LIBS CHARACTERIZATION OF IN-DEPTH COMPOSITION OF THERMAL SPRAY COATINGS MODIFIED BY COMPRESSION PLASMA FLOWS

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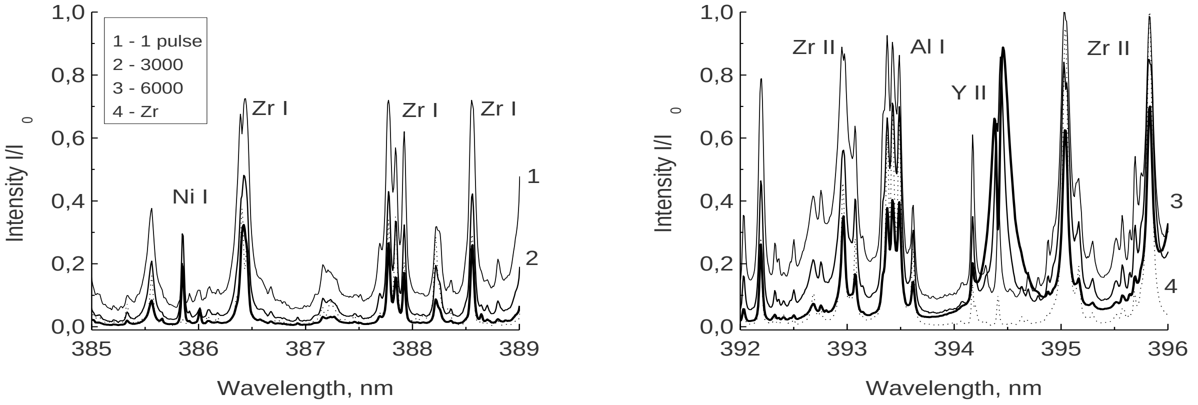
Laser-induced breakdown spectroscopy (LIBS) is obviously one of the most suitable method to analyze chemical composition of solid materials. As a rule, the LIBS measurements give surface composition data due to the surface irradiation by focused laser beams exciting laser plumes. Here, we examine LIBS potential to monitor composition evolution from the solid surface deep into the material acting with successive laser pulses onto a chosen point of the surface. Due to the surface erosion the laser plumes go deeper into the sample thus delivering information on in-depth distribution of the sample composition.

Samples of the two-layer coating consisting of a viscous NiAl metal layer on a base layer of solid ZrO_2 ceramics obtained by thermal plasma spraying have been used for the study. The samples have been further treated with compressed plasma flows (CPF) of a magneto-plasma compressor (MPC). Details of the sample preparation including CPF and MPC can be found elsewhere /1/.

The installation used for the LIBS analysis of the two-layer coating samples before and after the CPF treatment includes a double-pulse Nd:YAG laser at 1064 nm wavelength with the pulse energy of 100 mJ, 11 ns (at half intensity) duration of each pulse, 2 mrad divergence, and 10 μs inter-pulse interval.

The spectra have been recorded in the wavelength interval of 380-400 nm using a grating (1800 lines/mm) spectrometer with 850 mm focal length and 1/11 relative aperture. A lens of 13 cm focal length has been used to focus the laser beam on the sample. Recording of the laser plume emission has been realized by a CCD matrix (2048×64) in the line summation mode. The laser plume has been imaged 1:1 onto the entrance slit (30 μm width) using a lens with f=70 mm.

The laser plume spectra have been recorded for the action of 1 to 6000 laser pulses. The action has resulted in craters of 650 μm diameter for the sample metal part increasing up to 1500 μm at 6000 pulses. The crater total depth (after 6000 pulses) has reached 700 μm. So, the crater depth is related with a number of the laser pulses, and one can roughly accept that 1000 pulses correspond to a distance of 100 μm. Auxiliary spectra of Zr and Al samples have been also recorded. Two fragments of the recorded spectra are shown in Fig. 1 a,b.



a b

Fig. 1. Fragments (a, b) of the spectra resulted from the action of 1, 3000 and 6000 laser pulses onto CPF treated samples

Relative changes in concentration of basic elements of the sample composition from the sample surface deep into the coatings have been evaluated using the recorded spectra. Intensity ratios of the chosen spectral lines are supposed to correspond to concentration ratios of relevant elements. Spectral lines with close excitation (E_{ex}) and ionization (E_i) energy have been chosen to ensure the evaluation for the thermal equilibrium case. These lines are as follows: Ni I 385.830 nm (E_{ex}=3.63 eV), Zr I 388.541 nm (E_{ex}=3.23 eV), Al I 394.406 nm (E_{ex}=3.14 eV), Zr II 393.479 nm (E_{ex}=3.58 eV, E_i=6.84 eV), Y II (E_{ex}=3.24 eV, E_i=6.38 eV). Spectral profiles of the lines have been approximated with the Voigt contour, whose area is taken as intensity of the lines. Line intensity ratios of minor elements Al, Ni, Y to the basic Zr element of the coatings have been evaluated to increase the evaluation precision.

The evaluation results are presented in Fig. 2, 3. It is seen from the figures that Al content is varied in the coating composition most drastically increasing strongly with a distance from the surface. Changes in concentration of Y and Ni are much smaller with a slight growth from the surface. Fig. 3 shows possible errors in the content measurements because of using lines with a large difference in excitation-ionization energy.

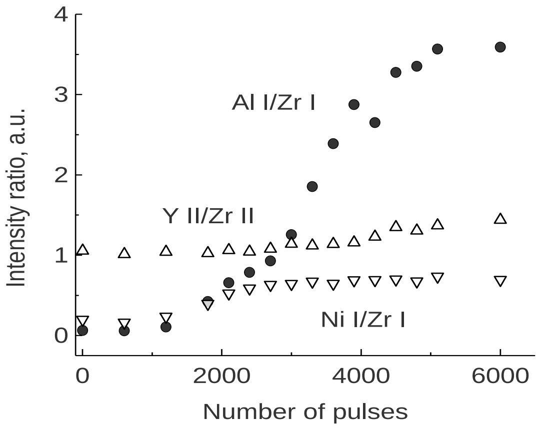
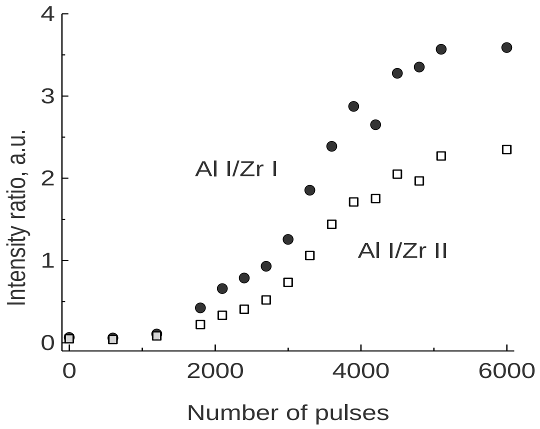
	

Fig. 2. Evolution of the coating composition with a distance from the surface	Fig. 3. Evolution of Al content relatively to Zr atom and ion

Additionally, the data for CPF treated and non-treated coatings have been compared (see Table below).

Ratio of spectral lines	For non-treated coating	For CPF treated coating
Ni I/Zr I	0.163	0.139
Al I/Zr I	0.021	0.012
Y II/Zr II	1.089	1.086

One can see from the Table that the CPF treatment hardly changes the coatings elemental composition influencing other properties, which are considered in other researches. A higher spatial resolution of the measurements would evidently give better results.

Thus, LIBS is shown to be a useful tool in studies of elemental composition of coatings capable to evaluate in-depth distribution of elements.

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References

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