TEA CO_2 Laser Surface Modification of Titanium Ceramic Thin Films

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ABSTRACT

The surface modification of titanium based ceramics thin films, induced by pulsed laser beam, was investigated in this work. Thin films of titanium nitride (TiN) and titanium diboride (TiB_2) were deposited on austenitic stainless steel substrate by two Physical Vapor Deposition (PVD) techniques and exposed in air atmosphere to a focused Transversely Excited Atmospheric (TEA) CO_2 laser irradiation. In these experiments two types of laser pulses have been used. One pulse was composed of an initial spike (FWHM = 120 ns) with a tail (duration about 2 microseconds) while the other contained only the initial spike (FWHM = 80 ns). Morphological changes of deposited ceramics, induced by successive laser pulses, have shown a dependence on the laser beam parameters (pulse energy, laser pulse duration, peak power density, number of pulses, etc.) and thin films characteristics. Thin films, investigated in this work, possessed reflectivity above 90% at wavelength of about 10 microns. Pulse peak power densities of 100 and 170 MW/cm^2 were used in these experiments and have induced the surface modifications of TiN and TiB_2 thin films. Depending on laser beam parameters, a change of color, grain growth, hydrodynamic effects, on TiN thin film were registered while on TiB_2 we noticed a change in color of the thin film, cracking and exfoliation.

Keywords: TEA CO_2, laser ablation, thin films, TiN, TiB_2, titanium ceramics.

1. INTRODUCTION

Titanium based ceramics possess excellent physico-chemical characteristics, such as, high melting and evaporation temperature, good chemical stability, high hardness, etc.[1,2]. Thin films and coatings of these ceramics, deposited on various substrates, retain similar properties. Furthermore TiN and TiB_2 thin films also exhibit good thermal and electrical conductivity. All these properties make TiN and TiB_2 thin films very attractive for various applications. The titanium diboride thin films have not been studied so frequently as titanium nitride. The investigations of laser beam interaction with thin films as well as their surface modifications are important not only for fundamental research, but equally so, for technological aspect. Laser interaction with materials could be described, in general, through the following stages: absorption of the laser beam-photon energy, transformation of this energy into radiative and/or nonradiative processes, desorption, fast heating and cooling of the target with or without damage, ablation, ejection of material from the interaction region and laser plasma formation [3-6].

Laser beam interactions with TiN thin films, deposited on various substrates, were studied in the papers 7-10. The most commonly used lasers for this purposes were Nd:YAG and excimer lasers[7-9]. The data of the interaction of TEA CO_2 laser beam with titanium diboride thin film deposited on steel substrate are insufficiently known in the literature.

The objective of this work was investigation of the surface modification of titanium-based ceramics, i.e. thin films of TiN and TiB_2 deposited on steel substrate, by pulsed TEA CO_2 laser – which emits infrared radiation of about 10 µm. Morphology changes of irradiated thin film surface were evaluated by means of optical and scanning microscopes

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(SEM, AFM). Special attention was devoted to monitoring of the surface morphology modification as a function of the laser pulse shape.

2. EXPERIMENTAL

Titanium based ceramic thin films, used in this work, were produced by physical vapor deposition (PVD) techniques, i.e. with: ion beam sputtering and direct evaporation technique. As substrates, for thin film deposition, high quality austenitic stainless steel was used. The substrates were of plate form with dimensions 2.5 cm x 1.3 cm x 0.2 cm (length x width x thickness). Before deposition, substrates were prepared by standard metalographycal procedure in order to obtain high quality layers with a low surface roughness. The TiN layer, thickness 850 nm, was deposited by Ar^+ ion sputtering of titanium target in the reactive atmosphere of nitrogen. The sputtering was performed in the SPUTTRON II BALZERS system[11]. The TiB_2 thin film was prepared[12] by direct electron beam evaporation of cold pressed powder in modified BAK BALZERS apparatus. The TiB_2 layer thickness was 800 nm.

The laser beam irradiation, Figure 1, of deposited TiN and TiB_2 thin films were performed with pulsed UV preionized TEA carbon dioxide laser.

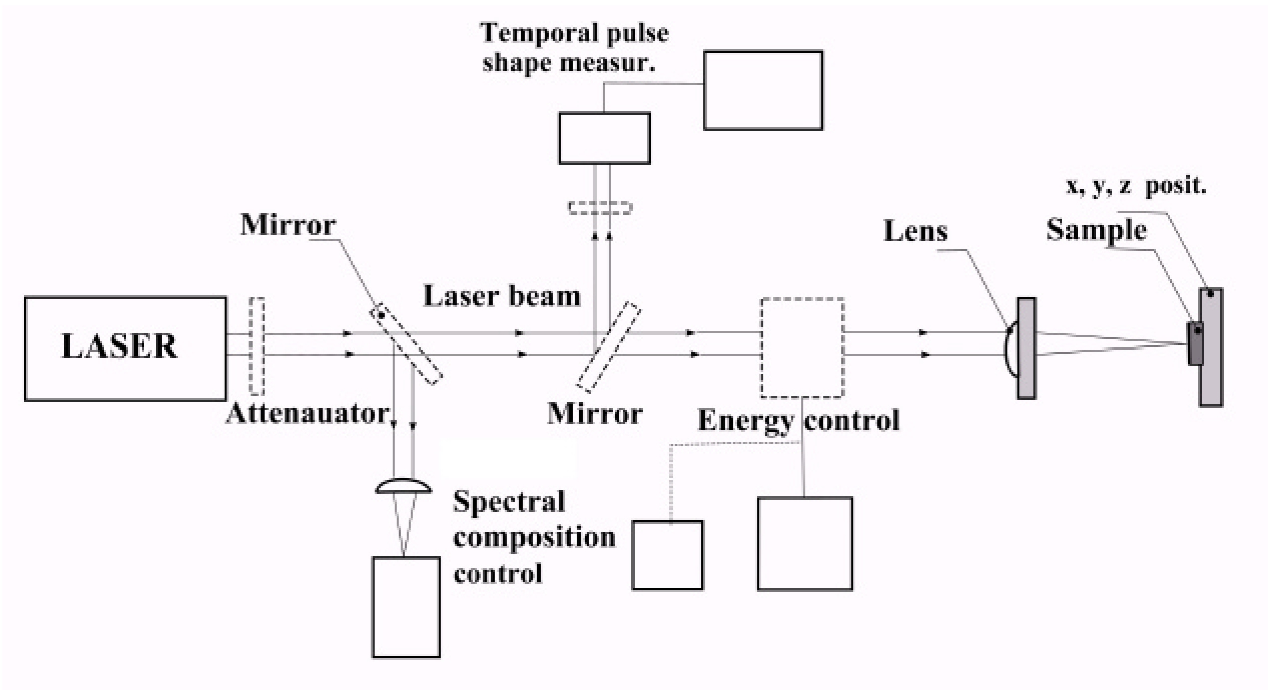


Figure 1. Experimental setup for TEA CO_2 laser surface modification of targets – TiN and TiB_2 thin films.

The samples were placed perpendicular to the incident laser beam, and before laser irradiation, the laser beam parameters were determined. For multi-pulse laser beam action the number of pulses per spot were varied. The targets were irradiated in air atmosphere; typically from 1 to 500 cumulative pulses were applied while, a peak power density was in the interval from 100 to 170 MW/cm^2. In the course of the experiment the laser pulse shapes were monitored by photon-drag detector, that output was connected to oscilloscope. Focusing of a laser beam on the target was done with NaCl lens, focal length of 6 cm.

The used laser, during experiment was running with non-typical gas mixtures[13] - ternary $CO_2/H_2/N_2$ or binary CO_2/H_2 - for difference of typically - ternary $CO_2/N_2/He$ and binary CO_2/He gas mixtures. In the case of ternary gas mixtures, the temporal shape of the pulse included a prominent first spike, followed by a tail of lower intensity. The full with of half maximum (FWHM) in the spike was 120 ns while, the tail duration was about 2 microseconds. This type of pulse was denoted as A-type. The absence of nitrogen, in binary gas mixture, results in a tail-free pulse with lasting of 80 ns (marked as B-type pulse). The laser runs in multymode regime. The beam cross-section is typically of quadratic form (1cm x 1cm) so that spatial – uniform distribution of intensity can be assumed. Detailed characteristics of the laser utilized in the experiment are presented in the Table 1.

Table 1. The typical TEA CO_2 laser operational conditions during the irradiation of thin films.

Laser parameters	**A-pulse**	**B-pulse**
Gas mixture	$CO_2/N_2/H_2$	CO_2/H_2
Content	1/1.6/1.4	1/1.3
Output pulse energy	to 220 mJ	to 40 mJ
FWHM	120 ns (initial spike) ~ 2 μs – pulse tail	80 ns
Peak power density	100 to 170 MW/cm^2	
Mode structure	Multimode output	
Laser cavity	Nondispersive	
Spectral composition*	Simultaneous two-lines operation in P- branch $00^01 \rightarrow 10^00$ vibration band	
Pulse repetition rate	2 Hz	

*The laser simultaneously operated at two wavelengths: 10.5709 μm and 10.5909 μm; P(18) and P(20) transitions. The P(20) transition mode is more intensive.

For the characterization of the titanium nitride and titanium diborade thin films, before and after laser beam irradiation, the various analytical techniques were used. The surface morphology was monitored by optical microscope (OM), by scanning electron microscope (SEM), with secondary (SE) and back-scattered electrons (BSE) detectors, and by atomic force microscope (AFM). The quantitative standardless compositional analysis has been performed by energy dispersive analyzer (EDAX). The phase composition and crystalline structure of thin films were determined by X-ray diffraction method (XRD). The radiation used was Cu Kα. Reflectivity characterization of targets, for a spectral region of 2.5 to 25 microns, was carried out by infrared spectrophotometer.

3. RESULTS AND DISCUSSION

X-ray diffraction measurements of TiN and TiB_2 thin films, before modification by laser beam, showed that TiN as well as TiB_2 possessed polycrystalline structure. TiN thin films shown face centered cubic structure of the bulk δ-TiN phase while, TiB_2 crystallites had has hexagonal structure like as bulk MB_2 (M-metal). SEM analyses of the thin films, also before laser beam irradiation, have confirmed their homogenous, polycrystalline and fine-grained structure, Figure 2. The established average grain sizes were up to 20 and 100 nm in diameter for TiB_2 and TiN, respectively [2,11]. These results were expected, since deposited temperatures were lower than $0.3T_m$ (T_m - melting temperature of deposited material). Both thin films, deposited on polished steel substrate, possessed mirror like surface with characteristic color (i.e. TiN has had gold while, TiB_2 - silver color) and high reflectivity. Reflectivity measurements showed the initial reflectivity of 96 and 90% for TiN and TiB_2 at 10.6 μm, respectively. It is well known that reflectivity of a target surface depends on the surface physical nature, its morphology, used radiation wavelength and previously accumulated laser pulses. Absorptivity of targets is in correlation to its reflectivity. The amount of absorbed energy into target has been increased, after multi pulse laser actions, in comparison with no laser action.

a. **b.**

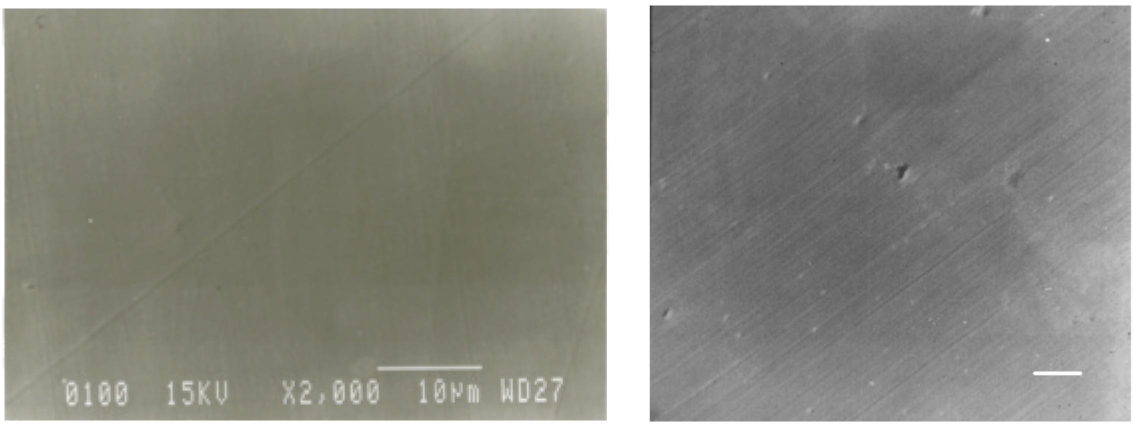
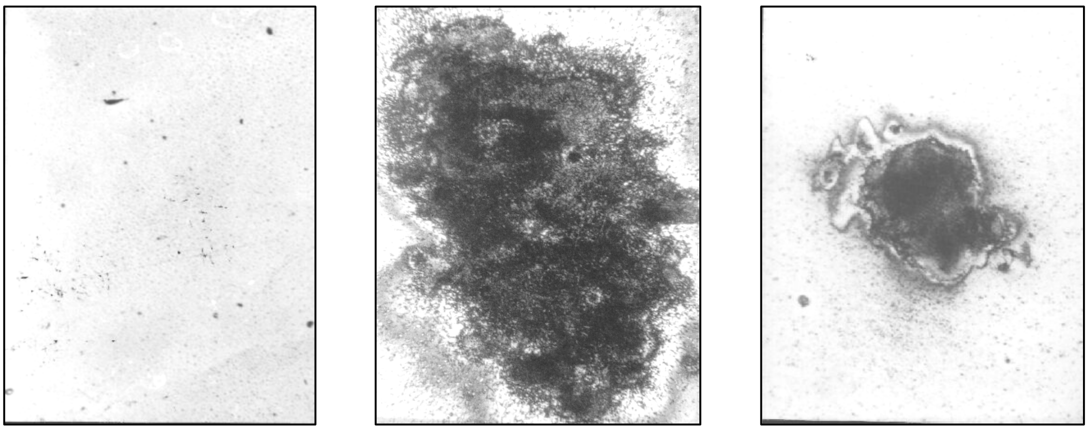


Figure 2. SEM microphotographs of the thin films before laser irradiation: (a) TiN and (b) TiB_2 film (in this case space bar is 2 microns).

Investigations of the thin films morphological changes, induced by the laser irradiation, have shown their dependence of beam characteristics: pulse energy, laser pulse duration, peak power density and number of pulses. The energy absorbed from the beam is converted into thermal energy, which generate a series of effects such heating, melting, vaporization of molten material, dissociation or ionization of the vaporized material and shock waves in the vapor and the solids. Optical microscope inspection of TiN and TiB_2 thin films is presented on Figure 3 and 4, respectively.

a. **b.** **c.**



200 mm

Figure 3. The surface appearance of the TiN thin film and changes induced by pulsed TEA CO_2 laser. (a) The surface of TiN thin films after deposition. The changes induced with 340 laser pulses: (b) action of laser pulses with tail, A-type pulse and, (c) action of tail-free pulses, B-type pulse. Peak power density was 170 MW/cm^2 for both laser pulses types.

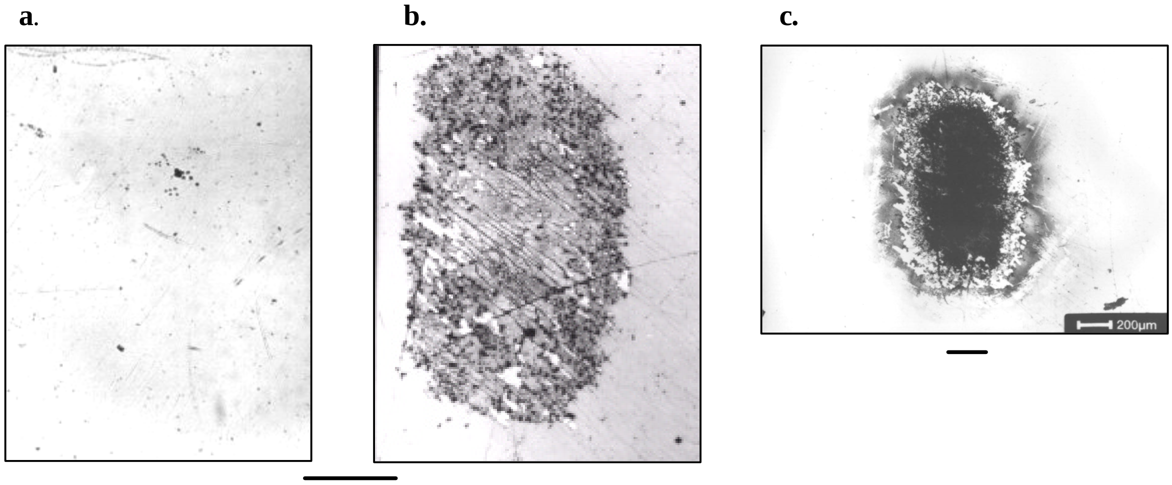


Figure 4. (a) As deposited TiB_2 thin films. Surface modification of same thin films by A-type pulses: after irradiation by 20 pulses – (b). and after 340 pulses – (c) (space bars = 200 microns; peak power density = 100 MW/cm^2).

The morphological changes of the thin film surface, induced by laser radiation, can be estimated via introduction of damage yield - DY. For damage yield a modified area on the thin film caused by multiple laser pulses, has been taken. This area was compared with those obtained for one laser pulse, reference 10. The damage yield depends on numerous laser parameters as well as from material properties. The damage yields for TiN and TiB_2 thin films as a function of accumulated laser pulses are presented in Figure 5 and 6.

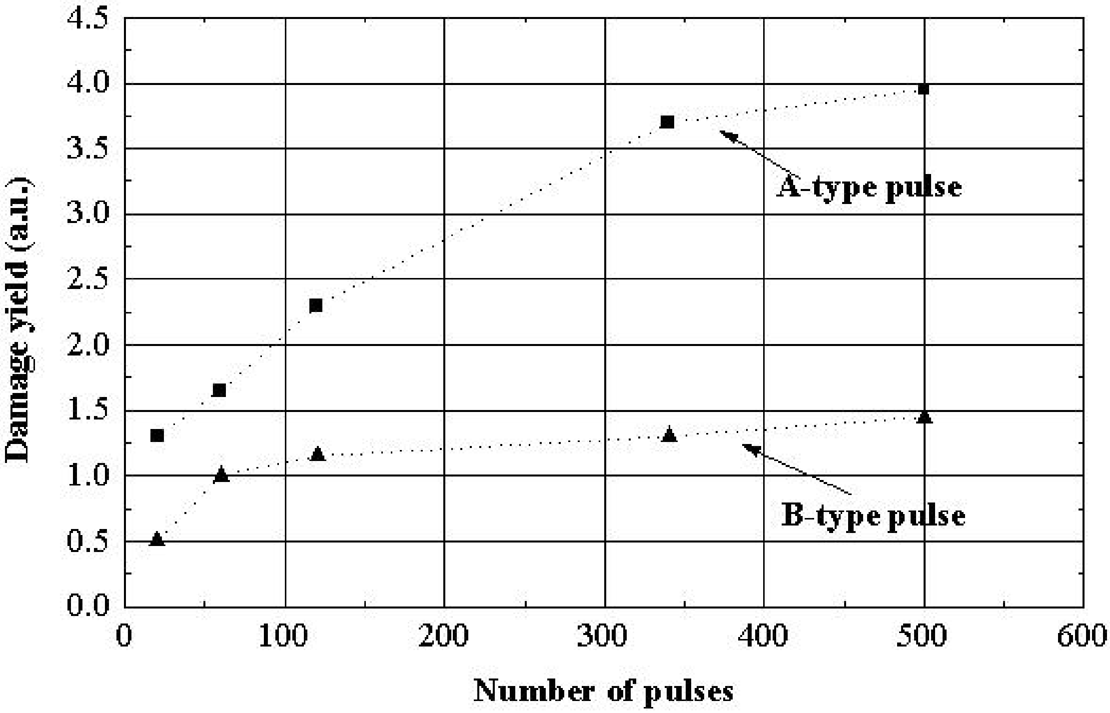


Figure 5 Damage yield (DY) of TiN thin film, as a function of a number accumulated laser pulses (A- and B- type of laser pulses). $DY = A_s/A_0$; As-sputtered targets area after numerous laser pulses and A_0-area after single pulse action (peak power density = 170 MW/cm^2).

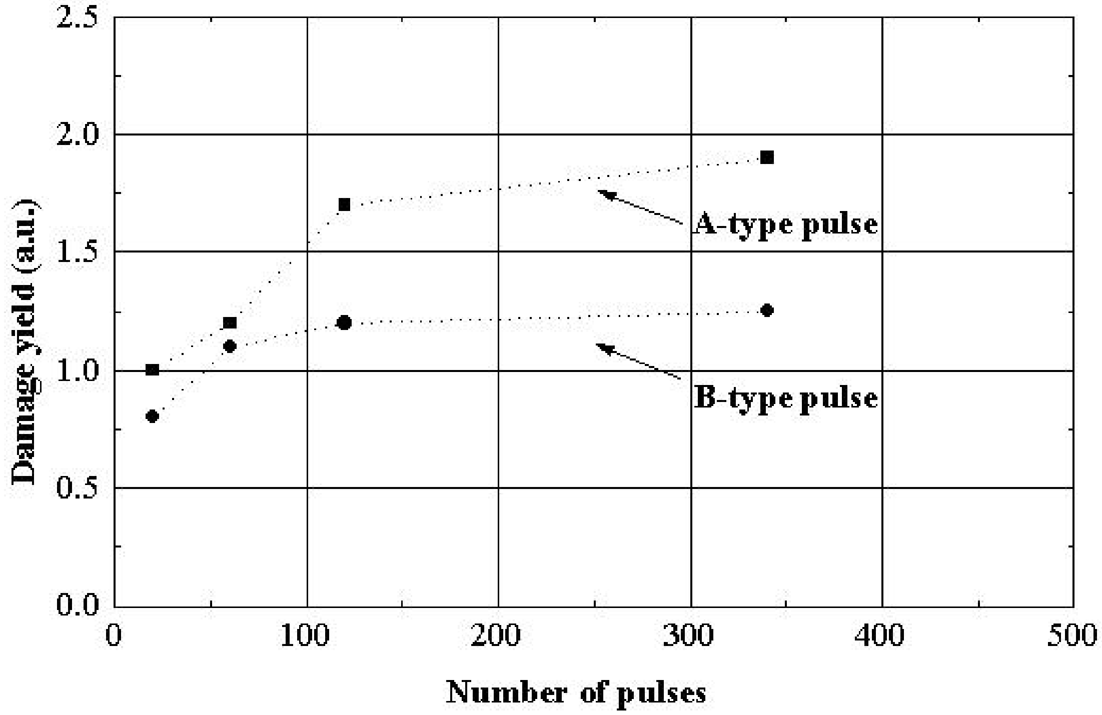
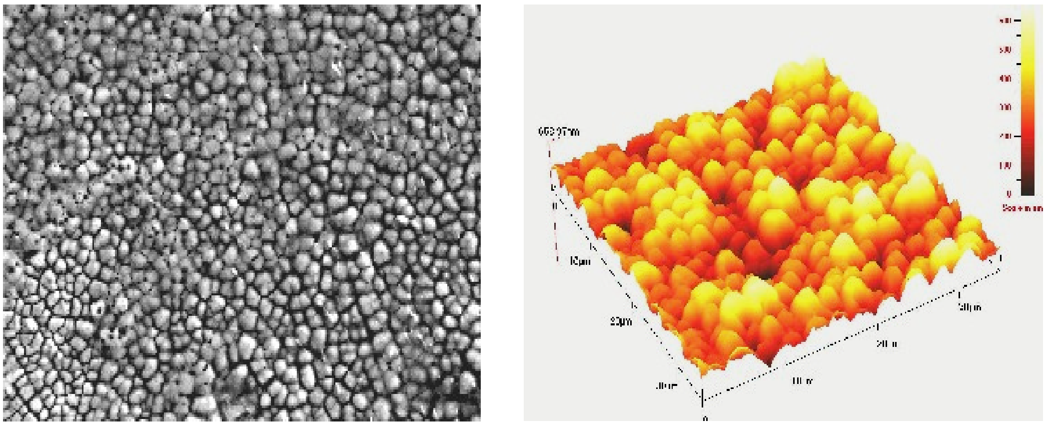


Figure 6. Damage yield for TiB_2 thin film, as a function of a number accumulated laser pulses (A- and B- type of laser pulses; peak power density =100 MW/cm^2).

The results have shown that for both thin films materials the damage yield was larger for the laser pulse with tail. This can be consequence of the fact that pulses with tail posses the higher energy. For TiN thin films, A-type laser pulses, the DY increases up to 340 pulses, Figure 5, and then it remained near constant. The constant value indicated that target modification performed in the bulk. For same target, B-type of laser pulses, DY increases up to 100 pulses. Similar behavior was registered for TiB_2 thin film. DY remained constant after action of 100 cumulative pulses for A- and B-(pulse) types.

a. **b.**



10mm

Figure 7. Morphological changes of the TiN thin film after action of 340 laser pulses (A-type pulse): (a) SEM microphotography and, (b) AFM microphotography of the same region (the square length is 35 microns)

TiN and TiB_2 posses similar values of thermal conductivity, i.e. 0.29 W/cmK for TiN and 0.26 W/cmK for TiB_2 at room temperature. It was expected that ratio between the maximums of damage yields for laser pulses A and B-type could be similar for both thin films materials. The rations, Figures 5 and 6, are different. The reason is probably in different adhesion between the thin film and substrate.

Twenty successive laser pulses were induced on TiN films the change of color and appearance of very fine like net structure while, the same number of pulses (but with the lower peak power density) on TiB_2 surface caused prominent cracking. The partial exfoliation of TiB_2 thin film was appeared, Figure 4 b.

The more precise microscopy of TiN and TiB_2 thin film surface modification, were conducted by SEM and AFM, Figures 7 and 8.

a. **b.**

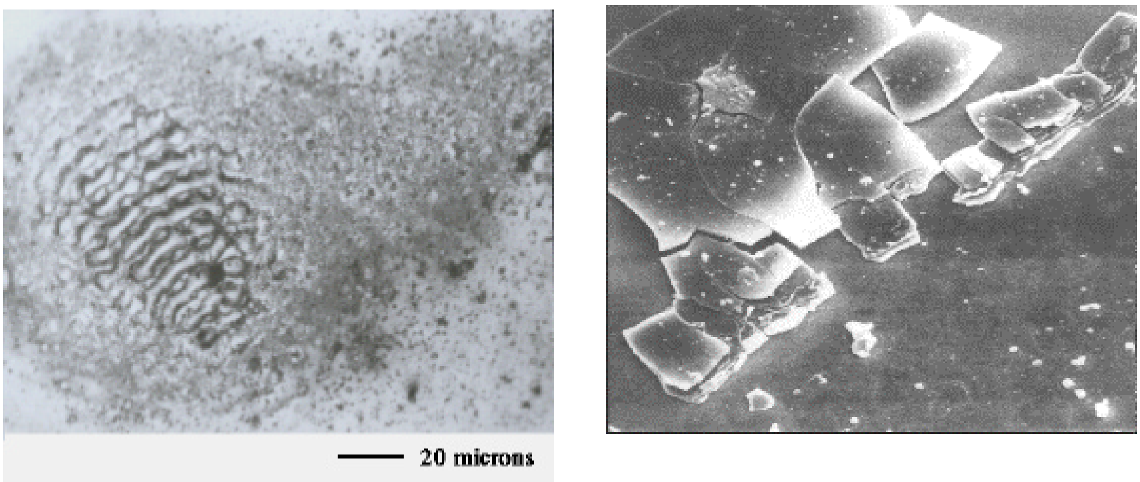


Figure 8. Morphology changes of the TiB_2 thin films after action of 340 laser pulses (A-type pulse): (a) Central part of irradiated area (OM) and, (b) periphery of the same area (with remained cracking part of thin film obtained by SEM).

The effects of laser beam irradiation on TiN and TiB_2 thin films could be described in general as follows:

The TiN thin film

Due to the high reflection and absorption coefficient value (at the IR wavelengths[14]), penetration depth of radiation into TiN can be small, estimated of about 20 nm. This indicating almost metallic optical properties of TiN and that low amount of energy was absorbed for the first pulse. Surface, in this case, was unchanged. After cumulative action of laser pulses (A and B-types), the absorbed amount of laser energy was increased and color of surface was altered. Darkening of the sputtered zone was detected. The change in color, of irradiated zone, can be result of chemical effect like oxidation and/or preferential sputtering of nitrogen.

The morphology changes of the surface were more prominent after action of 340 as well as 500 laser pulses. Both types of laser pulses (A- and B- types) caused the appearance of two zones – the central and the periphery zone[10]. In the central zone, Figure 7, the grainy hemispherical features, with diameter of 1–2 μm, was registered while, at the periphery zone there are visible hydrodynamic sputtering effects.

The laser ablation of the film with more than 120 laser cumulative pulses (of A-type) and more than 340 cumulative pulses (of B-type) was accompanied by plasma creation in front of the sample.

The TiB_2 thin film

For TiB_2, thin films/bulk, there are no accessible data of IR optical properties, like: absorption coefficient, reflectivity, etc. Based on experimentally obtained reflectivity could be estimated that the low amount of energy, in the first pulse, was absorbed at the thin film surface. For the difference of the TiN thin film here, in case of TiB_2 after the first laser pulse action the surface was modified. Plasma was created too during/after the first laser pulse. The following effects, after action of A- and B- types of laser pulses, are registered on surface of the TiB_2 film: cracking, partially and totally exfoliation. The total thin film exfoliation was observed for 120 laser pulses of A-type and for 60 laser pulses of B-type.

1. CONCLUSIONS

The morphology changes of the titanium based ceramics, in the form of TiN and TiB_2 thin films deposited on austenitic stainless steel substrate, induced by the TEA CO_2 laser irradiation, have monitored in this work.

Presence of laser plasma in front the samples were registered. Induced plasma for ablation of TiB_2 thin film was more prominent than for TiN thin films. Morphological changes of deposited ceramics, induced by successive laser pulses, have shown the dependence on laser beam parameters: pulse energy, laser pulse duration, peak power density, number of pulses, etc. and thin film characteristics. Used pulse peak power densities of 100 and 170 MW/cm^2 have induced the surface modifications of TiN and TiB_2 thin films, respectively. Depending on laser beam parameters, on TiN thin film, the changing of color, grain growth, and hydrodynamic effects were registered while, on TiB_2 thin films cracking and exfoliation were observed.

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REFERENCES

1. L.Toth, "Transition Metal Carbides and Nitrides", Acc. Press, New York and London 1971.
2. J. Sundgren, H. Hentzell, "A review of the present state of art in hard coatings grown from vapour phase", *J.Vac.Sci.Tech*, **A 4**, pp. 2259-2271, 1986.

3. R.F.Haglund, Jr., "Microscopic and mesoscopic aspects of laser-induced desorption and ablation", *Applied Surface Science***,** **96**, pp. 1-13 ,1996.
4. I. Boyd, "Laser processing of thin films and microstructure", *Springer Series in Mat. Sci.,*Springer-Verlag,1987.
5. I. Ursu, I. Mihailescu, A. Prokhorov, V. Konov, "Laser Heating of Metals", *Accad.R.S.R, Bucuresti*, 1991.
6. C. Boulmer-Laborge, J. Herman, B. Dubreuil, "Plasma formation resulting from the interaction of laser beam with a solid metal target in an ambient gas" *Plasma Sources Sci.Technol.,* **2,** pp. 219-226, 1993.
7. T. Nenadovic, T. Mihac, Z. Rakocevic, "Photo deposition sputtering of titanium and TiN thin films", *Thin Solid Films*, **218**, pp. 247-251, 1992.
8. J. Bonse, H. Sturm, D. Schmidt, W. Kautek, "Chemical, morphological and accumulation phenomena in ultrashort - pulse laser ablation of TiN in air", *Applied Physics,* **A 71**, pp. 657-665, 2000.
9. J. Bonse, M. Geus, S. Baudach, H. Sturm, W. Kautek, "The precision of the femtosecond-pulse laser ablation of TiN on silicon*", Applied Physics,* **A 69**, pp. S399-S402, 1999.
10. B.M. Gakovic, M.S. Trtica, T.M. Nenadovic and B.J. Obradovic, "TEA CO_2 laser-induced damage of low-thickness TiN coatings", *Thin Solid Films*, **343-344**, pp. 269-272, 1999.
11. T.M. Nenadovic, B.M. Gakovic, Z. Lj. Rakocevic," Implementation of solid surfaces with titanium ceramics deposited in vacuum", *Science of Sintering,* **31,** pp. 23-35, 1999.
12. B. Todorovic, T. Jokic, Z. Rakocevic, Z. Markovic, B. Gakovic, T. Nenadovic, "The effect of rapid thermal anniling on structural and electrical properties of TiB_2 thin films", *Thin Solid Films,* **300,** pp. 227-277, 1997.
13. M. S. Trtica, "A smal scale TEA-CO_2 laser utilizing nonconvential ternary $CO_2/N_2/H_2$ gas mixture", *SPIE Proceedings*, **1276**, pp. 106-109, 1990.
14. J. Bonse, S. Baudach, J. Kruger, W. Kautek, "Femtosecond laser micromachining of technical materials", *SPIE Proceedings,* **4065**, pp. 161-171, 2000.