METHODS AND APPARATUS FOR LAYERWISE ATOMIC EMISSION ANALYSIS OF MATERIALS AND PRODUCTS WITH NANOMETER RESOLUTION

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Double pulse LIBS is extensively used for quantitative analysis of various objects including the toolware manufactured of multicomponent alloys. 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. 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. 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 analysis of multilayer coatings on the curved surface.

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 Δt=0-100 μs (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 (Δt=0 μs) 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 about 50-100 μm. 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 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 a time interval between the double laser pulses is 10 μs, and for silicon – 7 μs.

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

- The «analysis blank sample» representing 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 V, thickness of the coating –1-2 μm.
- 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 pre-evacuated chamber up to the pressure 400 Pa. The power density of a stream was varying as $(1.5–3.5)\cdot 10^5$ 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 intermetallides. As a result, a multilayer structure was formed, with the thickness 10−15 μm.
- 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 μm in diameter, positioned at a distance of 50 μm from each other.
- The steel milling cutter manufactured by Guhring (Germany) having a multilayer PVD-coating (TiAlN/TiN).
- The defocusing method was proposed to reduce the flux density q and layer thickness h_0 [1]: positive and negative defocusing of the laser beam means focusing at some distance Δf above and below the surface of the ablated sample. In this case an analytical signal exceeds a background level by several fold even at h_0=0.1 μm [2]. As a minimal thickness of the coating in the samples under study amounted to ~ 1 μm, the measurements were performed for Δf=−10 mm to ensure, at least, 10 layers during the procedure of a layer-by-layer analysis.

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. 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: Ti λ=390.2 nm, Zr λ=360.1 nm, Si λ=390.6 nm, Al λ=396.2 nm, Fe λ=382.0 nm. Intensities of these spectral lines are given in fig. 1 as a function of the layer depth *h* for the protective Ti-Zr-coating before the surface treatment by the nitrogen plasma streams and after the treatment.

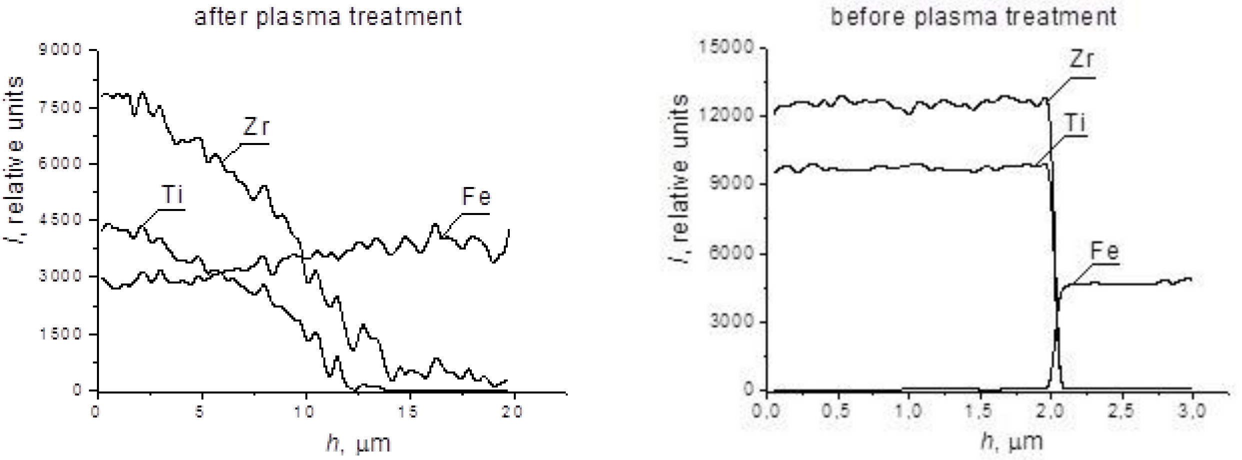

Fig. 1. Spectral line intensities of titanium λ_{Ti}=390.2 nm, zirconium λ_{Zr}=360.1nm, and iron λ_{Fe}=382.0 nm as a function of the coating depth before and after the surface treatment by the nitrogen plasma streams

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, e.g. atomic-emission analysis with electric arc or spark spectrum excitation, hardness tests, etc. As demonstrated by the experiments conducted, the use of double laser pulses, both focused on the surface (Δf = 0 mm) and defocused ($\Delta f \leq$ 10 mm), causes no destruction of the silicon substrate. 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 Si λ=390.6 nm and Ti λ=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 fig. 2.

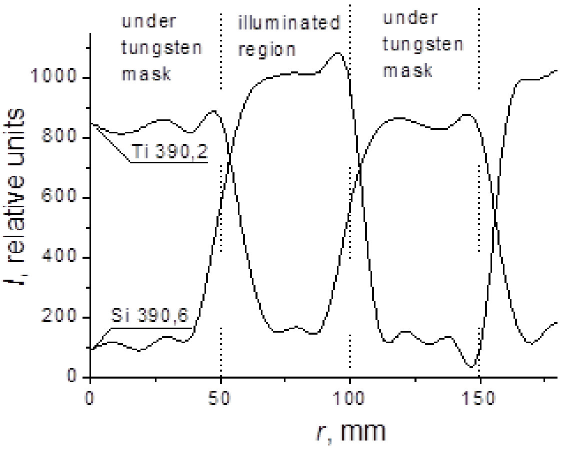

Fig. 2. Intensity distribution of spectral lines for Si λ=390.6 nm and Ti λ=390.2 nm over the surface of silicon plate after the nitrogen-plasma treatment through the tungsten mask with the holes 50 µm positioned at the distance 50 µm

To study a steel milling cutter with a PVD-coating (TiAlN/TiN), 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 (Fig. 3). 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 is identical, whereas a thickness of the side coating is greater (5.2 μ). This may be associated with peculiarities of the deposition procedure on cutting tools. As found, the PVD-coating under study comprises 10 layers of different thickness h_i, each of which has the characteristic content of the basic components (Ti, Al, 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, i.e. the closest to the steel base, layer of a PVD-coating with the thickness h_{10} = 1.7 μm is homogeneous as regards the content of Al and Ti.

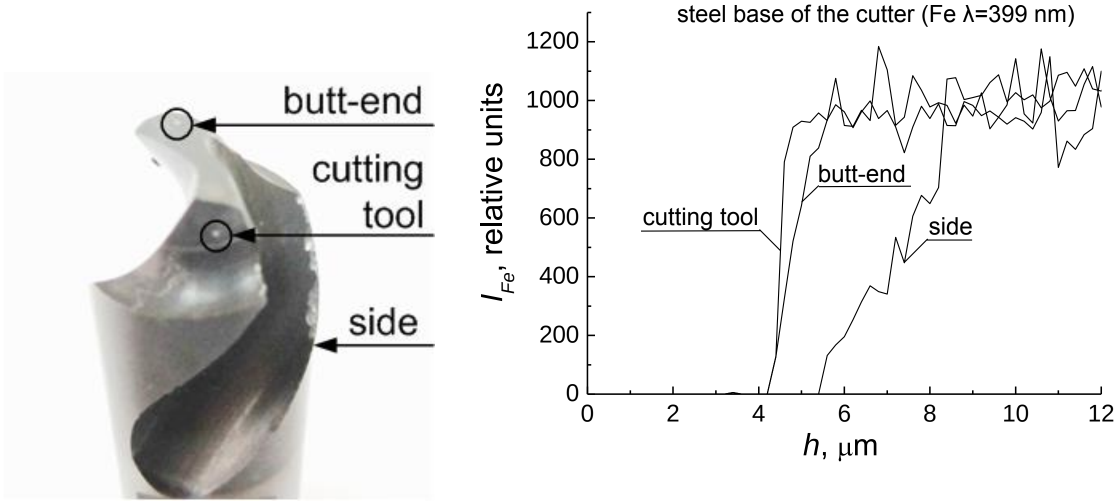

Fig. 3. Localized effect of laser radiation on milling cutter; the spectral line intensity λ_{Fe} = 399 nm of the steel base as a function of the radiation penetration depth

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 ($\Delta f = -10$ mm, E_{pul} = 75mJ, τ = 15 ns, $q = 3 \cdot 10^7$ W/cm^2, Δt = 10 μs). The curves for the spectral line intensities of titanium λ_{Ti} = 390.2 nm and aluminum λ_{Al} = 396.2 nm as a function of their concentration were constructed. Table 1 presents the results for a steel milling cutter.

Table 1. Layer thickness h_i and elemental content in PVD-coating on steel milling cutter
** Within the deepest layer with a thickness of 1.73 μm the content of titanium and aluminum linearly decreases with a growing depth*

Layer	1	2	3	4	5	6	7	8	9	10
h_i, μm	1,73	0,40	0,27	0,24	0,46	0,20	0,48	0,21	0,37	0,40
C_{Ti}, %	*29÷2,9	34	41	47	52	56	62	66	61	73
C_{Al}, %	*7÷0,6	9	11	12	14	15	16	18	16	19

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. 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.

Resources

1. K.F. Ermalitskaia, Y.S. Voropay, A.P. Zajogin, Dual-pulse laser-induced breakdown spectrometry of bronze alloys and coatings, J. of Appl. Spectroscopy 77 (2010) 153-159.
2. E. Voropay, K. Ermalitskaia, Spatial heterogeneity of the double-pulse laser plasma of copper alloys, Eur. Phys. J. D 64 (2011) 453–458.