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PHOTON-BEAM SPUTTERING AND SURFACE MORPHOLOGY OF TITANIUM-CERAMIC COATINGS

NAPRŠEVANJE S FOTONSKIM SNOPOM IN MORFOLOGIJA POKRITIJ IZ TITANOVE KERAMIKE

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The interaction of any energetic beam with a solid leads to a change in the solid's surface and the interior of the crystal. The induced changes depend on the beam's characteristics and the target properties. The interaction process, which is not a consequence of binary collision cascade, is the photon-beam sputtering with the incident laser beam. The mode of operation of the laser and the deposited energy in the bombarded area are important for both a fundamental investigation and technological applications. Laser systems - Nd:YAG and continous CO_2 - have been adopted for material processing. Generally, the continous CO_2 laser is an effective high-power laser that has found applications in cutting and drilling tools. The pulse (TEA) CO_2 laser is less used in practical applications. The interaction of laser light with materials has been investigated for many years, however, laser-beam sputtering of solid materials is still an expanding field in basic science, engineering and material processing.

The objective of this work was an investigation of surface modification, using photon-beam sputtering, of titanium-based ceramics (TiN, TiB_2) deposited on a steel substrate. The experiments were performed by focused TEA CO_2 (Transversaly Excited Atmospheric carbon dioxide) and Nd:YAG lasers (Neodymium Yttrium Aluminium Garnet - $Y_5Al_3O_{12}$) in an air atmosphere. Changes on the deposited coatings, induced by both lasers, showed the importance of the following laser-beam parameters: peak power density, wavelength and pulse number. Sputtering with the TEA CO_2 laser also showed that there was a dependence on the laser pulse shape.

Key words: laser sputtering, coatings, steel, TiN, TiB_2

Vsaka interakcija energijskega snopa s trdno snovjo spremeni površino in notranjost kristala. Nastale spremembe so odvisne od značilnosti snopa in od lastnosti tarče. Proces interakcije, ki ni posledica slapa zaradi binarnih trkov, je naprševanje s fotonskim snopom z vpadnim laserskim žarkom. Način dela laserja in energija, oddana na obsevani površini, sta pomembna za temeljne raziskave in tehnološko uporabo. Laserski sistemi - Nd:YAG in zvezni CO_2 - se uporabljajo za procesiranje materialov. V splošnem je zvezni CO_2-laser učinkovit za velike moči, ki se uporablja kot rezno in vrtalno orodje. Pulzni (TEA) CO_2-laser se v praksi manj uporablja. Interakcije laserske svetlobe se raziskuje že veliko let, in lasersko naprševanje trdnih snovi je še vedno rastoče polje temeljne znanosti, inženirstva in procesiranja materialov.

Cilj tega dela je bil raziskati spremembe površine zaradi naprševanja z laserskim snopom na titanovi keramiki (TiN, TiB_2), naneseni na jekleno podlago. Eksperimenti so bili izvršeni s fokusiranimi TEA CO_2 (Transversaly Excited Atmospheric carbon dioxide) in Nd:YAG (Neodymium Yttrium Aluminium Garnet - $Y_5Al_3O_{12}$)-laserji na zraku. Spremembe na površini nanosov zaradi učinka obeh laserjev so pokazale pomen naslednjih parametrov laserskega snopa: največja gostota moči, valovna dolžina in število pulzov. Pri laserju TEA CO_2 se je pokazal tudi vpliv oblike pulza.

Ključne besede: lasersko naprševanje, prekrivanje, jeklo, TiN, TiB_2

1 INTRODUCTION

Titanium-based ceramic coatings play an important role in many applications because of their hardness, high evaporation temperature, good chemical stability, metallic brightness, etc. The most thoroughly investigated thin film and coating of titanium-based ceramics is titanium nitride (TiN), which exhibits good thermal and electrical conductivity. Because of its unique combination of properties, TiN has a broad range of applications. Titanium diboride (TiB_2) coatings have not been studied as much as titanium nitride or carbide coatings. TiB_2 is also very hard and chemically stable, but very brittle. TiB_2 coatings are considered as a candidate material for some parts of the next generation of tokamak.

The processing of these materials, bulk or coating, is difficult due to their high hardness and brittleness. The solution is to use laser beams. Laser-beam sputtering can cause the rapid removal of surface material as well as thermal and non-thermal effects. The process may be divided into laser-induced ablation, which is a high-yield sputtering process, and laser-induced desorption, which includes low-yield sputtering. Generally, the process of laser-beam interaction with materials can be described, in terms of a few characteristic stages: absorption of the laser beam's photon energy, transformation of this energy in radiative and/or non-radiative processes, fast heating and cooling of the target with or without damage, ejection of material from the interaction region and laser plasma formation [1]. The photon-beam sputtering induced changes depend on the beam's characteristics and the target properties. The interaction of laser light with materials has been investigated for many years. However, laser sputtering of solid materials continues to be an expanding field in fundamental science, engineering, and material processing technologies [2,3].

The objective of this work was to investigate the surface modification of titanium-based ceramics (TiN, TiB_2), deposited on a steel substrate, using photon-beam sputtering. Experiments were performed in an air atmosphere using a focused TEA CO_2 laser, which was operated in two pulse regimes, and using a Nd:YAG laser.

2 EXPERIMENTAL

2.1 Sample preparation

Titanium-based ceramic coatings were produced using two physical vapor deposition (PVD) techniques: ion-beam sputtering and direct evaporation. Before the deposition the substrates, austenitic stainless steel (dimensions 20 mm × 13 mm × 1.5 mm), were prepared using a standard metallographic procedure in order to obtain coating surfaces with a low roughness. The TiN layer, thickness 850 to 2200 nm, was deposited by Ar^+ ion sputtering of a titanium target in a reactive atmosphere of nitrogen (N_2). The d.c. reactive sputtering was performed in a BALZERS SPUTTRON II [4]. The TiB_2 coating was prepared by direct electron-gun evaporation of cold-pressed powder in a modified BAK BALZERS apparatus [5]. The layer thickness was 360 to 950 nm.

2.2 Photon-beam sputtering

The photon-beam sputtering of TiN and TiB_2 coatings was performed with pulsed TEA CO_2 and Nd:YAG lasers, using a zero angle of incidence. The important laser-beam parameters for both lasers are presented in **Table 1**.

The pulsed UV pre-ionized TEA carbon-dioxide laser was operated with non-typical ternary ($CO_2/H_2/N_2$) or binary (CO_2/H_2) gas mixtures. For the case of the ternary gas mixture, the temporal shape of the pulse included a prominent first spike followed by a tail of lower intensity. The full width at half maximum (FWHM) of the spike was 120 ns and the tail duration was about 2 microseconds, denoted as A-type pulse. The absence of nitrogen resulted in a tail-free pulse shape that lasted 80 ns, denoted as B-type pulse. The temporal shape of the Nd:YAG laser pulse is similar to the B-type pulse, but lasting only 15 ns. The photon-beam sputtering in these experiments was performed with a similar peak power density and a nanosecond laser-pulse duration, but with different photon energies ($E_{Nd:YAG}$ = 1.17 eV and E_{TEA} = 0.117 eV). Samples were positioned perpendicular to the incident laser beam, and before any laser irradiation the laser-beam parameters were determined (**Figure 1**). For multi-pulse photon-beam sputtering the number of pulses per spot was varied with a constant pulse duration and a fixed pulse energy. The targets were irradiated in an air atmosphere with 1 to 500 consecutive pulses; the peak power density was in the interval from 100 to 170 MW/cm^2.

2.3 Sample characterization

Before and after the photon-beam sputtering experiments the TiN and TiB_2 coatings were analyzed. For the characterization of the samples the following techniques were used: (i) optical microscope (OM), scanning electron microscope (SEM) and atomic force microscope (AFM), for surface morphology observation; (ii) X-ray diffraction analysis (XRD), for determination of the phase composition and the crystallographic structure; (iii) an energy-dispersive analyzer (EDAX), for quantitative compositional analysis; and (iv) an infrared spectrophotometer, for reflectivity characterization.

3 RESULTS AND DISCUSSION

Both deposited coatings possessed a mirror-like surface (color: TiN gold and TiB_2 silver) and high a reflectivity. Reflectivity measurements in the spectral region from 1 to 14 μm showed an initial reflectivity of (i) 96% for TiN and 90% for TiB_2 coatings at 10.6 μm; and (ii) 84% for TiN and 80% for TiB_2 coatings at 1.06 μm. It is well known that the reflectivity of a target's surface depends on the surface's physical nature and the morphology, the radiation wavelength and the previously accumulated laser pulses. The reflectivity of targets is directly correlated to their absorptivity. The amount of absorbed energy per pulse increased after several pulse actions.

An analyses of the deposits (XRD, EDAX) before laser-beam sputtering showed their homogenous, polycrystalline and fine-grained structure. Inspections of the cross-section showed a columnar equiaxial crystal

Table 1: The characteristics of the lasers' pulse for the photon-beam sputtering experiments
Tabela 1: Značilnosti laserskega pulza pri poskusih napreševanja z laserskim snopom

Laser pulse type	Wavelength (μm)	Pulse energy (mJ)	Pulse duration (FWHM, ns)	Peak power density (MW/cm^2)	Pulse repet. (Hz)	Structure mode operation
Nd:YAG	1.06	10-150	15	10^6 - 10^9	10	single
TEA CO_2 (A-type)	10.6	20-220	120	10^6 - 10^8	2	multimode (two-line)
TEA CO_2 (B-type)	10.6	5-40	80	10^6 - 10^8	2	multimode (two-line)

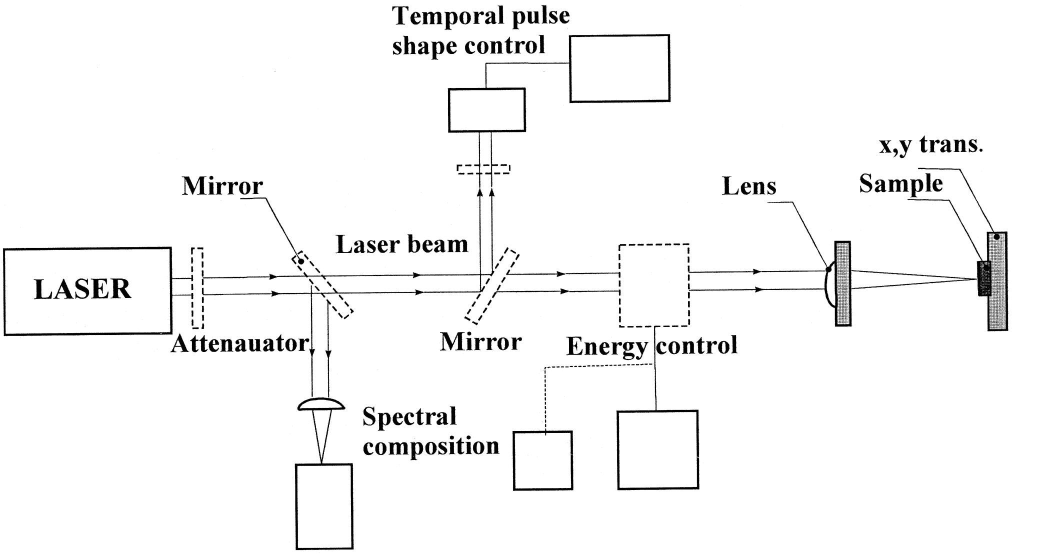

Figure 1: Experimental set up. The LASER denoted pulsed lasers TEA CO_2 or Nd:YAG.
Slika 1: Eksperimentalna naprava. Z besedo laser je označen pulzni laser TEA CO_2 ali Nd:YAG.

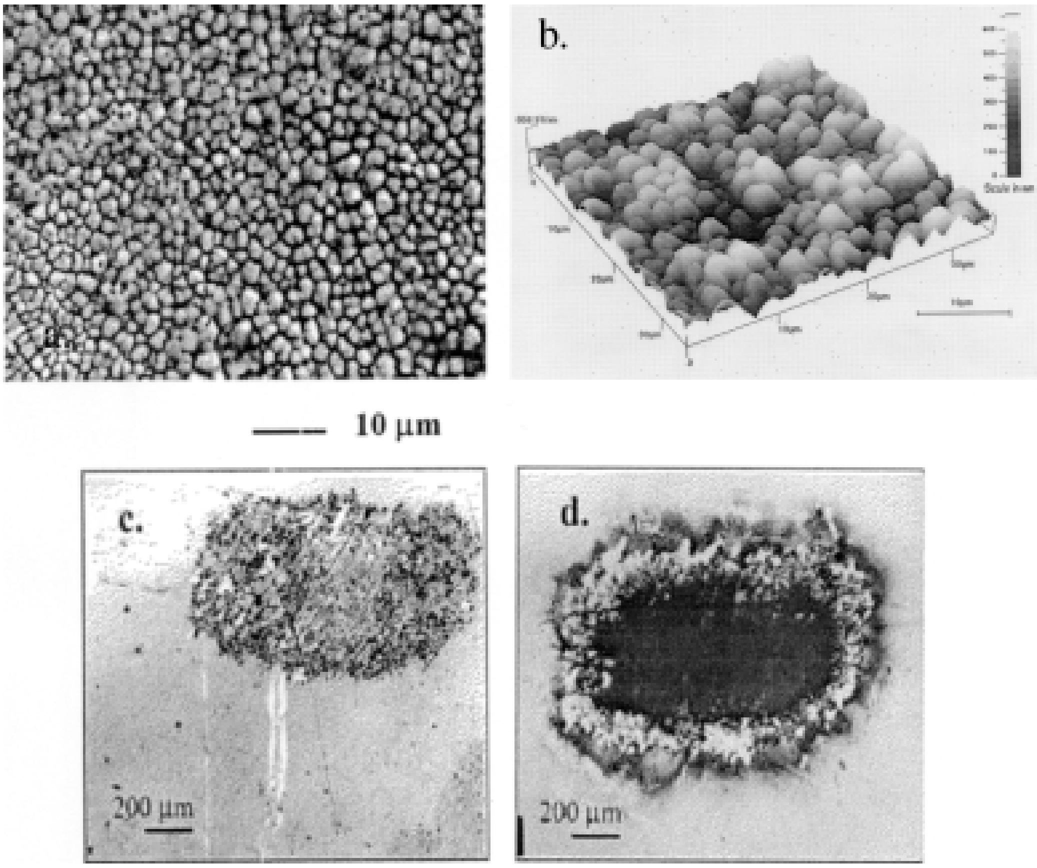

Figure 2: The morphology changes induced by the TEA CO_2 laser. The TiN coating sputtered with 340 laser pulses of B-type: (a) center of damaged area by SEM analyses and same area by AFM. The TiB_2 coating sputtered with (c) 20 laser pulses and (d) with 340 A-type pulses.
Slika 2: Oblika sprememb zaradi obsevanja s TEA CO_2-laserjem. Plast TiN, obsevana s 340 laserskimi pulzi vrste B: (a) središče poškodovane površine, posnetek v SEM in ista površina v AFM. Plast TiB_2, obsevana s (c) 20 laserskimi pulzi in (d) 340 pulzi vrste A.

structure typical for low-temperature crystal growth. The average grain sizes were up to 20 nm in diameter for TiB_2 and up to 100 nm for TiN. These results were expected from the Thorton diagram since the deposition temperature was lower than $0.3T_m$ (T_m is the deposit melting temperature) [3,6].

With an optical microscope we made an initial inspection of the irradiated surface regions. Using a SEM and an AFM we made a more detailed characterization of the morphological changes in the laser-modified areas. The AFM registered topographical changes of the irradiated surface in three dimensions. Investigations of the laser-beam sputtering morphological changes showed the dependence on the sputtered materials, the laser-pulse power density, the wavelength of the laser light, the temporal pulse shape, and the pulse number. The same results for photon-beam sputtering of TiN and TiB_2 coatings with a TEA CO_2 laser are presented in **Figure 2a-d**.

The effects of laser-beam sputtering of TiN and TiB_2 coatings can be described as follows.

(a) TEA CO_2 (10.6 μm wavelength)

The TiN coating

Due to the high reflection and the absorption coefficient value ($\alpha = 4.5x10^5$ cm^{-1}), the penetration depth of the light was found to be 22 nm. This indicated almost metallic-like optical properties and only a small amount of energy for each pulse was absorbed at the surface. In the case of a few successive laser pulses (A- and B-types), with maximum peak power density, optical microscopy showed darkening of the sputtered zone. The degree of darkening increased with the number of laser pulses applied to the same spot. This change in color of the affected zone can arise from chemical changes like oxidation and/or the preferential sputtering of nitrogen. After 20 successive laser pulses, the SEM inspection confirmed the morphological changes. Laser-induced changes in the central part of the irradiated area created grainy hemispherical features (diameter 1-2 μm). With an increased number of pulses the surface changes increased, and the difference in sputtering with the two pulse types (A-type or B-type) was pronounced. The action of A-type laser pulses produced wavy-like forms [6]. The increase in the number of pulses caused an initial enlargement of the sputtered zone, after which it remained constant (**Figure 3a**). An increase in the number of pulses (up to 500) during the sputtering did not lead to exfoliation of the coating. The photon-beam sputtering was accompanied by plasma creation in front of the coating (after 120 laser pulses of A-type and 340 pulses of B-type).

The TiB_2 coating

The almost metallic-like optical properties of the surface were remained in the case of TiB_2 coating. The small amount of energy in the first pulse was absorbed at the surface, but the single laser pulse with maximum peak power density caused plasma formation. The coating cracked for 20 pulses A- and B-type and complete layer exfoliation occured for 120 pulses of A-type and 60 pulses of B-type. An increase in the number of pulses caused enlargement of the sputtered zone, after which it remained constant (**Figure 3b**). An SEM analysis confirmed that the changes were inside the substrate.

The differences in the surface morphology for the case of the different types of TEA CO_2 laser pulses, at the same peak power density, originated from a different deposited energy per pulse.

(b) Nd:YAG (1.06 μm wavelength)

The TiN coating

Besides the high surface reflectivity of the coating, and the small penetration depth, the laser plasma appeared after a single pulse irradiation of the sample. The reason might be a higher photon energy for this wavelength. Another reason could be a different mode of

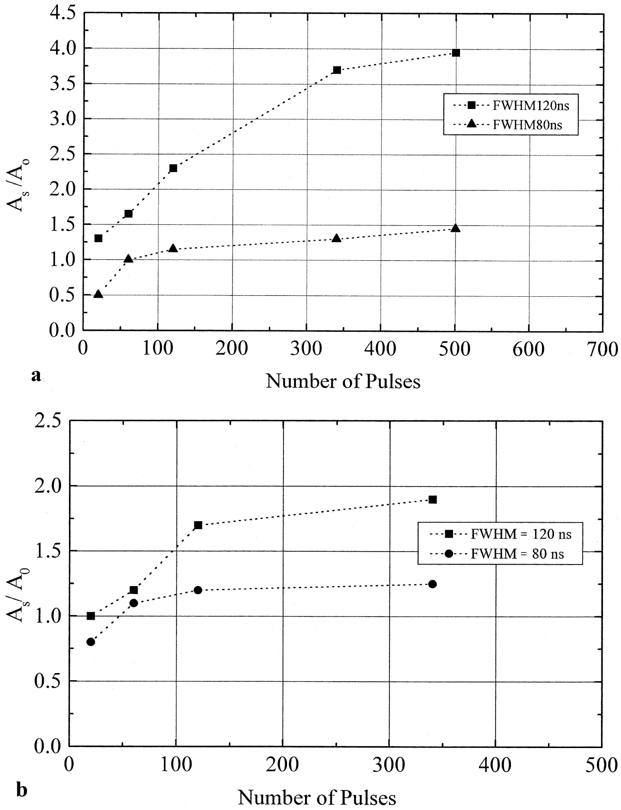

Figure 3: Damage yield (DY) vs. number of accumulated A- and B-type laser pulses: (a) TiN and (b) TiB_2 coatings ($DY = A_s/A_0$; As-sputtered targets area after numerous laser pulses and A_0-area of single pulse action). The peak power densities were 170 and 100 MW/cm^2, respectively.

Slika 3: Stopnja poškodovanosti (DY) v odvisnosti od skupnega števila A- in B-laserskih pulzov: (a) TiN- in (b) TiB_2-plast ($DY = A_s/A_0$; As-obsevana površina po številnih laserskih pulzih in A_0-površina, obsevana z enim pulzom). Intenziteti največje moči 170 in 100 MW/cm^2.

laser operation, and different physical mechanisms of plasma formation. The single pulse sputtering indicated surface morphology changes that depended on the pulse energy. It was possible to obtain the sputtering yield from the crater-like form. The photon-beam sputtering was comparable with ion-beam sputtering. The sputtering yield, the amount of sputtered material per incident photon energy, can be estimated [7]. An increase in the pulse energy or the number of laser pulses causes coating removal.

The TiB_2 coating

The laser plasma appeared in front of the surface for the single pulse irradiation of the sample. The photon-beam sputtering yield of TiB_2 is a function of the laser-beam power density. It increases with the increase in the power density, showing a maximum at a certain value and then decreases [3].

4 CONCLUSIONS

According to the difference in characteristic parameter values, laser-material interaction leads to morphology changes, heating/removal of larger material volume with the 10.6 μm wavelength, with the A-type pulse, and more intense evaporation phenomenon with the 1.06 μm wavelength. In the case of sputtering, with photons of 1.06 μm wavelength the obtained values of sputtering yields for TiN and TiB_2 coatings were lower than those obtained for pure titanium [3,7].

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