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NANOSTRUCTURES ASSISTED TEA-CO_2 BASED LIBS: IMPROVEMENT OF THE LIMIT OF DETECTION

SANJA ŽIVKOVIĆ[1], JELENA PETROVIĆ[1], MILOŠ OGNJANOVIĆ[1], JOVAN CIGANOVIĆ[1], DAMJAN BLAŽEKA[2], NIKŠA KRSTULOVIĆ[2] and MILOŠ MOMČILOVIĆ[1]

[1] *VINČA Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, PO Box 522 11351 Belgrade, Serbia, E-mail sanjaz@vinca.rs*

[2] *Institute of Physics, Bijenička cesta 46, 10000 Zagreb, Croatia*

Abstract. We report preliminary results of an innovative approach based on nanomaterials deposition on the sample surface for the improvement of the limit of the detection of Laser-Induced Breakdown Spectroscopy (LIBS) analysis of trace elements in aluminum alloys. For this purpose, Ag-TiO_2 bimetallic nanoparticles were synthesized and used to enhance the emission signal of laser-induced plasma.

1. INTRODUCTION

Laser-Induced Breakdown Spectroscopy (LIBS) technique has been recognized as a modern, fast, and direct method for multielement material analysis for more than 20 years. Specific advantages of LIBS include a very small amount of the sample required for the analysis with little or no sample preparation and no consumable or waste products. Despite the intrinsic benefits of the LIBS method with respect to other standard analytical techniques (ICP-OES, XRF, AAS), some fundamental limitation in sensitivity and reproducibility of the analytical results has limited the establishment of this method (Zivkovic et al. 2017). Recently, one of the signal enhancement methods has emerged as a possible solution. This promising variant of the LIBS technique, namely Nanoparticle - Enhanced LIBS (NELIBS) is based on the use of metallic nanoparticles which can be determinant in controlling the laser-matter interaction, by directly affecting the coupling of incoming laser electromagnetic field with the irradiated material (Dell'Aglio et al. 2018).

In this work, silver-titanium dioxide bimetallic nanoparticles (NPs) were prepared and used to perform preliminary NELIBS analysis of aluminum alloy samples. Preliminary results have shown that enhancement of the LIBS signal can be achieved using this kind of NPs.

2. EXPERIMENTAL

With the Pulsed Laser Deposition (PLD) method thin film is prepared by the simultaneous ablation of two targets: silver and titanium dioxide. As the thin film substrate pure silica is used. PLD was performed in vacuum using 5 ns Nd:YAG laser operating at 1064 nm, 300 mJ of output energy and repetition rate of 5 Hz. Laser pulses were focused onto the target yielding laser fluence of about 30 mJ/cm^2. PLD setup is shown in (Meljanac *et al.* 2016). Uniformity of the prepared thin layer was tested by LIBS analysis.

Silver-titanium dioxide bimetallic (Ag-TiO_2) nanoparticles were produced by the laser ablation method. A thin layer film obtained by PLD was placed in a glass and covered with 10 ml of bidistilled water. Laser applied was the picosecond Nd:YAG system, operating at 1064 nm with a 150-ps pulse length, pulse energy 40mJ pulse energy, and irradiation time of 30 minutes. The size distribution of the obtained colloid solution of nanoparticles was analyzed by dynamic light scattering (DLS) technique using a *Zetasizer Nano ZS90* (Malvern, UK) with 633-nm He-Ne laser and 90° detection optics. The zeta potential was measured at pH 5 at 25 ± 0.1 °C in a disposable zeta cell (DTS 1070) of a *Nano ZS90* device.

LIBS measurements were conducted using a unique developed LIBS system based on pulsed gas TEA CO_2 laser and time-integrated spatially resolved spectroscopy (TISR). All aluminum alloy samples were mechanically treated with corundum abrasive paper to increase the absorptivity of applied TEA CO_2 laser wavelength. After the samples were clean from the residue of mechanical treatment, samples were coated with a thin layer of nanomaterial dispersion droplets and then were dried. The schematic diagram of the experimental arrangement is shown in Figure 1.

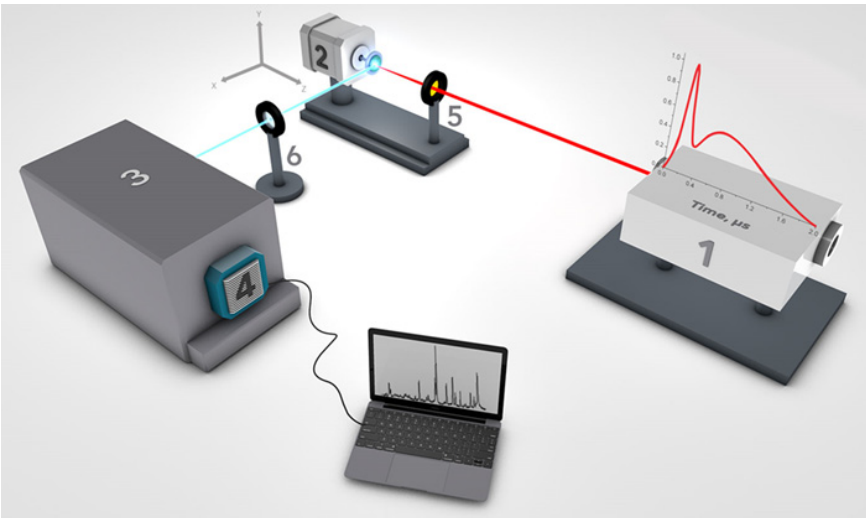

Figure 1: Experimental setup for TEA CO_2 laser-based LIBS

The plasma was generated by focusing a pulsed TEA CO_2 laser that emits at 10.6 µm on the aluminum target with Ag-TiO_2 NPs on the surface at atmospheric pressure. All measurements were taken at the focal point. Applied laser energy was 200 mJ with a repetition rate of 1 Hz and the shot to shot fluctuation of its energy was about 5%. Optical emission from the induced plasma was collected on the entrance slit of a Carl Zeiss PGS2 monochromator by using an achromatic lens with magnification 1:1. LIBS analysis was conducted in time-integrated mode during 10 s using CCD Apogee Alta F1007 camera as a detector. The TISR measurements were performed at the atmospheric pressure in the air. Production of stable and reproducible plasma required fresh area at the target surface which was achieved by target rotation using a continual motor. All measurements were carried out in triplicate and obtained spectra present average values of line intensities from 10 different parts of the sample surface.

3. RESULTS AND DISCUSSION

Uniformity of the PLD thin film was confirmed by the LIBS method. Average spectra consist of several Ti I and Ti II lines and Ag I emission line, Figure 2.

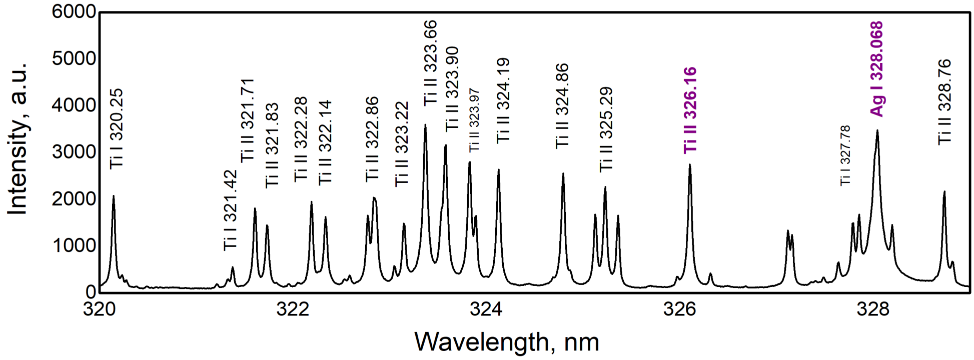

Figure 2: LIBS analysis of Ag:TiO_2 thin film

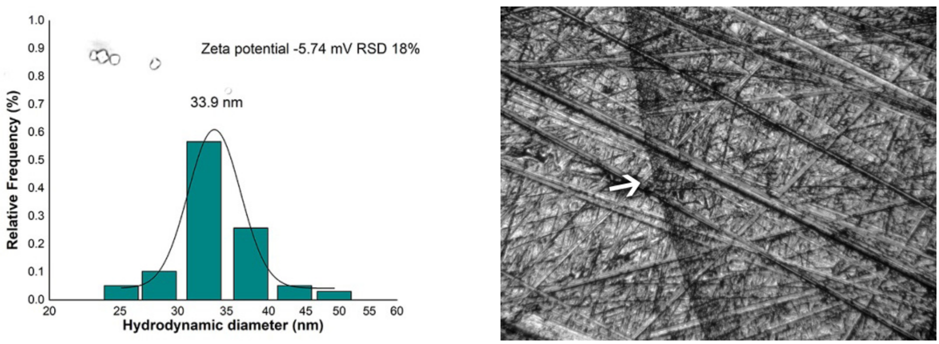

Figure 3: a) Size distribution of NPs; b) Front of NPs dispersion layer applied on a sample surface

The size distribution of synthesized NPs is shown in Figure 3a.

The LIBS spectra segments of the analyzed sample with a focus on the copper line are shown in Figure 4a. Each spectrum represents an averaged spectrum from 10 laser pulses. Considering that TISR method utilizes the fact that intense continuum emission is mostly emitted from a region close to the sample surface, the best signal to background (SBR) value was achieved by changing the viewing position of plasma along its expanding direction of toward the laser beam. Distance between the focusing lens and a target was constant and optimal SBR ratios were obtained at 1 mm in front of the target. For determination limits of detection (LOD) of applied technique, the standard calibration method was chosen. The linear dependency of measured LIBS intensity towards the concentration of Cu in samples was obtained for both LIBS and NELIBS, Figure 4b. The main difference between calibration plots is the incensement of a slope which corresponds to the incensement of method sensitivity. Using a formula $LOD = 3\sigma_B/b$, where σ_B is the standard deviation of background surrounding the selected emission line, and b is the sensitivity defined as the slope of the calibration curve, we estimated that $NELIBS_{LOD}$ is 2.5 times less than $LIBS_{LOD}$.

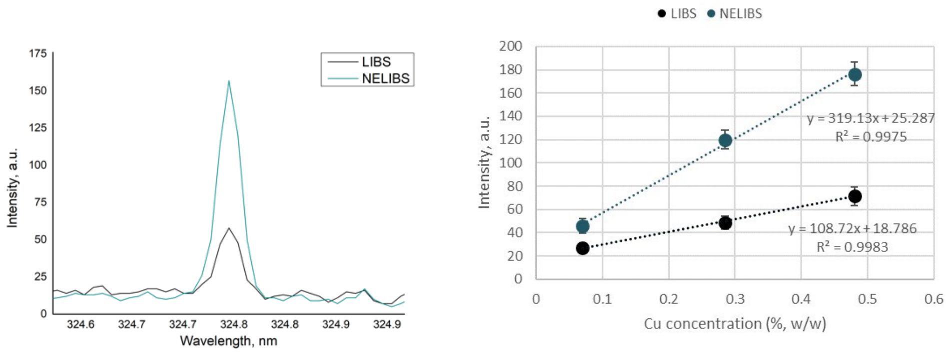

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Figure 4: a) Segments of LIBS spectra with focus on Cu I 324.754 line; b) Calibration plots for two applied techniques

We believe that some methods could additionally lower the LOD: (1) optimized conditions to obtain thin film by PLD (2) the LIBS spectral characteristics will be improved by optimization dimensions of bimetallic nanoparticles. We will further study the above methods and present the results in our future publications.

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