same for untreated we presented on figure 2. The XPS analysis indicated that the O/Ti atomic ratio is in the range of (2.6-3.1), which was calculated by the peak areas of the O1s and Ti2p3/2, normalized by the corresponding photoionization cross–sections. The value of O/Ti ratio increase with the increasing of the scanning velocity of the laser beam.

Table 2. The calculated concentrations of chemical elements on the surface after laser treatment with scanning velocity from 5mm/s to 1280mm/s.

| scanning velocity | C [at. %] | O [at. %] | Ti [at. %] | N [at. %] | O/Ti |
|-------------------|-----------|-----------|------------|-----------|------|
| 5mm/s             | 46.1      | 38.6      | 15.0       | 0.3       | 2.6  |
| 40mm/s            | 48.4      | 36.7      | 14.4       | 0.5       | 2.6  |
| 80mm/s            | 51.4      | 34.4      | 13.4       | 0.8       | 2.6  |
| 160mm/s           | 51.1      | 34.9      | 13.0       | 1.0       | 2.7  |
| 320mm/s           | 53.5      | 33.5      | 12.1       | 0.9       | 2.8  |
| 640mm/s           | 61.6      | 28.1      | 9.7        | 0.6       | 2.9  |
| 1280mm/s          | 67.1      | 24.4      | 7.9        | 0.6       | 3.1  |

We recorded the Ti2p and O1s core level spectra. The binding energies of the Ti2p and O1s lines give information about the oxidation state of the titanium targets. Figure 3 shows the O1s core level spectra of titanium wafers. The O1s peaks are wide with an asymmetric shoulder. They are deconvoluted by Lorentzian–Gaussian curve fitting into two components at 530.0eV and 531.8eV, respectively (figure 4). The first component with the lower binding energy is attributed to O2− ions in the TiO2 lattice and the second one with the higher binding energy is ascribed to oxygen atoms in hydroxyl groups [5].
Figure 3. O1s core level spectra on the surface of the titanium wafers.

Figure 4. Deconvolution of O1s peak treated with beam velocity 5mm/s.

Figure 5 shows the Ti2p core level spectra of titanium plates prepared with different velocities of the laser beam. The Ti2p spectra are symmetric with a maximum at 458.6eV. Ti2p peak has significantly split spin-orbit components (Δmetal=6.1eV). Splitting-value varies with chemical state (Δnitride=6.0eV, Δoxide=5.7eV). Typically FWHM for each spin-orbit component is the same, but for Ti2p the Ti2p<sub>1/2</sub> component is much broader than the Ti2p<sub>3/2</sub> peak. Post-ionization, Ti2p<sub>1/2</sub> state is very short lived compared to Ti2p<sub>3/2</sub> state.

The observed peak position, the doublet separation between the 2p<sub>1/2</sub> and 2p<sub>3/2</sub> peaks of ~5.7eV and the satellite at 14eV from the main peak are characteristic of TiO<sub>2</sub>. 
4. Conclusion

XPS analysis indicated that the treatment with UV laser leads to formation of oxide layer on the surface of the plates. The oxide layer covered by hydroxyl species is formed by O$_2$ and water vapor present in air. The TiO$_2$ layer is nonstoichiometric which was proved by the calculation of the O/Ti atomic ratio.

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