

NANOSTRUCTURES

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Surface nanotexturing of tantalum by laser ablation in water

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Abstract. **Surface nanotexturing of tantalum by ablation with short laser pulses in water has been studied experimentally using three ablation sources: a neodymium laser with a pulse duration of 350 ps, an excimer laser (248 nm) with a pulse duration of 5 ps and a Ti : sapphire laser with a pulse duration of 180 fs. The morphology of the nanotextured surfaces has been examined using a nanoprofilometer and field emission scanning electron microscope. The results demonstrate that the average size of the hillocks produced on the target surface depends on the laser energy density and is $\sim$ 200 nm at an energy density approaching the laser-melting threshold of tantalum and a pulse duration of 350 ps. Their surface density reaches 10^6 cm^{-2}. At a pulse duration of 5 ps, the average hillock size is 60 – 70 nm. Nanotexturing is accompanied by changes in the absorption spectrum of the tantalum surface in the UV and visible spectral regions. The possible mechanisms of surface nanotexturing and potential applications of this effect are discussed.**

Keywords: *laser ablation, surface nanotexturing.*

1. Introduction

The interaction of laser radiation with solids is accompanied by various instabilities, which may lead to the formation of surface textures. These are as a rule divided into large- and small-scale textures. The large-scale textures result from the capillary motion of the melt produced by laser pulses striking the target. Under ordinary conditions, their characteristic length scale is tens of microns. The length scale of the finer surface textures is of the same order as the laser wavelength, and they originate from the interference of the incident laser radiation and the electromagnetic wave photogenerated on the surface of the solid. The resulting interference pattern is stationary because the waves are in phase, and the corresponding surface morphology is determined by a variety of processes (oxidation, sublimation, and others), whose rate is temperature-dependent.

Laser ablation of solids in liquids is also accompanied by surface texturing of the target, but this is due to other mechanisms because the liquid adjoining the melt on the target surface undergoes a phase transition. Sufficiently high laser energy densities give rise to surface melting of the target, solid at room temperature. As a result, its environment, liquid under normal conditions, vaporises. Sufficiently short pulses produce not only superheated liquid but also a zone of elevated pressure near the target, which may transfer the substance adjoining the target to a supercritical state. The pressure wave interacts with the melt layer on the target surface, changing its configuration. At a pulse duration below 1 ns, this viscous interaction leads to nanotexturing of the solid surface. Nanotextures were first observed on silver [1] and then on gold [2], after laser ablation of Ag and Au targets in some liquids. Nanotexturing is accompanied by changes in the absorption spectrum of the target: additional bands emerge near the plasmon resonances of metal nanoparticles.

At the present stage, surface nanotexturing in response to the ablation of targets with short laser pulses in liquids defies theoretical interpretation. To handle this complicated problem, one must jointly solve the heat equation and the Navier – Stokes equation for hydrodynamic flow when the two media in contact, a metal and a liquid, undergo phase transitions. Therefore, accumulation of experimental data on surface nanotexturing of various materials is of interest per se. In view of this, in the present study tantalum was used as target material.

Another reason is that tantalum possesses unique physicochemical properties. This refractory metal, with a melting point of $\sim$ 3000 °C, offers high chemical stability. Its natural oxide, Ta_2O_5, has high electric strength and passivates the metal surface, preventing oxidation even at elevated temperatures. These advantages make tantalum an attractive material for a variety of applications: from medical to microelectronic.

The objective of this work was to produce surface nanostructures on tantalum by ablation with picosecond laser pulses in water and to study their morphology in relation to process parameters.

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2. Experimental

As targets we used 100-μm-thick tantalum plates. Prior to irradiation, the targets were abrasively ground or polished to the desired surface quality and placed on the bottom of a glass cuvette, which was then filled with water.

To produce nanostructures on tantalum, three ablation sources were used. One of them was a 1.064-μm pulsed Nd : YAG laser (pulse duration is 350 ps; repetition rate is 300 Hz). The cuvette was then mounted on a computer-controlled stage which ensured a constant translation velocity. Another source was a KrF laser (248 nm) with a pulse duration of 5 ps and repetition rate of 10 Hz, which was used for stationary irradiation. The third source was a Ti : sapphire laser operating at a repetition rate of 1 kHz (180-fs pulses at 800 nm).

In all cases, the laser beam was focused onto the target through a water layer several millimetres in thickness. The spot area was determined from the dimensions of the modified zone.

The surface morphology of the Nd : YAG irradiated target was examined using an NPX 2000 nanoprofilometer/atomic force microscope (AFM), and that of the other targets was examined with a field emission scanning electron microscope. The absorption spectra of nanotextured tantalum were measured with a Shimadzu UV-3600 spectrometer in a specular reflection mode and with a Perkin – Elmer integrating sphere spectrometer.

3. Experimental results and discussion

Figure 1 illustrates the initial surface morphology of the tantalum targets. The surface was abrasively polished and had an rms roughness value of about 50 nm. The surface morphology of tantalum after ablation with 350-ps Nd : YAG pulses in water is illustrated in Fig. 2. The surface of the tantalum target is covered with nanohillocks 200 – 250 nm in height. Their lateral size depends on the laser energy density delivered to the target surface. To assess this effect, we measured the average lateral size of the nanohillocks as a function of energy density. As seen in Fig. 3, with decreasing energy density the average size of the nanohillocks drops to 200 – 300 nm, and the percentage of hillocks on the order of 1 μm in lateral size markedly decreases. After KrF laser irradiation, the average lateral size of the nanohillocks was about a factor of 5 smaller. A general view of the surface is presented in Fig. 4a.

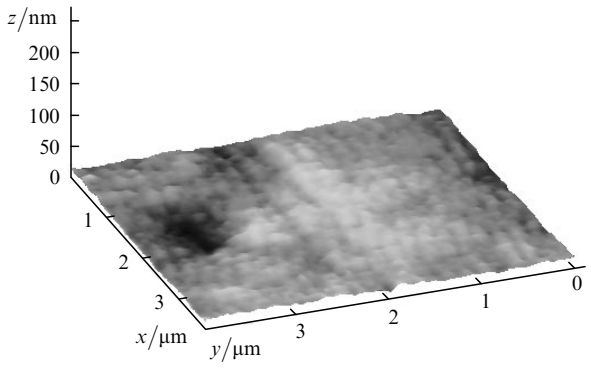


Figure 1. AFM image of an unirradiated tantalum target.

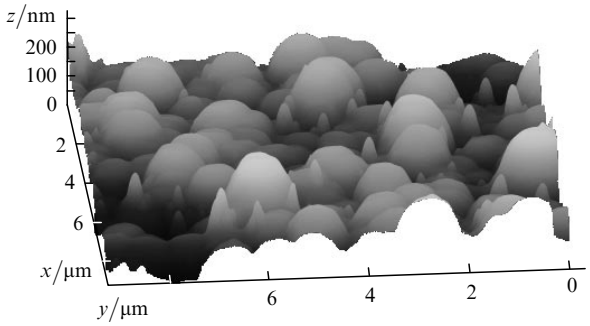


Figure 2. AFM image of a tantalum target irradiated through a water layer to an energy density of 0.31 J cm^{-2}. Pulse duration, 350 ps; wavelength, 1.06 μm.

Note that laser ablation in water significantly increases the surface area of the target. The surface density of nanohillocks as estimated from Fig. 4 is 10^6 cm^{-2}. Laser ablation produces not only elevations but also numerous depressions, valleys etc. Each nanohillock is surrounded by four to six pits with nearly hexagonal symmetry (in Fig. 4b the centres of six pits are marked by a hexagon). It seems likely that the hillocks grow by drawing the melt from the neighbouring pits. This is indirectly evidenced by the presence of solidified metal jets ending with a rounded droplet (Fig. 4a). The symmetric arrangement of the pits around nanohillocks in Fig. 4b seems to result from the symmetry of the superheated water vapour flows over the melt surface, which are generated by each laser shot and persist for some time thereafter [1]. The melting point of tantalum is $\sim 3000\,^{\circ}$C, and the water layer adjoining the melt is also flashed to this temperature. The melt moves from pits to the centre of symmetry by virtue of viscous interaction and then solidifies, as evidenced by the smooth surface of the nanohillocks. Their smooth domes suggest that dissolution of the target material in supercritical water, if at all occurs, contributes little to nanotexturing. Indeed, if tantalum were partially dissolved in supercritical water, precipitation of the dissolved material from the super-

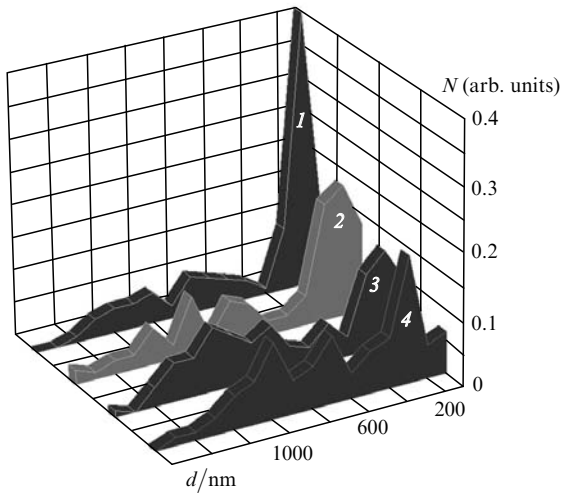


Figure 3. Lateral size (d) distribution for nanostructures on the tantalum surface irradiated with 350-ps laser pulses through a water layer to an energy density $J = 0.29$ (*1*), 0.36 (*2*), 0.43 (*3*) and 0.45 J cm^{-2} (*4*).

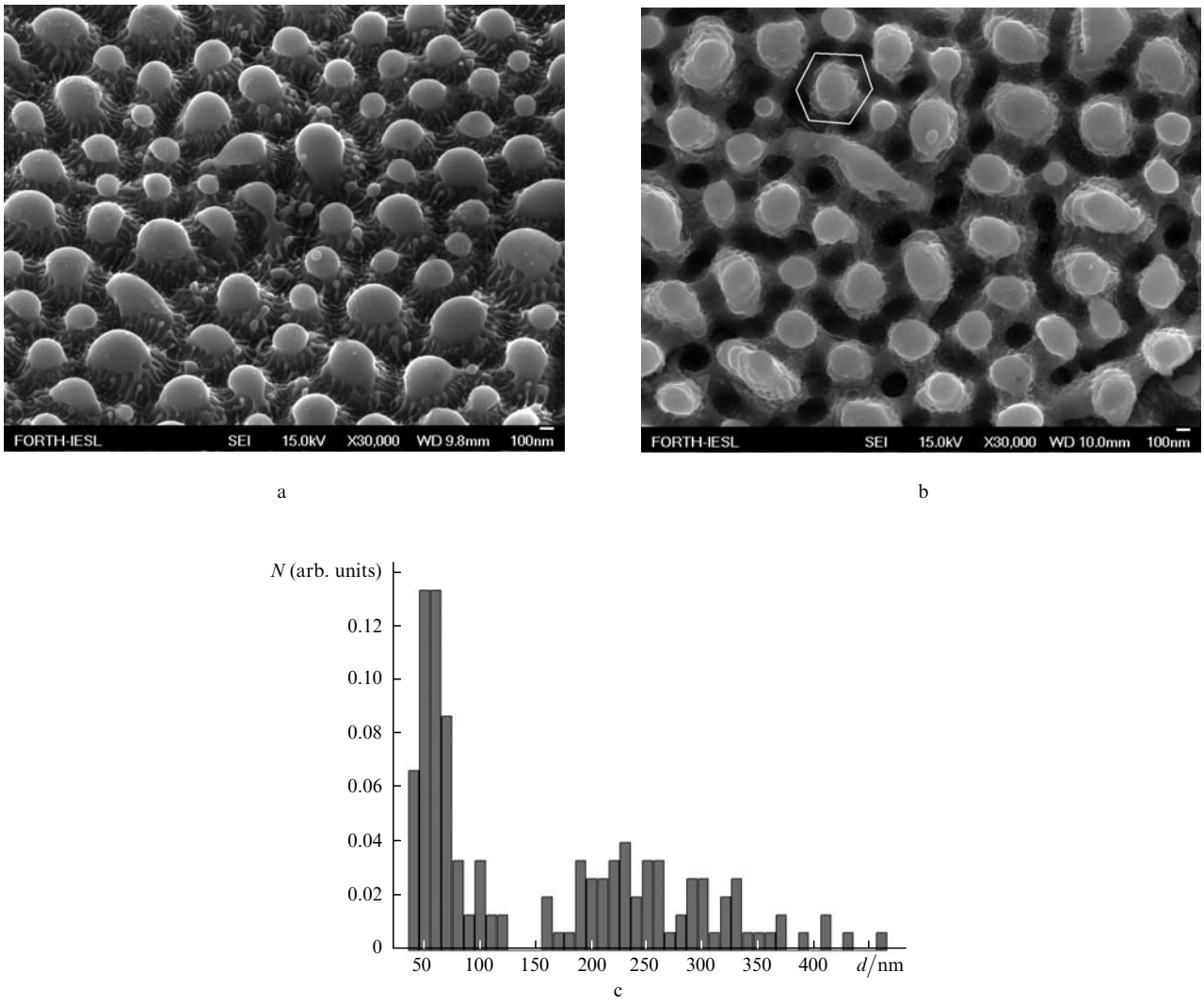


Figure 4. Nanotextured tantalum surface after irradiation with 5-ps, 248-nm laser pulses: (a) general view, (b) normal incidence image. (c) Lateral size (d) distribution for the nanostructures.

saturated aqueous solution after cooling would result in dendritic morphology and not in smooth shapes. Moreover, dissolution in pure supercritical water occurs more slowly than in aqueous solutions of salts and alkalis, as was demonstrated for sapphire dissolution via laser irradiation of its surface in contact with aqueous solutions [3].

The observed symmetric arrangement of the pits may be due to the development of instability at the interface between the superheated water and melt layer. Of all known instabilities, this effect is most similar to the Rayleigh–Taylor instability: the formation of periodic closed vortices in liquid placed between two rotating cylinders [4]. In the case under consideration, a pit on the target surface, which is far from being perfectly polished, may be an analogue of a cylinder. Another possible mechanism behind the symmetric arrangement of the pits is defect-strain instability which develops in response to multipulse laser ablation of the target [5]. Such instabilities, however, have no definite length scale, with a characteristic lateral size from 100 to 200 nm. They may develop concurrently with hydrodynamic instability at the melt–superheated water interface. Thus, the mechanism of the nanotexturing induced by laser ablation in liquids remains unclear.

It is worth noting that field emission scanning electron microscopy provides more detailed images of nanotextures in comparison with AFM images.

Figure 5 shows nanostructures produced on tantalum by Ti : sapphire laser ablation. Note small-scale periodic structures that originated from the interference of the incident laser beam and the surface electromagnetic wave generated by it.

Given that surface nanotexturing of silver and gold produces changes in their absorption spectra [1, 2], we measured the absorption spectra of tantalum surfaces before and after laser ablation. The spectra of nanotextured tantalum contain peaks near the calculated position of the plasmon resonance of tantalum nanoparticles. The peak positions calculated for 10-nm tantalum particles are about 280 and 640 nm [6], whereas we observe peaks in the ranges 280–300 and 620–640 nm, depending on the laser ablation parameters (Fig. 6). By analogy with previous data on surface nanotexturing of silver [1], this coincidence can be understood in terms of plasmon oscillations in nanostructures on the surface of the tantalum target. It is not surprising that the observed peak positions differ slightly from the calculated ones because the size of the

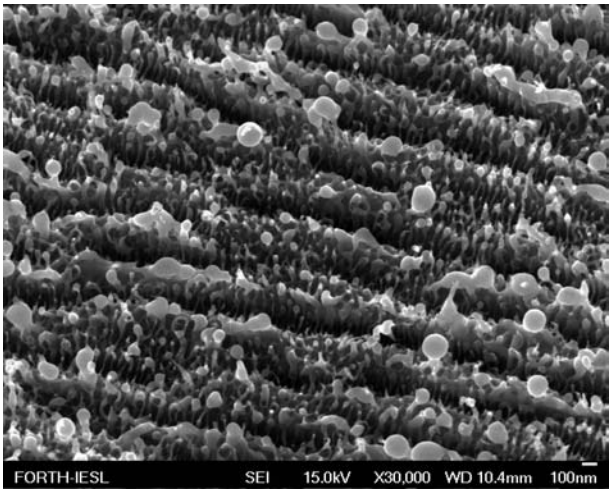


Figure 5. Surface morphology of tantalum after exposure to femtosecond laser pulses.

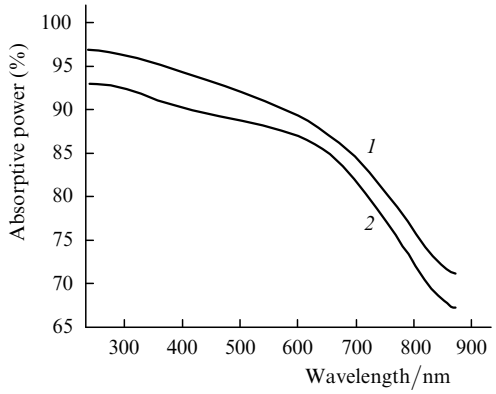
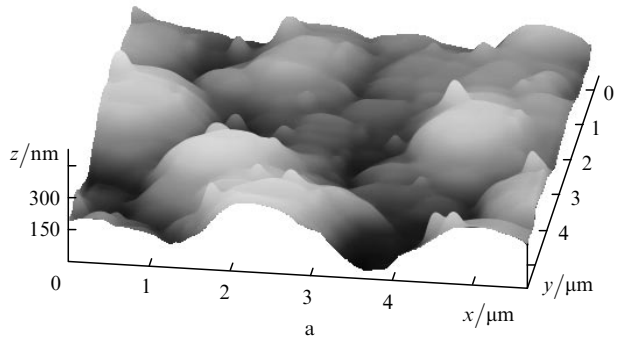


Figure 6. Absorption spectra of (*1*) an unirradiated tantalum surface and (*2*) a nanotextured surface produced by 350-ps, 1.06-μm laser pulses. The spectra are normalised to the absorption spectrum of polished aluminium.

nanohillocks on tantalum substantially exceeds 10 nm. The presence of both small-scale periodic structures and nanostructures typical of ablation in liquids clearly demonstrates that they differ in origin.

It can be seen in micrographs that many nanohillocks have a small spike on top. Similar morphologies were observed earlier on the surface of some metals after ablation in liquids. Figure 7 compares nanotextures on tantalum and tungsten surfaces, the latter after ablation with 20-ns copper vapour laser pulses in ethanol [7]. The formation of tungsten nanospikes (Fig. 7b) was attributed to the melt flowing along the surface of the microcones under the action of the vapour of the liquid heated by the target surface. Clearly, a similar process occurs on a considerably smaller length scale, comparable to the size of the nanostructures studied. The melt is forced out from the pits surrounding a hillock and spreads over the lateral surface of the latter, reaching its top. At a sufficiently high energy density, the melt layer is rather thick, and part of it may separate from the target surface to form nanoparticles in the liquid [8].



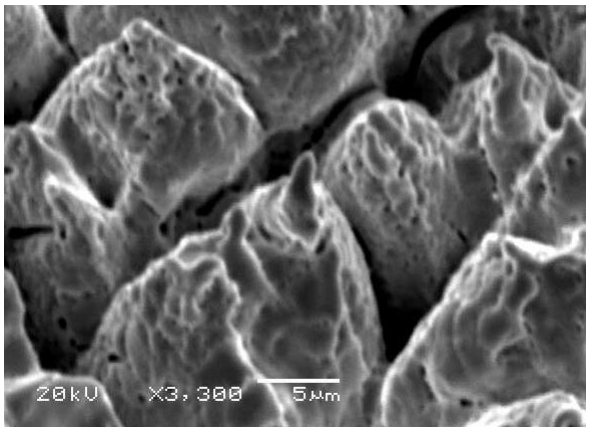


Figure 7. Surface morphologies of tantalum and tungsten after ablation in liquids at different laser pulse durations: (a) Ta, 350 ps, water, this work; (b) W, 20 ns, ethanol [7].

4. Conclusions

Surface nanotexturing of tantalum by ablation with short (180 fs to 350 ps) laser pulses in water was studied experimentally. The characteristic size of the resultant hillocks is ~200 nm at a pulse duration of 350 ps and 60–70 nm at a pulse duration of 5 ps, and depends not so much on the laser wavelength as on the laser energy density on the target. A typical surface density of hillocks is 10^6 cm^{-2}. Ablation of tantalum with femtosecond pulses produces not only nanohillocks but also small-scale periodic structures with a period comparable to the laser wavelength. The nanotexture produced on tantalum gives rise to additional UV and visible bands in the absorption spectrum of the target. Their position is well described in terms of the plasmon resonance in nanotextured tantalum. Surface nanotexturing of tantalum via laser ablation in liquids is of interest for medical, electronic, and other applications.

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