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纳秒、皮秒和飞秒激光脉冲对材料表面的改性

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摘要：对基体材料镉镍铁合金 600 和多层 TiAlN/TiN 涂层的激光表面改性在基础研究和实际应用中有着很好的前景。本文观察了由超短脉冲(fs 和 ns)和短脉冲(ns)激光器引起的镉镍铁合金 600 和 TiAlN/TiN 镀层的表面变化。结果显示，3 种激光都能使靶面发生形态改变，超短脉冲的破坏轮廓更为清晰。与 ps 激光脉冲相比，fs 激光脉冲能产生更严重的破坏。与产生半球体形状的 ps 激光束相反，fs 激光脉冲产生的破坏斑是圆锥形的。另外，ns 脉冲辐照时热效应占支配地位，且所有的辐照都伴随着等离子体。

关　键　词：纳秒脉冲；皮秒脉冲；飞秒脉冲；Inconel 600 镀层；TiAlN/TiN 镀层；激光改性
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Material surface modification by ns, ps and fs laser pulses

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Abstract: The laser surface modifications of a bulk material Inconel 600 and a multilayered titanium-aluminium-nitride/titanium-nitride(TiAlN/TiN) coating are of great interest for fundamental and practical aspects. Observation of surface changes of the Inconel 600 and TiAlN/TiN induced by ultra-short (fs and ps) and short (ns) lasers is considered. It is shown that all laser systems can stimulate morphological changes at the target surface, and the irradiation with ultra-short pulses results in a better definition of the damage. Fs laser pulses can produce a sharper destruction in comparison to the ps pulses and it gives the conical cross section of the crater, which is in contrast to the semispherical

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shapes ps laser beams. Furthermore, thermal effects are dominant in the case of ns pulse, and all irradiations are accompanied by the plasma.

Key words: ns pulse; ps pulse; fs pulse; Inconel 600 coating; TiAlN/TiN coating; laser modification

1 Introduction

Research of the surface modifications of materials by short or ultra-short laser beams and basic principles of the coupling between laser radiation and surface[1] are necessary from fundamental and practical reasons. The targets we have studied so far, such as Inconel 600, TiAlN/TiN multilayer, and titanium show extraordinary physico-chemical characteristics. Due to this, laser surface modifications of these targets are very important not only for the technological but also for biomedical applications. Preliminary studies show that these materials could have a potential for implant applications[2], which is already well known for Ti/Ti-based alloys[3-7]. The states of their surfaces are important for bio-compatibility and bio-integration with human body. It has to be contaminant-free, while the optimal surface roughness is significant for the tissue integration. These implants are corrosion resistant to electrolytes (such as physiological solution) and inert to the body fluids. They can be used as orthopaedic, dental, heart, *etc*. implants.

The interest in the laser beam interaction with these targets has generally increased, especially in the last two decades. The main investigations were focused on the usage of short laser pulses (ns/μs domain). Treatment of these targets with the ultra-short laser pulses (ps/fs) is scarce in literature. In the present paper, our emphasis is on studying the effects of ultra-short and short laser pulses on Inconel 600 and TiAlN/TiN targets.

2 Experiments

The target Inconel 600 was prepared by a standard metallographic procedure. The multilayer TiAlN/TiN was deposited on a polished steel H11 plate by magnetron sputtering. Thickness of the multilayer coating was about 2.17 μm. Total thickness of the samples was in the millimetre range.

The irradiation of targets was carried out in air, at the pressure of 1.013 bar and a standard relative humidity. The laser beams were perpendicular to the material surfaces. The targets were irradiated by focusing laser beam using quartz lenses (12 cm focal length for a ps laser, *i.e.* 15 mm for a fs laser) and KBr lens (6 cm focal length for a ns system). During the irradiation process, the lasers were operated typically in the fundamental transverse mode. Picosecond laser used was Nd : YAG laser[3]. The laser pulse energy is the order of mJ, pulse length is 40 ps, wavelengths are 1 064 nm/532 nm/266 nm and the pulse repetition rate is 2 Hz. For femtosecond domain, the Ti:sapphire laser was employed[8]. The laser pulse energy is the order of nJ, pulse length is 160 fs, wavelength is 800 nm and the pulse repetition rate is 75 MHz. A typical experimental setup for the irradiation of samples is shown in Fig. 1 for the fs laser. Nanosecond pulses were obtained by using a TEA CO_2 laser with the following characteristics: the pulse energy order of tens of mJ, pulse length 100 ns (initial spike), wavelength 10.6 μm and the pulse repetition rate 2 Hz.

Various analytical techniques were used for characteriing the samples before and after laser irradiations. The phase composition and crystalline structures of the samples were identified by an X-ray diffraction. The surface morphology was monitored by an Optical Microscopy (OM) and a Scanning Electron Microscopy (SEM). The SEM was connected to an energy dispersive

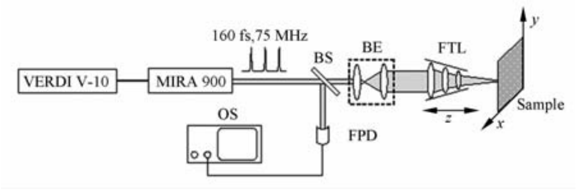


Fig. 1　Experimental setup for irradiation of Inconel 600 by fs laser. VERDI V-10 and MIRA 900 are pumping solid-state Nd: YVO_4 laser, and femtosecond Ti: sapphire laser, respectively (BS: beam splitter, BE: beam expander, FTL: focusing triplet lens, FPD: fast photodiode and OS-oscilloscope)

analyzer (EDX) for determining the surface composition of targets. Profilometry and focused ion beam (FIB) techniques were used for specifying the geometry of ablated/damaged areas.

3　Results and discussion

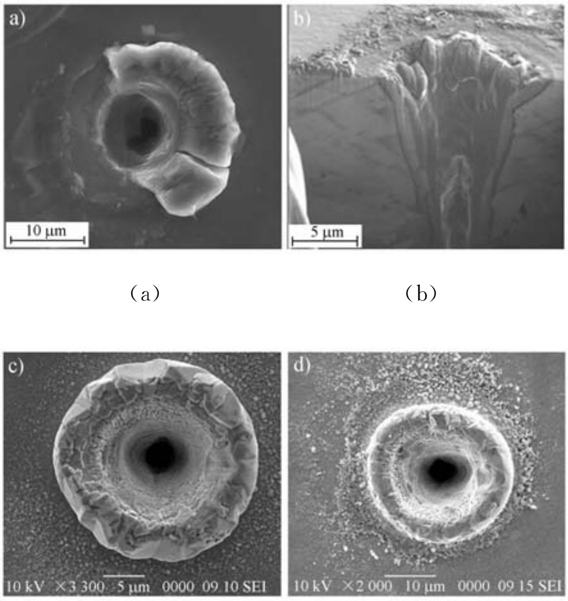
XRD phase compositional analysis of targets shows that both Inconel 600 and TiAlN/TiN are polycrystals. The main alloying elements in Inconel 600 incorporated into the lattice are highly predominant Ni ($w = 76\ \%$), as well as Cr ($w = 15.5\ \%$) and Fe ($w = 8\ \%$). This alloy has a face centred cubic (fcc) nickel structure. Although TiAlN/TiN system was composed of 45 alternating layers, it also retained single-phase fcc structure of TiN. The coating showed preferential orientation (111), which is the same as individual components of the bilayer (TiAlN/TiN).

Investigations of the surface changes of Inconel 600 and TiAlN/TiN have shown their dependence on laser beam characteristics, primarily on the energy density (fluence), peak power density, number of accumulated pulses, wavelength, *etc*. Surface modifications of these targets are presented in Fig. 2－5. The results of the induced modifications are given below:

3.1　Nickel-based superalloy, Inconel 600

3.1.1　Irradiation with fs laser pulses

Fig. 2 shows the damages on Inconel 600 target induced by fs pulses after 10 s and 5, 7 min. These morphology changes are highly expressed in both time ranges despite of very low pulse energy, due to large number of the delivered pulses, *i.e.* relatively high average power. The material expelled during irradiation formed a surrounding hillock-like rim around the deep crater. In contrary to the minute time range [Fig. 2(c), (d)], the adhesion of the accumulated rim for second irradiation time [Fig. 2(a), (b)] with the surface was low and its species/fragments could easily be mechanically removed.



(a)　(b)

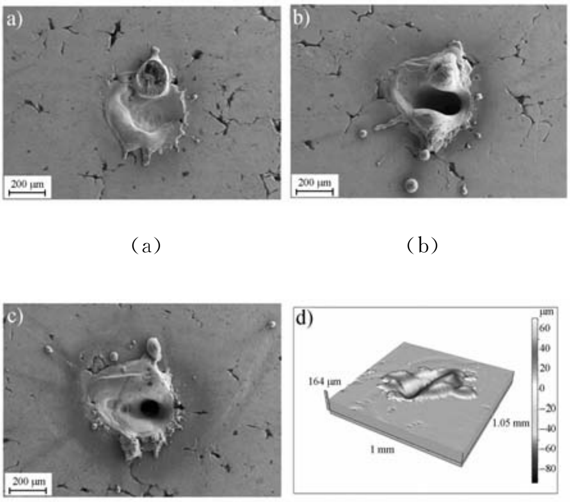
(c)　(d)

Fig. 2　Effect of 20 nJ, 160 fs laser pulses on superalloy Inconel 600, as a function of irradiation time: (a) and (b) 10 s, (c) 5 m, (d) 7 min (laser intensity $\approx 10^{11}$ W/cm^2, $\lambda = 800$ nm, pulse repetition rate is 75 MHz; (a), (c), (d) SEM analysis; (b) FIB analysis

Surface changes/phenomena can be summarized as follows: (i) intensive removal of surface material with crater like features; (ii) sporadic appearance of cracking effect at the accumulated material; (iii) appearance of nano-structures (droplets) in near and father periphery and, (iv) creation of the plasma in front of the target. The crater formed by fs-laser beam after short irradiation time is strongly defined on the surface with the diameter of about 300 μm, whereas its depth is of the order of tens of microns. The cross-section of the crater is conical.

3.1.2 Irradiation with ps laser pulses

Irradiation of Inconel 600 with picosecond laser is shown in Fig. 3.



(a) (b)

(c) (d)

Fig. 3 Effect of Nd:YAG laser pulses on superalloy Inconel 600, as a function of number of pulses: (a) 1, (b) 5, (c) and (d) 50 pulses. (Laser intensity ≈ 10^{11} W/cm^2, $\lambda = 1\ 064$ nm, pulse repetition rate is 2 Hz; (a)-(c) SEM analysis; (d) profilometry analysis.

In this case the radiation intensity was similar to the fs laser, however thermal effects are present. The surface features/phenomena induced by this laser can be characterized as: (i) violent removal of material and crater production; (ii) appearance of hydrodynamic changes (like resolidified droplets), and (iii) creation of the plasma in front of the target. The crater formed by the ps laser beam is not so sharp as in case of the fs laser. The damage diameter is larger (about 300 μm), while the profilometry analysis showed semi-spherical cross-section.

3.1.3 Irradiation with ns laser pulses

Irradiation of Inconel 600 target with nanosecond laser pulses is performed by using a pulsed TEA CO_2 system. This laser typically produces the initial spike (FWHM ~ 100 ns) and tail (duration ~ 2 μs). The laser intensity was optimal (10^8—10^9 W/cm^2) but lower with respect to the ultra-short lasers (fs or ps systems). The surface features induced by the lasers can be described as: (i) superficial damage with expressed thermal effects, (ii) intensive appearance of cracking areas and (iii) appearance of the plasma in front of the target, much stronger than in the case of ps and fs pulses. The damage formed by ns laser beam is large with a diameter about 500 μm.

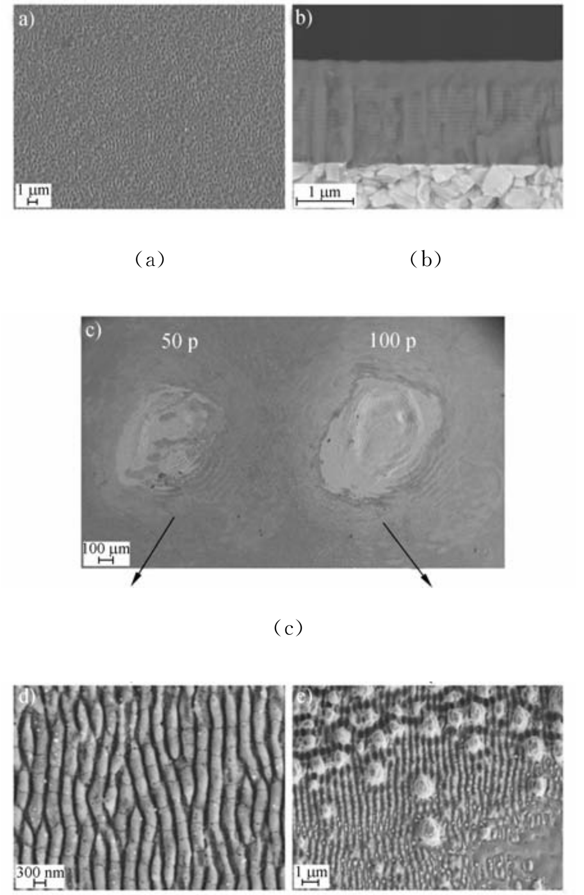
Generally, assuming that the laser emits energy near the damage threshold, its radiation is absorbed via free electrons existing in the metal. This process is fast, and is followed by the thermalisation of electron and lattice subsystems. Finally, the phenomena of ablation can also be present. The Heat Affected Zone (HAZ) strongly depends on the duration of laser pulse. For fs, as well as ps lasers (if the pulse duration is several ps), the HAZ is minimals thus the high precision of surface modification can be achieved. For ns laser pulses, the HAZ is significant and thermal effects are present[9].

3.2 TiAlN/TiN multilayered coating

3.2.1 Irradiation with ps laser pulses

Irradiation of multilayered TiAlN/TiN/steel system with ps laser pulses is shown in Fig. 4.

The target consists of 45 alternating layers Fig. 4(b). The first layer to the steel substrate (bright-white colour) is TiAlN, the subsequent is TiN, *etc.* [10]. Laser induced surface features/phenomena can be summarized as follows: (i) intensive removal of coating in the central irradiation zone, (ii) appearance of wave-like periodic structures at the periphery, and (iii) creation of the plasma in front of the target. The damages formed by ps-laser beam are shallower compared to the fs regime. Periodicity of the laser induced periodic surface structures is in nano-domain (approximately 300 nm)[Fig. 4(d), (e)].



(a)　(b)

(c)

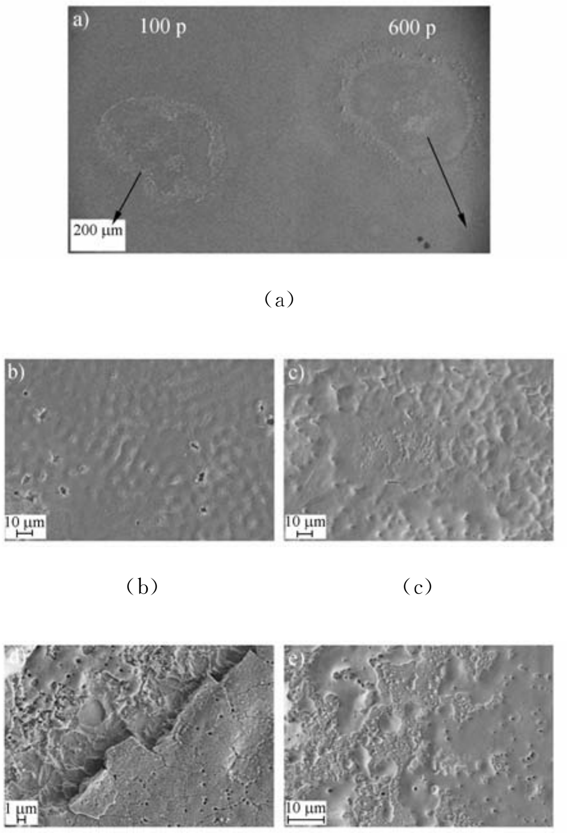
(d)　(e)

Fig. 4　SEM analysis of TiAlN/TiN multilayer: (a) and (b) before irradiation (the surface and cross section of the coating, respectively); (c)－(e) after irradiation with 50 and 100 pulses of ps Nd: YAG laser [(d) and (e) show periodic structures at the periphery]. Laser intensity is about 10^{11} W/cm^2, $\lambda=532$ nm and pulse repetition rate is 2 Hz.

3.2.2　Irradiation with ns laser pulses

The irradiation of multilayered TiAlN/TiN/steel system with ns laser pulses is shown in Fig. 5.

The irradiation with one laser pulse was sufficient to induce visible surface changes. Increasing the pulse count to 100 led to a noticeable enlargement of the damage spot size, but without complete coating removal from the substrate [Fig. 5(b), (d)]. A detailed analysis, Fig. 5(b), revealed periodic surface structures at a micrometer scale. The periodicity of these structures is about 10 μm, close to the laser wavelength. The phenomenon of the surface electromagnetic waves could be responsible for this effect. The irradiation of the target with 600 pulses resulted in coating ablation in the central zone [Fig. 5(c)] and creation of resolidified regions at the periphery. The irradiation was accompanied by strong plasma appearance on the target.



(a)

(b)　(c)

(d)　(e)

Fig. 5　SEM analysis of TiAlN/TiN multilayered coating after irradiation with 100 and 600 TEA CO$_2$ laser pulses. The view of the centre and the periphery: (b) and (d) after 100 pulses, (c) and (e) after 600 pulses, respectively. Intensity is obout 10^8 W/cm^2, $\lambda=10.6$ μm, pulse repetition rate is 2 Hz.

4　Conclusions

A study of surface features of Inconel 600 and TiAlN/TiN/steel target induced by an ultra-short (fs and ps laser system) and short (ns laser system) is considered. It is shown that ultra-short as well as short laser system stimulated morphological changes at the target surface for the laser intensities used. The irradiation of the targets with ultra-short laser pulses, as a rule, resulted in a better definition of the damage comparing to the nanosecond pulses. In case of nanosecond pulses, the thermal effects are dominant. Regarding ultra-short laser interaction, the fs laser pulses produced sharper damage compared to the ps pulses. The obtained crater shapes are quite different. The fs laser beam gave the conical cross section, contrary to the ps laser beam producing a semispherical shape.

The interaction of ultra-short, as well as short laser pulses with Inconel 600 and TiAlN/TiN/steel target was accompanied by the appearance of plasma in front of the target. The plasma, especially in the case of short pulses, together with high surface temperatures achieved, can be used for sterilization. This enables contaminant-free conditions, necessary for the potential implant applications.

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Author's biography：

Dr Milan S. Trtica (Full Res. Professor), was born in Banatsko Veliko Selo, Serbia, received his BS, MS and Ph. D degrees in physical chemistry at the University of Belgrade in 1974, 1979 and 1987, respectively. In 1980 he was on a specialization at the University of Southern California, Los Angeles, USA, and in 1989 at the HeriotWatt University, Edinburgh, UK. The subjects of his specialization were LIF spectroscopy, chemical lasers and pulsed molecular gas lasers. From 2005 to 2010 (in four visits), he was at the Bicocca University, Milano, Italy, as a visiting scientist. During his work experience, he was employed: (i) from 1975 to 1989 at the Institute of Physics, Belgrade as the head of the Laser Group; (ii) from 1989 to date at the Institute of Nuclear Sciences VINCA. He is now the head of the Group for Lasers and Applications. He is also a director of the Department of Physical Chemistry (since 2002) of the VINCA Institute as well as the project leader (project no. 142065) with the Ministry of Science (from 2006 to 2010). His current research interests comprise: (i) phenomena associated with laser beam interactions with materials (including phenomena under ultra-high intensity); (ii) modifications of materials at micro- and nano-levels, and (iii) physics/physical chemistry of pulsed gas lasers. E-mail: etrtica@vinca. rs

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●下期预告

非零位补偿检测大口径非球面反射镜技术

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为了无需零位补偿就能够实现对大口径非球面的测量，阐述了利用圆形子孔径拼接和环形子孔径拼接检测非球面的方法。对该技术的基本原理和基础理论进行了分析和研究，并基于齐次坐标变换、最小二乘拟合建立了综合优化和误差均化的拼接数学模型。分别开发了圆形子孔径拼接和环形子孔径拼接检测非球面的算法软件；设计和搭建了子孔径拼接干涉检测装置，并分别利用圆形子孔径拼接和环形子孔径拼接实现了对一口径为 350 mm 的双曲面的检测；同时，对待测非球面进行了零位补偿检测实验，圆形子孔径拼接与全口径补偿测量结果的 PV 值和 RMS 值的偏差分别为 0.031λ 和 0.004λ；环形子孔径拼接与补偿测量结果的 PV 值和 RMS 值的偏差分别为 0.028λ 和 0.006λ。3 种方法测量所得的面形分布都是一致的，从而提供了除零位补偿检测以外的另一种定量测试大口径非球面的手段。