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Applied Surface Science 252 (2005) 474–482
applied surface science
www.elsevier.com/locate/apsusc

Surface modifications of TiN coating by pulsed TEA CO_2 and XeCl lasers

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Received 14 September 2004; accepted 22 January 2005
Available online 5 March 2005

Abstract

Interactions of a transversely excited atmospheric (TEA) CO_2 laser and an excimer XeCl laser, pulse durations ~2 μs (initial spike FWHM ~100 ns) and ~20 ns (FWHM), respectively, with polycrystalline titanium nitride (TiN) coating deposited on high quality steel AISI 316, were studied. Titanium nitride was surface modified by the laser beams, with an energy density of 20.0 J/cm^2 (TEA CO_2 laser) and 2.4 J/cm^2 (XeCl laser), respectively. The energy absorbed from the CO_2 laser beam is partially converted to thermal energy, which generates a series of effects such as melting, vaporization of the molten material, shock waves, etc. The energy from the excimer XeCl laser primarily leads to fast and intense target evaporation. The calculated maximum temperatures on the target surface were 3770 and 6300 K for the TEA CO_2 and XeCl lasers, respectively. It is assumed that the TEA CO_2 laser affects the target deeper, for a longer time than the XeCl laser. The effects of the XeCl laser are confined to a localized area, near target surface, within a short time period.

Morphological modifications of the titanium nitride surface can be summarized as follows: (i) both lasers produced ablation of the TiN coating in the central zone of the irradiated area and creation of grainy structure with near homogeneous distribution; (ii) a hydrodynamic feature, like resolidified droplets of the material, appeared in the surrounding peripheral zone; (iii) the process of irradiation, in both cases, was accompanied by appearance of plasma in front of the target.

Target color modifications upon laser irradiation indicate possible chemical changes, possibly oxidation.

Keywords: Laser surface modification; TiN coating; Grainy microstructure; Pulsed TEA carbon-dioxide laser; Pulsed excimer XeCl laser

1. Introduction

Surface modification studies of titanium-based ceramic coatings, especially titanium nitride (TiN) deposited on steel substrates, by various types of

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doi:10.1016/j.apsusc.2005.01.029

energetic beams, including laser beam, are of great fundamental and technological interest. The last decade saw most of the studies of laser beam interaction with titanium nitride. Beams of the ruby- [1], Nd:YAG- [2], Ti:sapphire- [3], excimer XeCl-[4], and CO_2- [5,6] lasers have so far been employed for this.

Interaction of pulsed TEA CO_2 or XeCl laser beams with titanium nitride are not extensively reported in literature [4–7]. Titanium nitride has extraordinary physical and chemical properties, like high melting point, thermodynamic stability, high hardness, etc. [8]. It is thus used in many applications (e.g. microelectronics, tool protection, sensor technologies, etc.), and is very attractive in nuclear technology. The quality of fusion plasma in a thermonuclear device depends not only of the reactor design, but also on proper selection of the reactor vessel wall material, especially the plasma facing materials [9]. High quality steels, like austenitic stainless steel, can be used as plasma facing materials. These materials must be additionally protected by coatings. Oxides, nitrides and borides have recently been considered as suitable materials for this purpose [9]. Titanium nitride is a serious candidate in that respect, as a refractory transition metal nitride with excellent properties.

The present paper deals with effects of a pulsed TEA CO_2 laser emitting in the IR region (~10 μm) and a XeCl excimer laser in the UV region (0.308 μm) on polycrystalline titanium nitride coatings deposited on high quality steel AISI 316. Special attention was paid to morphological surface modifications of TiN. Studies presented here are strongly complementary with investigations presented in Ref. [10].

2. Experimental

The TiN coatings (thickness 1 μm, typically) used in the experiment were deposited on a steel substrate via a plasma assisted vacuum process [11] as a shift from our recently published studies [4,10] where a reactive dc magnetron sputtering was applied. The substrate (steel type AISI 316) was prepared by the standard metallographic procedure. This included polishing, rinsing and drying. Bulk dimensions of rectangularly shaped substrates were typically 20 mm × 12 mm × 2 mm.

Sample irradiations were performed with laser beams focused by a KBr/quartz lens, for the TEA CO_2/XeCl laser radiation, focal lengths 6.0 and 10 cm, respectively. In the case of the XeCl laser, a 5 mm diameter aperture diaphragm placed in front of the quartz lens was used to form a circular laser spot on the target surface. The angle of incidence of the laser beam with respect to the surface plane was 90°. The irradiation was carried out in air, at a pressure of 1013 mbar and relative humidity of 60%.

The TEA CO_2 laser was operated in the transverse fundamental mode or the multimode regime, whereas XeCl laser was operated only in the fundamental mode. Conventional (1 atm) $CO_2/N_2/He$ gas mixtures were used for the TEA CO_2 laser [12] yielding pulses with a gain switched peak followed by a slowly decaying tail, see Fig. 1(A). The XeCl excimer laser was operated with typical HCl/Xe/Ne gas mixtures

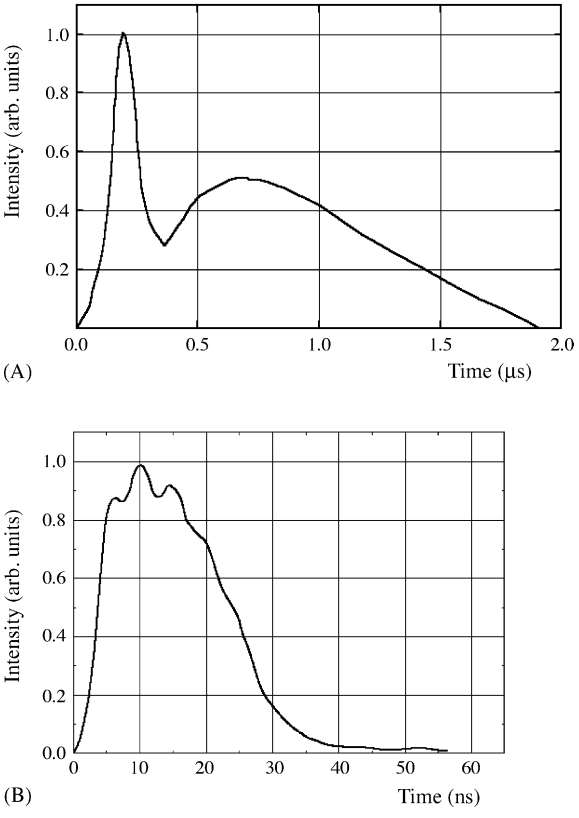

Fig. 1. Temporal shape of the TEA CO_2 (A) and XeCl (B) laser pulses: horizontal scale, 0.5 μs/div (A) and 10 ns/div (B); FWHM, ~100 ns (of the first peak) and ~20 ns, respectively.

Table 1
Typical experimental conditions used for TEA CO_2 and XeCl laser

	Type of laser system	
	TEA CO_2 laser	XeCl laser
Gas mixture	$CO_2/N_2/He$	HCl/Xe/Ne
Operational gas mixture pressure (atm)	1	3
Output pulse energy (mJ)	To 85	To 16
FWHM[a] (ns)	~100 (initial spike)	~20
Mode structure	TEM_{00}/multimode	TEM_{00}
Peak power density (MW/cm^2)	To 120	To 123
Spectral emission[b] (μm)	10.5709 and 10.5909	0.308

[a] Full width at a half maximum. The TEA CO_2 laser pulse, for difference from XeCl system, consists of an initial spike and a tail. The tail duration is about 2 μs.
[b] Only the TEA CO_2 laser simultaneously operates at two wavelengths, i.e. 10.5709 and 10.5909 μm, P(18) and P(20) transitions.

[13] at pressure of 3 atm. A typical shape of the laser output pulses is given in Fig. 1(B). Detailed characteristics of the lasers used in the experiments are given in Table 1.

Various analytical techniques were used for characterization of the samples. X-ray diffraction (XRD) was employed for identifying crystal phases, growth orientation, etc. Surface morphology was monitored by optical microscopy (OM) and by scanning electron microscopy (SEM) with secondary electron (SE) and back-scattered electron (BSE) detectors. The profilometer was used to characterize surface roughness as well as topographic changes of the irradiated area. Reflectivity of the coating in the infrared spectral region was measured by an infrared spectrophotometer prior to laser action.

3. Results and discussion

X-ray analysis of the TiN coating prior to laser irradiation confirmed its polycrystalline structure. The coating showed a cubic B1 structure of the NaCl-type. Cross-section analysis of the coating has shown columnar crystal structure. The TiN coating had a stoichiometric composition of [Ti]/[N] = 1.

Laser-induced TiN morphological changes showed dependence on beam characteristics: primarily on the energy density, peak power density, pulse duration, number of pulses and wavelength.

Morphological changes of the TiN for 120 and 500 accumulated TEA CO_2 laser pulses are presented in

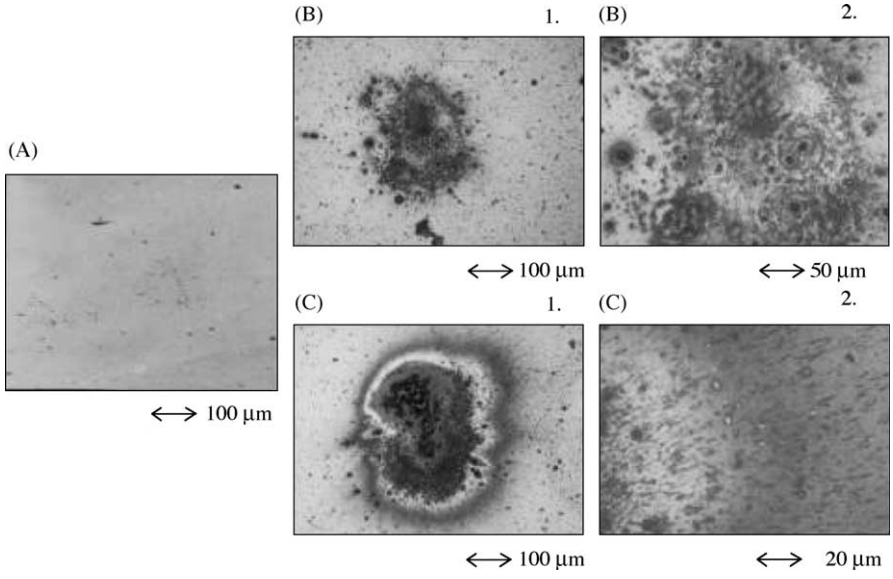

Fig. 2. TEA CO_2 laser-induced morphology changes of TiN coating (thickness, 1 μm)/steel AISI 316. Analysis was carried out by optical microscopy. Laser was operating in TEM_{00} mode; pulse with tail (Fig. 1A); energy density, 20 J/cm^2: (A) the view of TiN coating prior laser action; (B) TiN coating after 120 laser pulses action ((1, 2) represents entire spot and part of damage area, respectively); (C) TiN coating after 500 laser pulses action ((1, 2) represents entire spot and periphery of damage area, respectively).

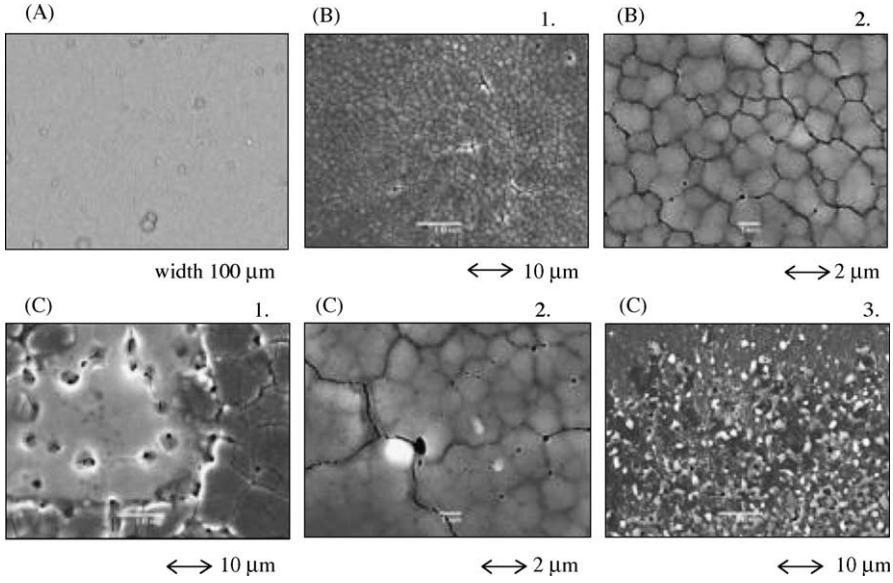

Fig. 3. TEA CO_2 laser-induced morphology changes of TiN coating (thickness, 1 μm)/steel AISI 316. Analysis was carried out by scanning electron microscopy. Laser was operating in TEM_{00} mode; pulse with tail (Fig. 1A); energy density, 20 J/cm^2: (A) the view of TiN coating prior laser action; (B) TiN coating after 120 laser pulses action ((1, 2) the center of the damage area – different magnification); (C) TiN coating after 500 laser pulses action ((1, 2) the center of the damage area – different magnification and (3) periphery of the damage area).

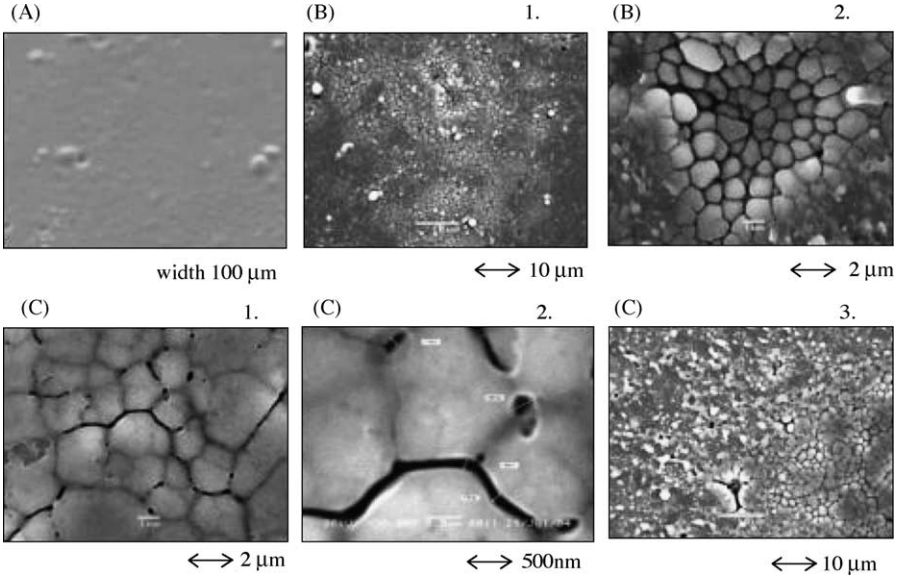

Fig. 4. TEA CO_2 laser-induced morphology changes of TiN coating (thickness, 3 μm)/steel AISI 316. Analysis was carried out by scanning electron microscopy. Laser was operating in TEM_{00} mode; pulse with tail (Fig. 1A); energy density, about 20 J/cm^2: (A) the view of TiN coating prior laser action; (B) TiN coating after 120 laser pulses action ((1, 2) the center of the damage area – different magnification); (C) TiN coating after 500 laser pulses action ((1, 2) the center of the damage area – different magnification and (3) periphery of the damage area).

Figs. 2–4, and for 1, 20 and 500 XeCl laser pulses in Figs. 6 and 7. Laser radiation energy densities of 20.0 J/cm^2 (TEA CO_2 laser) and 2.4 J/cm^2 (XeCl laser) induce significant surface modifications of the TiN surface. The induced modifications can be presented as follows.

3.1. The TEA CO_2 laser

After 120 and 500 pulses at 20.0 J/cm^2 (Figs. 2, 3B and C) the damage of the TiN coating can be clearly recognized. In the central part of the damaged area cracks were typically found, along with appearance of a grainy structure, Fig. 2B(1) and C(1), and Fig. 3B(1, 2) and C(1, 2). On the periphery of the damaged zone hydrodynamic effects become visible after about 500 accumulated pulses, Fig. 2C(2) and 3C(3). After 500 pulses (Figs. 2 and 3), the effects can be summarized as follows: (i) ablation of the TiN coating in the interaction area, (ii) forming of a grainy structure in the central zone and cracking of the TiN thin film and (iii) appearance of three almost concentric outer damage zones with hydrodynamic features like resolidified droplets of the material. Similar modifications were also reported in our previous paper [10], although, apart from the 1 μm thickness of the sample, all other conditions were different, e.g. energy density and the method of film deposition.

Distribution of the grainy structure was near uniform for the sample with a TiN thickness of 1 μm (Fig. 3B(1, 2) and C(2)). Irradiation of a thicker, 3 μm, TiN film sample with similar laser energy density leads to a non-homogeneous distribution of the grainy structure, Fig. 4B(1, 2) and C(1). The average diameter of the grain, Figs. 3 and 4, was estimated to be about 1 μm with a tendency of forming tandems. The widths of the cracks were estimated at about 200 nm in the case of the 3 μm thick sample, Fig. 4C(2).

The process of the TEA CO_2 laser interaction with the TiN coating during the first pulses was not accompanied by any appearance of plasma in front of the target. A form of spark-like plasmas started appearing after about 30 cumulated pulses.

Generally, the energy absorbed from the TEA CO_2 laser beam is assumed to be converted to thermal energy, which causes melting, vaporization of the molten material, dissociation or ionization of the vaporized material and shock waves in the vapor and the solid. Surface temperature as a function of time for the laser pulse shape used (Fig. 1(A)) was calculated by Eq. (1) of our Ref. [10], i.e. Eq. (2) of Ref. [14]. The equation comprises absorptivity, A, specific heat, c, thermal diffusivity, κ, target density, ρ, and the laser beam intensity, I. It was solved numerically. For a given TEA CO_2 laser pulse shape with I_{max} = 120 MW/cm^2 and an absorptivity of A = 0.09 the calculation yields a temporal temperature evolution shown in Fig. 5. After the first peak of about 0.2 μs the temperature slightly decays before reaching a maximum of 3770 K, approximately after 1.2 μs. It follows that the laser energy contained in the tail essentially affects surface modification of the target. It is interesting to note that the maximum temperature is greater than the decomposition temperature of TiN, which is about 3220 K.

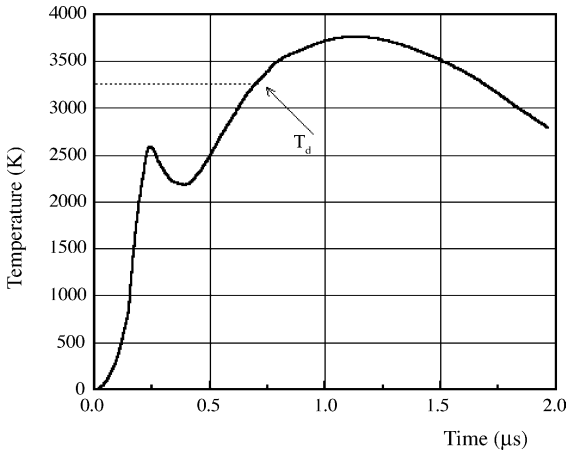

Fig. 5. Surface temperature variation of a sample during irradiation process with TEA CO_2 laser (T_d denotes the decomposition temperature of the TiN coating).

3.2. The XeCl laser

The XeCl laser radiation at an energy density (ED) of 2.4 J/cm^2 modified the TiN coating, although the ED was approximately, by a factor of 8, lower than that of the TEA CO_2 laser. Irradiation of TiN coatings with 500 accumulated laser pulses resulted in a more pronounced surface modification than obtained with 1 or 20 pulses, Fig. 6. Changes on the surface can be summarized as follows: (i) ablation of the TiN coating in the central zone, Fig. 6C and D(1), (ii) appearance of accumulation of material in the peripheral direction, particularly visible after 20 and 500

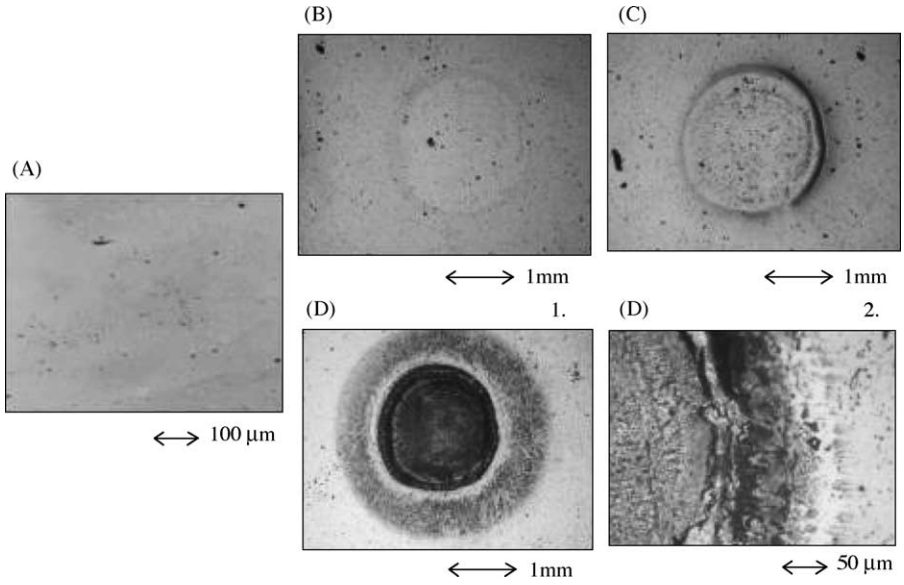

Fig. 6. XeCl laser-induced morphology changes of TiN coating (thickness, 1 μm)/steel AISI 316. Analysis was carried out by optical microscopy. Laser was operating in TEM_{00} mode; pulse width, 20 ns (FWHM, Fig. 1B); energy density, 2.4 J/cm^2: (A) the view of TiN coating prior laser action; (B), (C) and (D) TiN coating after 1, 20 and 500 laser pulses action, respectively. D(1) and D(2) entire spot and periphery of the damage area, respectively.

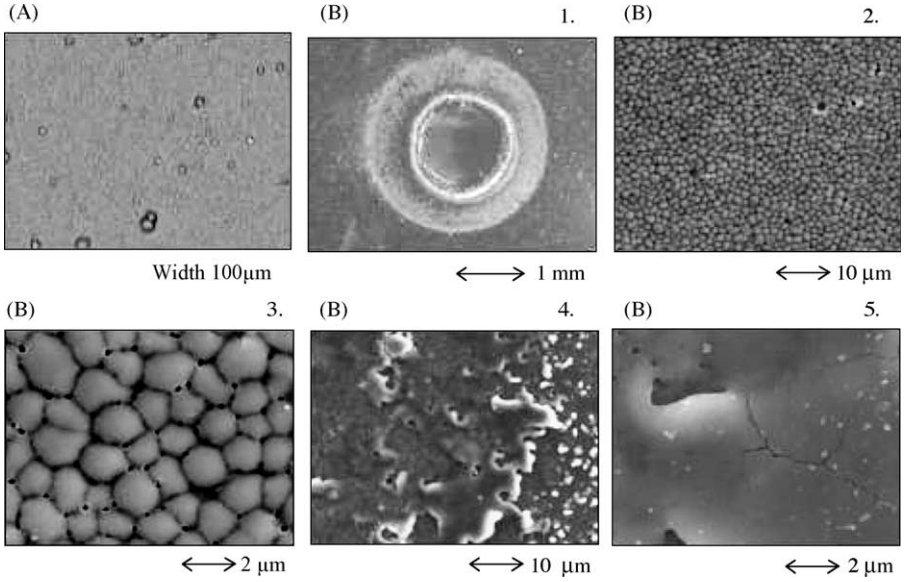

Fig. 7. XeCl laser-induced morphology changes of TiN coating (thickness, 1 μm)/steel AISI 316. Analysis was carried out by scanning electron microscopy. Laser was operating in TEM_{00} mode; pulse width, 20 ns (FWHM, Fig. 1B); energy density, 2.4 J/cm^2: (A) the view of TiN coating prior laser action; (B) TiN coating after 500 laser pulses action ((1) entire spot; (2, 3) center of the damage area – different magnification; (4, 5) periphery of the damage area – different magnification).

cumulated pulses, Fig. 6C and D(1), and (iii) appearance of four concentric damaged zones in the periphery with additional hydrodynamic features, Fig. 6D(2). In contrast to the KrCl laser action on the TiN coating [10], the XeCl laser did not produce periodic microstructures here. Analysis of the central zone of interaction, after 500 laser pulses, Fig. 7B(2) and B(3), showed a fine and homogeneous distribution of the grainy structure. An average diameter of the grain was about 2 μm. Hydrodynamic effects in the form of resolidified droplets of the material can be observed in Fig. 7B(4) and B(5).

The degree of TiN ablation obtained with the XeCl laser is presented in Fig. 8. It is evident that ablation was present upon irradiation with laser energy density of 2.4 J/cm^2. Depths of ablation for two TiN thicknesses of 1 and 3 μm are different. For the thickness of 1 μm, the average depth of ablation (ADA) was estimated at about 0.5 μm, Fig. 8(A), whereas it was about 0.8 μm for the 3 μm sample, Fig. 8(B). The efficiency of the energy transfer between the coating and the steel substrate material may be responsible for this behaviour. These results indicate that the ablation rate of the TiN coating was minimal, i.e. about 1 and 1.6 nm per pulse for TiN thicknesses of 1 and 3 μm, respectively.

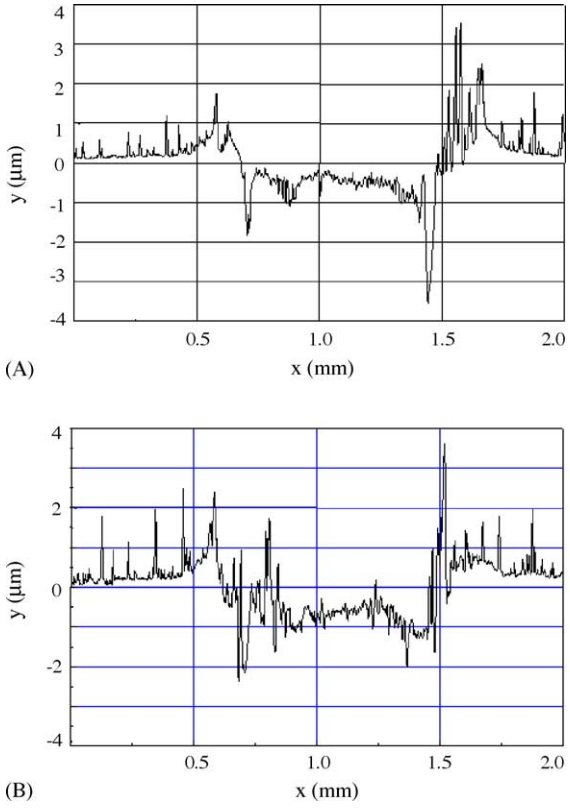

Fig. 8. Profilometry analysis of the damage area, after 500 laser pulses action, for the sample thickness of 1 μm (A) and 3 μm (B). TiN coating was deposited on AISI 316 substrate. XeCl laser; Laser was operating in TEM_{00} mode; pulse width, 20 ns (FWHM, Fig. 1B); energy density, about 2.4 J/cm^2.

It should be emphasized that under the present exposure conditions, XeCl laser causes ignition of plasmas already during the first and all subsequent laser pulses. The plasma appeared in the form of plasma jets.

Generally speaking, TiN pulsed irradiation with the XeCl laser (2.4 J/cm^2) yields better coupling of the laser energy with the target [15] than the TEA CO_2 laser (20.0 J/cm^2). This means also that higher sample surface temperatures are obtained. The XeCl laser irradiation of TiN results in a quick and intense target evaporation. It can also be assumed that the plasma, which appears above the target surface, contains target atoms and ions. Processes like multiphoton ionization, photoionization from excited states, etc. are responsible for plasma ignition [16].

The XeCl laser-induced TiN surface temperatures versus time were calculated using Eq. (1) of our Ref. [10], i.e. Eq. (2) of Ref. [14], as a function of the available energy density and pulse shape (Fig. 1(B);

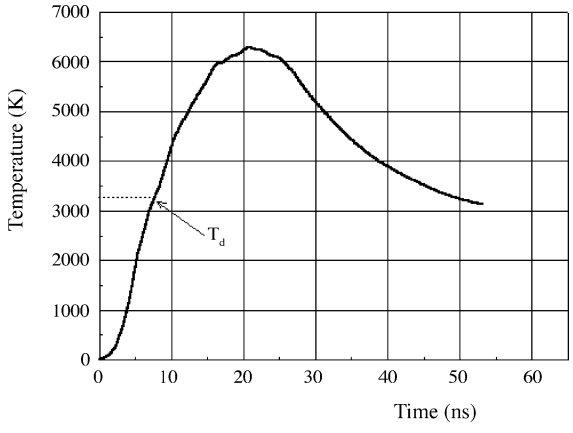

Fig. 9. Temperature surface variation of a sample during irradiation process with XeCl laser (T_d denotes the decomposition temperature of the TiN coating).

I_{max} = 122 MW/cm^2 and A = 0.6 [15]). The resulting plot of temperature versus time is presented in Fig. 9. A maximum of somewhat above 6300 K is achieved after about 21 ns (corresponding to about half of the pulse duration). The higher temperatures achieved with the XeCl laser than the TEA CO_2 laser are explained primarily by the almost six-fold higher absorptivity, i.e. much better coupling of XeCl laser radiation with target. This temperature, 6300 K, is lower in comparison to 8300 K obtained during KrCl laser irradiation. The main contribution can, in this case, be attributed to the much greater power density of the KrCl laser compared to the XeCl laser applied.

The main error in these calculations, as well as in our recently published paper [10], is introduced by the uncertainty concerning absorptivities, A. For TiN, A at 0.308 μm was estimated using data from Ref. [15].

4. Conclusion

A qualitative study of morphological changes on titanium nitride coatings deposited on high quality steel AISI 316, induced either by a TEA CO_2 laser or a XeCl laser is presented. It is shown that both lasers induce structural changes in the titanium nitride coating. Laser energy densities of 20.0 J/cm^2 in the case of the TEA CO_2 laser and 2.4 J/cm^2 with the XeCl laser system were found to be sufficient for inducing surface modifications of the samples.

The energy absorbed from the CO_2 laser beam is mainly converted into thermal energy, causing melting, vaporization and shock waves in the vapor and the solid-state material. Energy absorbed from the XeCl laser leads primarily to a quick and intense target evaporation. It can be assumed that the TEA CO_2 laser affects the target within a deeper zone than the XeCl laser due to the longer exposure time (pulse). In contrast, XeCl laser-induced target effects are localized and confined to the target surface and its vicinity. The temperatures of the target surfaces were calculated to be 3770 K for the CO_2 laser and 6300 K for the XeCl laser. It should further be recognized that different mechanisms were responsible for plasma formation above the target. In the case of the TEA CO_2 laser, the plasma was ignited similarly as in the case of gas breakdown. In the case of the XeCl laser, it was initiated and developed in the form of evaporated metallic vapor consisting of target atoms and ions.

Qualitatively, the morphological modifications of the TiN target can be summarized as follows: (i) for both laser types, ablation of the TiN coating in the central zone of the irradiated area was recorded, with creation of a grainy structure with near homogeneous distribution, (ii) appearance of a hydrodynamic feature, like resolidified droplets of the material, in the surrounding peripheral zone and (iii) the process of sample irradiation, in both cases, was accompanied by the appearance of plasma in front of the target.

Color modifications upon laser irradiation of the target indicate possible chemical changes, like oxidation.

Acknowledgements

This research was financially supported by the Ministry of Science and Environmental Protection of the Republic of Serbia, contract nos. 1995 and 2018, and as well as by ISTC (Russia), project no. 1206. The work is partially the result of cooperation in research in the field of gas lasers and their applications between Vinča Institute of Nuclear Sciences, Belgrade, Serbia and Montenegro, and the Institute of High Current Electronics (Siberian Branch, Russian Academy of Sciences), Tomsk, Russia (document no. 1629 of November 2001). The authors have benefited considerably from discussions with Prof. Š.S. Miljanić, Faculty of Physical Chemistry, University of Belgrade. We are also grateful to Prof. Dr. Peter Panjan and Dr. Miha Čekada from Jožef Štefan Institute, Ljubljana, Slovenia. Authors would like to thank Dr. N.N. Koval and Dr. I.M. Goncharenko from the Institute of High Current Electronics for carrying out of TiN film deposition.

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