

Research Article

Double Pulse LIBS of Titanium-Based PVD-Coatings with Submicron Resolution

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The possibility for double pulse LIBS in the process of a direct layer-by-layer analysis of the titanium-based PVD-coatings on polished flat blank samples of steel and silicon and also of the TiAlN/TiN-coating on a milling cutter is considered. A method is proposed to control thickness of the radiation evaporated layer by defocusing the laser beam with respect to the surface, making it possible to attain the depth resolution of 0.1 μm . The Ti and Ti-Zr-coatings produced using the ion-assisted condensation method and subjected to streams of the nitrogen plasma in a magnetic-plasma compressor are studied.

1. Introduction

Double pulse LIBS is extensively used for quantitative analysis of various objects including the toolware manufacture of multicomponent alloys [1, 2]. This method is characterized by such advantages as a low degree of sample destruction, no need in chemical or mechanical pretreatment of the surface. Because of this, LIBS is one of the primary direct analysis methods for thin protective coatings which effectively improve the performance of the products contributing to their resistance to wear and durability. But the papers devoted to LIBS of thin coatings on commercial samples are few [3, 4], whereas quantitative analysis of massive objects manufactured of multicomponent alloys has been comprehensively studied and adequately described in the literature [1, 2, 5, 6]. In the majority of the works devoted to LIBS of thin layers the attention is focused on analysis of the samples with single-component coatings (e.g., zinc-coated steel or copper foils attached to steel and aluminum substrates) [3, 4]. However, the performance of various tools is improved mainly with the use of multicomponent coatings commonly formed by physical vapor deposition (PVD). During this procedure the metal surface is treated in vacuum by molecules of other metals (titanium, zirconium, aluminum, tungsten, molybdenum, iron, copper, nickel, and their alloys) in three stages:

vaporization of the particles involved in the deposition process; transport of vapor to the substrate; vapor condensation on the surface with the formation of a coating. Though this surface-modification technique has been in use for more than thirty years, previously only a single-layer coating of titanium nitride (TiN) was deposited. Now multilayer coatings of titanium-aluminum nitride (TiAlN) are formed, featuring high heat and wear resistance. At the present time for the performance improvement, the leading world producers of drilling and cutting tools use the combined TiAlN/TiN-coating 3–5 μm thick. Owing to the PVD-technique, the surface is modified, whereas the properties and biochemical functions of the base material are retained. The coating is uniformly formed on the substrate without microcracks, providing a protective layer resistant to abrasion and scratches.

PVD-coatings are deposited on the finished drilling and cutting tools often featuring very intricate forms. To realize the quality control, a similar deposition is performed for a flat blank sample whose coating may be studied using an electron microscope and an X-ray spectroscopic analysis. Unfortunately, there are some problems with uniformity of the deposited layer on an intricate surface of the drill as well as with the elemental concentration control in the layers of a tool at different points of the cutting rim. It is impossible to perform by the standard methods a submicron-resolution

TABLE 1: Analyzed samples and their main characteristics.

Number of the sample	Sample name	Material of the coating	Thickness of the coating	Coating method
1	Analysis blank sample (steel)	Ti-Zr	1-2 μm	Ion-assisted condensation
2	Blank sample (steel)	Ti-Zr/TiN/ZrN/steel	10–15 μm	Nitrogen plasma streams
3	Silicon plates	Ti		Ion-assisted condensation
4	Steel milling cutter	(TiAlN/TiN)	Unknown	Physical vapor deposition

analysis of multilayer coatings on the curved surface. The principal objective of this work is to study the possibilities offered by double pulse laser atomic-emission spectroscopy during a direct layer-by-layer analysis of PVD-coatings and the development of techniques for submicron analysis of the coatings deposited on various objects.

2. Experimental

The experiments were performed with the help of a LSS-1 laser spectrometer produced by the Belarusian-Japanese joint venture LOTIS-TII (Minsk). The plasma was generated at the fundamental wavelength (1064 nm) of a nanosecond Q-switched double pulse Nd:YAG laser with a pulse width of 15 ns and repetition rate of 10 Hz. Double laser pulses with the interpulse interval $\Delta t = 0\text{--}100\ \mu\text{s}$ (1 μs step) were used to vaporize the sample and to excite the atomic spectra. The effect of double laser pulses with zero interpulse interval ($\Delta t = 0\ \mu\text{s}$) was identical to that of a single pulse of the doubled energy. Laser pulses with the energy ranging from 10 to 70 mJ were focused by a lens of 100 mm focal length with the spot diameter of about 50–100 μm . A laser beam was aligned horizontally at right angles to the sample surface, and the plasma was generated in the air at atmospheric pressure.

An analytical signal was recorded synchronously with the arrival of the second pulse in order to eliminate registration of continuous spectra of the air. The continuum emitted by the leading front of the plasma formed by the second pulse was much weaker because of the reduced particle density of the surrounding atmosphere in the near-surface region. Radiation of the sample plasma was collected by two achromatic objectives into two SDH-1 compact polychromators (SOLAR Laser Systems, Minsk) with the working ranges 190–340 nm and 265–800 nm, respectively. In both cases the recorded spectral width was $\sim 150\ \text{nm}$; range of the second polychromator was retuned by a microscrew. The SDH-1 polychromator (grating 1200 lines/mm; the average inverse linear dispersion 5.3 nm/mm; spectral resolution 0.12 nm) was a diffraction spectrograph providing a linear spectral scan for the recording system based on a 3648-pixel multichannel TCD1304AP detector (Toshiba).

The crater depth on the sample surface and the layer thickness were determined using a Linnik MII-4 microinterferometer. The measurements performed demonstrate that, compared to single pulses, the use of double laser pulses at the invariable total power leads to a multiple increase in the intensity of spectral lines (Figure 1) with a thickness of the evaporated layer, increasing by a factor of 1.5 only. A maximum intensity of spectral lines for titanium is observed when

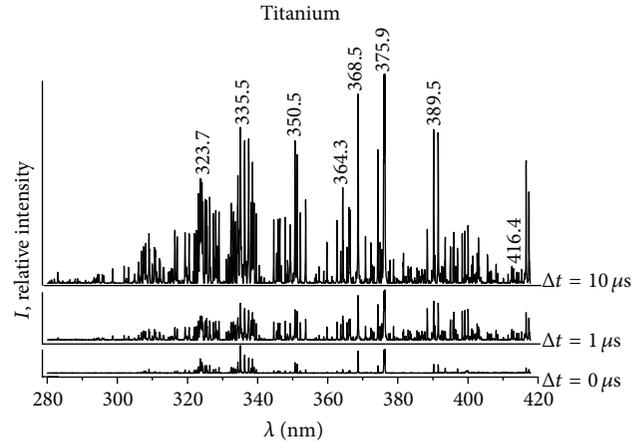


FIGURE 1: Fragment of spectra recorded for titanium in the case of single ($\Delta t = 0\ \mu\text{s}$) and double laser pulses ($\Delta t = 1\ \mu\text{s}$ and $10\ \mu\text{s}$) with the total energy $E_{\text{pul}} = 60\ \text{mJ}$.

a time interval between the double laser pulses is 10 μs and for silicon – 7 μs [7].

In the process of studies four different objects with PVD-coatings have been analyzed (Table 1):

- (i) The “analysis blank sample” represents a flat steel plate polished to high finish that was titanium coated using the ion-assisted condensation method. This system was subjected to the effect of the combined and separate plasma streams formed in vacuum-arc discharges. The arc current was 100 A, negative reference voltage $-120\ \text{V}$, and thickness of the coating – 1-2 μm .
- (ii) The “blank sample” was additionally treated with the use of the nitrogen plasma streams formed in a magnetic-plasma compressor with different numbers of plasma pulses (ranging from 1 to 5) during the period of about 100 μs . The experiments have been performed in the “residual atmosphere” regime: the plasma-forming substance—nitrogen—was injected into the preevacuated chamber up to the pressure 400 Pa. The power density of a stream was varying as $(1.5\text{--}3.5) \cdot 10^5\ \text{W/cm}^2$; this was sufficient for melting of the surface layers and for doping of steel by the coating components and plasma-forming substance (nitrogen) with possible formation of nitride phases, solid solutions, and intermetallics. As a result, a multilayer structure was formed, with the thickness 10–15 μm [8].

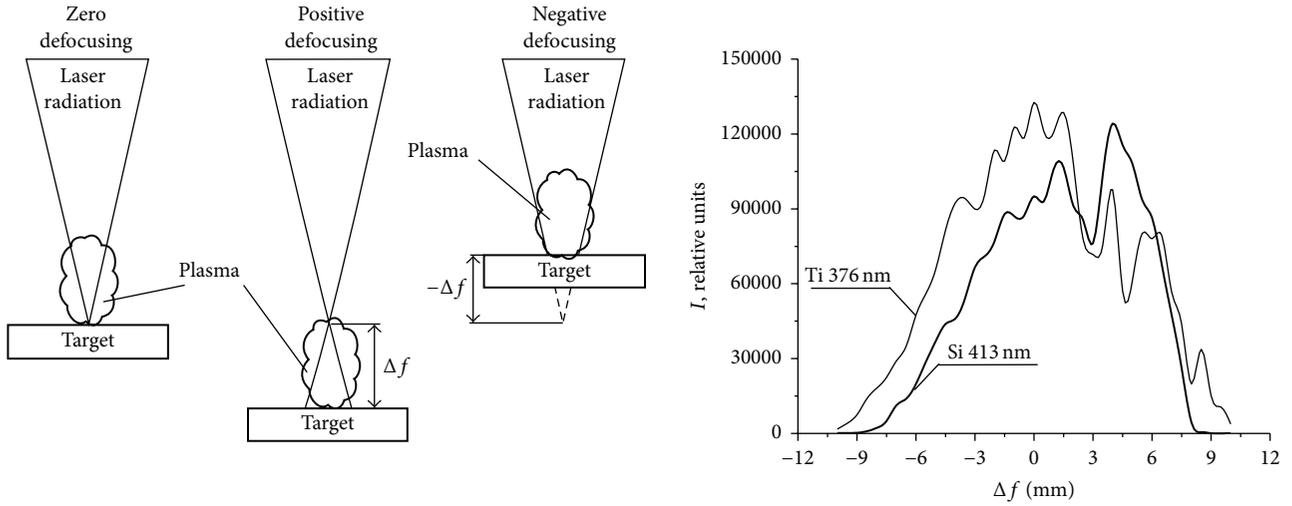


FIGURE 2: Schematic for defocusing of laser radiation; the spectral line intensities of titanium $\lambda = 376$ nm and silicon $\lambda = 413$ nm as a function of the distance Δf from the sample surface to the laser beam focus.

- (iii) Silicon plates with a titanium coating deposited using the ion-assisted condensation method, the discharge parameters being the same as for the blank sample of steel. Some of the silicon plates with titanium coating, similar to the blank sample, were subjected to the effect of the nitrogen plasma. Before the treatment, the initial silicon plates were covered by a high-melting mask of tungsten with the holes $50 \mu\text{m}$ in diameter, positioned at a distance of $50 \mu\text{m}$ from each other [8].
- (iv) The steel milling cutter was manufactured by Guhring (Germany) having a multilayer PVD-coating (TiAlN/TiN).

A source for a direct layer-by-layer analysis of thin coatings should meet the following requirements [9, 10]:

- (i) The constant minimal evaporated thickness of a substance offers the possibility for analysis procedures at the spatial resolution of the coating thickness 0.1.
- (ii) Uniform evaporation over the whole effective area of the erosion spot ensures that the substance ingress into the analytical plasma is related only to the layer under study rather than to the previous or subsequent layer.
- (iii) An intensity of the analytical spectral lines for all the coating components should be higher than the background level severalfold.

An amount of the vaporized substance was determined from the radiation flux density q on the sample surface:

$$q \approx \frac{E_{\text{pul}}}{\tau S_{\text{eff}}}, \quad (1)$$

where E_{pul} and τ were the pulse energy and duration at half height and S_{eff} was effective area of the laser spot on the target. For $E_{\text{pul}} = 60$ mJ and $q \sim 10^{10}$ W/cm², the average

crater depth on the sample surface after one laser shot was $5 \mu\text{m}$. Because of this, double laser pulses with these radiation parameters could not be used as a substance evaporation and spectrum excitation source for a layer-by-layer analysis of micron coatings.

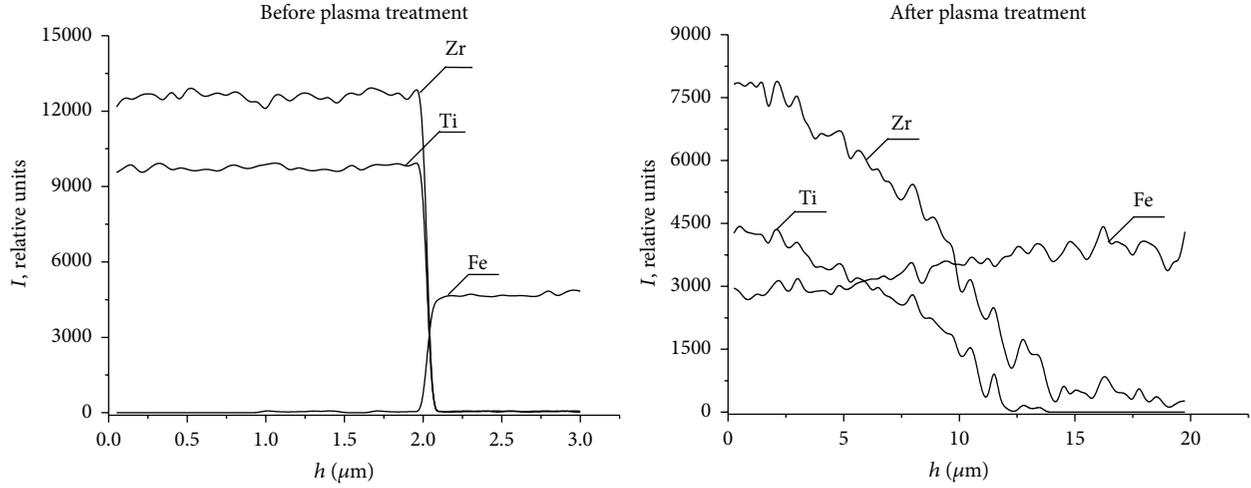
Three methods were proposed to reduce the flux density q and layer thickness h_0 [9]:

- (i) Lowering of the pulse energy: in this case a decrease in the temperature, density, and coefficient of the radiation absorption by plasma leads to passing almost without energy absorption of the second laser pulse directly to the sample surface. This results in a greater degree of the surface destruction [11, 12].
- (ii) Use of light filters (optical glasses) with different transmission coefficients for laser radiation: an amount of the vaporized substance is decreased with the use of light filters due to a decrease in q . As a result, intensities of spectral lines of the investigated elements (Ti, Zr, Si, Fe, Al, and N) were at a background level for the required thickness of the analyzed layer and hence this method for decreasing q could not be used for analytical purposes.

Positive and negative defocusing of the laser beam means focusing at some distance Δf above and below the surface of the ablated sample (Figure 2). As this takes place, a decrease of the radiant flux density q occurs simultaneously with a decrease in the effective area S_{eff} of the erosion spot associated with evaporation. Based on the optical scheme of a LSS-1 spectrometer, it is possible to record a signal from the plasma evaporated from a greater ($\sim 1\text{--}3 \text{ mm}^2$) surface area [13]. In this case an analytical signal exceeds a background level severalfold even at $h_0 = 0.1 \mu\text{m}$. As demonstrated by the conducted experiment elucidating the effect of a defocused laser radiation on silicon and titanium plates (sample 1 and sample 3), with a minor change in Δf the spectral line intensities of Ti and Zr are changed stepwise (Figure 2).

TABLE 2: Radiant flux density q and thickness h_0 at different distances Δf for negative defocusing.

Δf , mm	-1	-2	-3	-4	-5	-6	-7	-8	-9	-10
$q \cdot 10^7$, W/cm ²	1500	370	170	93	59	41	30	23	18	15
h_0 , μm	3	1.5	1	0.5	0.35	0.2	0.15	0.12	0.105	0.10

FIGURE 3: Spectral line intensities of titanium $\lambda_{\text{Ti}} = 390.2$ nm, zirconium $\lambda_{\text{Zr}} = 360.1$ nm, and iron $\lambda_{\text{Fe}} = 382.0$ nm as a function of the coating depth before and after the surface treatment by the nitrogen plasma streams.

This is due to the plasma blooming for laser radiation at a lower radiant flux density q and also due to spatial inhomogeneity of the ablation plasma formed [10]. By studies of the surface destruction under the effect of a defocused radiation it has been found that double laser pulses completely meet the requirements to the spectrum excitation sources in a direct layer-by-layer analysis of thin coatings with a submicron resolution.

In Figure 2 it is seen that in the case of a negative defocusing when $\Delta f \leq -3$ mm, in contrast to the positive defocusing, an intensity of spectral lines exhibits a monotonic decrease with a growing distance from the surface to the focal point. This is associated with the fact that at the focal point for $\Delta f > 0$ mm the initiation of so-called laser spark—break-down of the propagating plasma—is possible. So, the proposed method for lowering the radiant flux density may be used for analytical purposes at a negative defocusing with $\Delta f \leq -3$ mm only. The thickness h_0 of the layer evaporated by a defocused radiation was determined by an abrupt, during 1-2 pulses, intensity drop for the spectral line of Ti when the blank sample 1 had a marked interface between the titanium coating and steel base. Table 2 gives the values of the radiant flux density q and of the thickness h_0 at different distances Δf in the case of a negative defocusing [13, 14].

As a minimal thickness of the coating in the samples under study amounted to $\sim 1 \mu\text{m}$, the measurements were performed for $\Delta f = -10$ mm to ensure, at least, 10 layers during the procedure of a layer-by-layer analysis. The optimum parameters of laser radiation to provide a maximal value of the spectral line intensity for the coating components and for the base material in the studied samples have been found experimentally: $E_{\text{pul}} = 70$ mJ, $\Delta t = 10 \mu\text{s}$.

3. Results

A lowered density of the radiant flux q with a defocused radiation leads to the decreased quantity of a substance ingressed into the ablation plasma and hence to the decreased line intensities [11–14]. Because of this, for analytical applications it is expedient to select the lines with the highest intensity for all the components in the spectral range of interest: $\lambda_{\text{Ti}} = 390.2$ nm, $\lambda_{\text{Zr}} = 360.1$ nm, $\lambda_{\text{Si}} = 390.6$ nm, $\lambda_{\text{Al}} = 396.2$ nm, and $\lambda_{\text{Fe}} = 382.0$ nm.

Intensities of these spectral lines are given in Figure 3 as a function of the layer depth h for the protective Ti-Zr-coating before the surface treatment by the nitrogen plasma streams (sample 1) and after the treatment (sample 2).

In the process of a qualitative layer-by-layer analysis of Ti-Zr coating using double pulse LIBS it has been found that the ion-assisted condensation method enables one to form a layer of titanium and zirconium actually homogeneous to the depth on the polished steel substrate [7]. An abrupt drop in the intensities of spectral lines for titanium and zirconium occurring simultaneously with an increase of I for the line of iron supports the conclusion that a defocused radiation of double laser pulses results in uniform evaporation of the substance from the sample surface. In this case the crater is practically cylindrical in its form, and the contribution into the analytical signal due to fluorescence of the atoms arriving into the plasma on ablation from the crater walls may be neglected. Thermal diffusion of the elements when the surface is subjected to the effect of nitrogen plasma leads to the formation of a three-component coating with the content varying over the depth (sample 2). The components of PVD-coating penetrate in depth of the steel plate within a distance

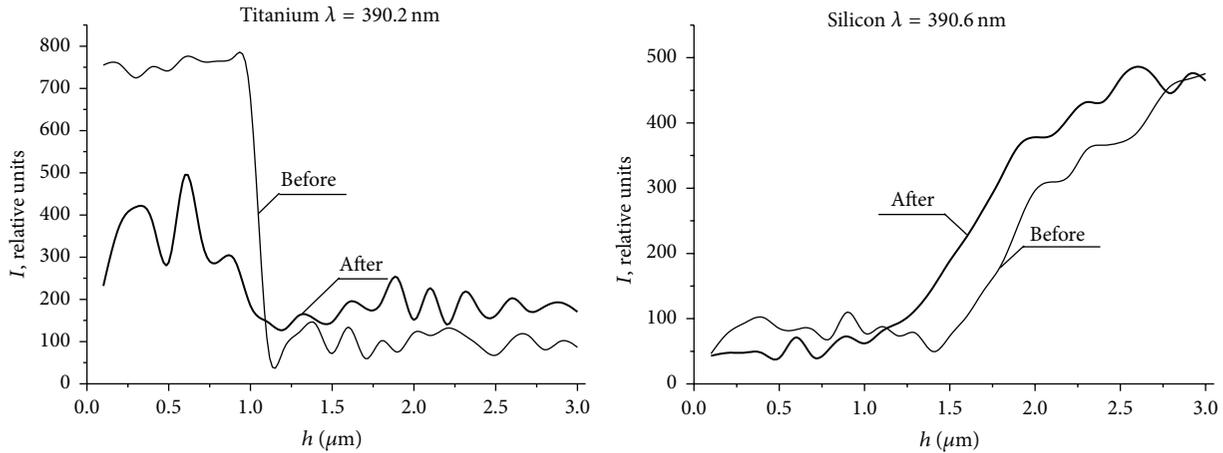


FIGURE 4: Spectral line intensities of titanium $\lambda = 390.2$ nm and silicon $\lambda = 390.6$ nm as a function of the layer depth h in PVD-coating on silicon plate before and after the nitrogen plasma treatment.

of 10–15 μm , and iron atoms from the substrate arrive to the very surface. A thickness of the three-component system formed is dependent on the power density and on the number of the plasma pulses formed in a magnetic-plasma compressor.

During analysis of a PVD-coating one should take into account that the base of Si is very fragile and nonconducting. Because of this, many standard methods are inapplicable, for example, atomic-emission analysis with electric arc or spark spectrum excitation and hardness tests. As demonstrated by the experiments conducted, the use of double laser pulses, both focused on the surface ($\Delta f = 0$ mm) and defocused ($\Delta f \leq 10$ mm), causes no destruction of the silicon substrate (sample 3). Though focused radiation could not be used for a layer-by-layer analysis of PVD-coating, laser pulses with such values of Δf and q enable one to study the spatial distribution of titanium on the plate surface at the points directly subjected to the effect of the nitrogen plasma and hidden by the tungsten mask. The spectral line intensities of titanium $\lambda = 390.2$ nm and silicon $\lambda = 390.6$ nm as a function of the layer depth h in a PVD-coating on a silicon plate before and after the treatment with the nitrogen plasma are given in Figure 4.

Similar to the case of a steel plate with a Ti-Zr coating, the plasma treatment results in diffusion of the atoms associated with a homogeneous micron coating to the depth of the base, forming a two-component system several micrometers thick on the surface. Due to the use of a tungsten mask, the penetration depth of titanium into silicon after irradiation is considerably lower than in the case of a similar treatment for the Ti-Zr coated steel sample, being less than 5 μm . The intensity distribution of spectral lines for $\lambda_{\text{Si}} = 390.6$ nm and $\lambda_{\text{Ti}} = 390.2$ nm over the surface of a silicon plate after the nitrogen plasma treatment using the tungsten mask, with the holes 50 μm in diameter positioned at a distance of 50 μm from each other, is shown in Figure 5.

The obtained results point to spatial inhomogeneity of the coating subjected to the nitrogen plasma but it has been found experimentally that the high-energy treatment without the tungsten mask leads to the sample destruction.

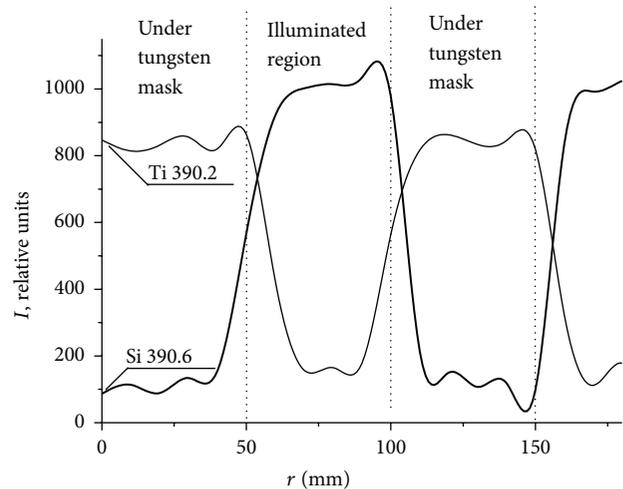


FIGURE 5: Intensity distribution of spectral lines for $\lambda_{\text{Si}} = 390.6$ nm and $\lambda_{\text{Ti}} = 390.2$ nm over the surface of silicon plate after the nitrogen plasma treatment through the tungsten mask with the holes 50 μm positioned at the distance 50 μm .

To study a steel milling cutter with a PVD-coating (TiAlN/TiN) (sample 4), the authors have analyzed layer by layer the deposited coating at three different points arbitrary designated as a side, a cutting tool, and a butt-end (Figure 6). A thickness of the coating was established by the appearance of the spectral lines for iron from the steel base of the cutting tool. As found in the process of experiments, a thickness (4.2 μm) and a spatial distribution of the elements on the butt-end and on the cutter are identical, whereas a thickness of the side coating is greater (5.2 μm); see Figure 6. This may be associated with peculiarities of the deposition procedure on cutting tools. Then the PVD-coating has been scanned in layers by steps of 0.1 μm , and a relative in-depth spatial distribution of components in the deposited layer normalized to the maximal value has been analyzed (Figure 7). As found, the PVD-coating under study comprises 10 layers of different thickness

TABLE 3: Layer thickness h_i and elemental content in PVD-coating on steel milling cutter.

Layer	1	2	3	4	5	6	7	8	9	10
$h_i, \mu\text{m}$	1.73	0.40	0.27	0.24	0.46	0.20	0.48	0.21	0.37	0.40
$C_{\text{Ti}}, \%$	*29–2.9	34	41	47	52	56	62	66	61	73
$C_{\text{Al}}, \%$	*7–0.6	9	11	12	14	15	16	18	16	19

*Within the deepest layer with a thickness of $1.73 \mu\text{m}$ the content of titanium and aluminum linearly decreases with a growing depth.

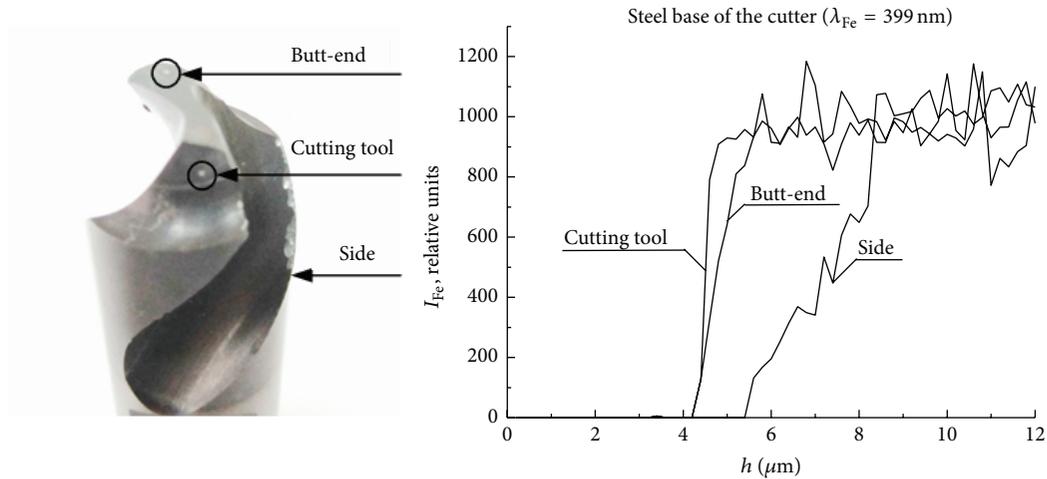


FIGURE 6: Localized effect of laser radiation on milling cutter; the spectral line intensity $\lambda_{\text{Fe}} = 399 \text{ nm}$ of the steel base as a function of the radiation penetration depth.

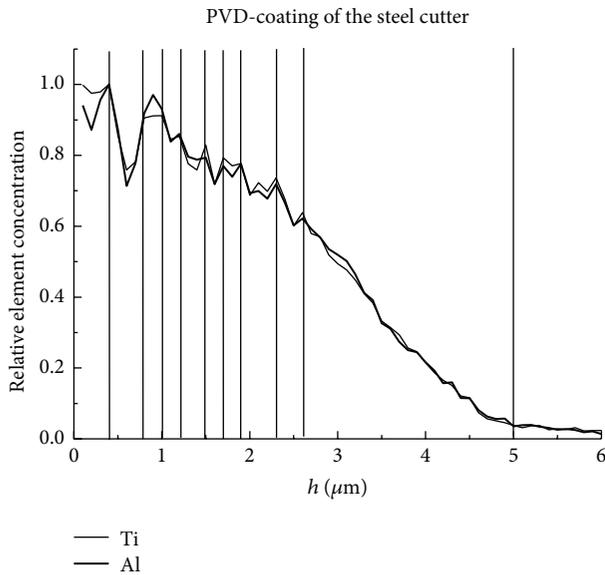


FIGURE 7: The maximum-normalized relative content of titanium Ti and aluminum Al in PVD-coating of milling cutter as a function of the layer depth.

h_i , each of which has the characteristic content of the basic components (Ti, Al, and N). The number of layers and the elemental concentrations at the three indicated points of the milling cutter are identical, while a thickness of each layer at the side surface is greater. The deepest, that is, the closest to

the steel base, layer of a PVD-coating with the thickness $h_{10} = 1.7 \mu\text{m}$ is homogeneous as regards the content of Al and Ti.

However, in Figure 7 it is seen that the concentration of aluminum and titanium decreases practically linearly. This is due to the fact that the surface of a workpiece for milling cutter is not polished before deposition; the surface exhibits microroughness in the form of “horns” the size of which diminishes with a distance from the piece center.

To perform a layer-by-layer quantitative analysis of a PVD-coating, spectra have been recorded for 10 standard samples with a specified concentration of titanium and aluminum at similar parameters of laser radiation ($\Delta f = -10 \text{ mm}$, $E_{\text{pul}} = 75 \text{ mJ}$, $\tau = 15 \text{ ns}$, $q = 3 \cdot 10^7 \text{ W/cm}^2$, and $\Delta t = 10 \mu\text{s}$). The curves for the spectral line intensities of titanium $\lambda_{\text{Ti}} = 390.2 \text{ nm}$ and aluminum $\lambda_{\text{Al}} = 396.2 \text{ nm}$ as a function of their concentration were constructed. Table 3 presents the results for a steel milling cutter.

The developed technique for a direct layer-by-layer elemental analysis of coatings using double pulse LIBS may be applied in submicron-resolution quantitative studies in the case of PVD-deposition.

4. Conclusions

Double pulse LIBS is a very effective technique of a direct layer-by-layer analysis of micron PVD-coatings, enabling studies of the curved surface of samples without the preliminary chemical or mechanical treatment in the air. To control a thickness of the evaporated layer by changes in the radiant flux density, one should use the defocusing method when

double laser pulses meet all the requirements to the spectrum excitation source for a direct layer-by-layer analysis of thin coatings.

The developed analytical techniques may be used in quantitative and qualitative analysis in layers of PVD-coatings on metal and nonmetal objects including metal and nonmetal objects, both flat blank samples and commercial products of intricate form.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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