Laser induced breakdown spectrometry for elemental mapping of wear resistant coatings synthesized by laser cladding

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Abstract. Three dimensional multielemental mapping of composite wear resistant by laser induced breakdown spectroscopy has been demonstrated for the first time. Individual clads of 1560 nickel alloy reinforced with tungsten carbide were synthesized by co-axial laser cladding technique. Electron energy X-ray dispersive spectroscopy revealed elemental maps for major elements (W, Ni, Co, Cr, Fe, Si) but failed to measure carbon. Laser induced breakdown spectroscopy was utilized for elemental mapping of carbon and all other elements under interest. It was demonstrated that for depths beyond few microns three dimensional elemental profiling requires substantial laser spot overlapping in order to achieve ±2 µm accuracy of depth measurements. Elemental maps for nickel, tungsten and carbon were quantified for 900x900x45 µm volume with 30 µm lateral and 4 µm depth resolution in case of tungsten carbide particles in nickel alloy.

1. Introduction

Additive technologies fast growth in last decades resulted in producing new composite materials with desired properties. Among numerous additive technologies laser cladding technique provides several advantages like 3D structures production, capability to synthesize composite materials and fast cladding process [1,2]. However, laser cladding technique is still under development due to complexity of numerous parameters influence on production sample quality. Knowledge of the chemical composition and elemental mapping is of fundamental importance for composite materials. Chemical analysis maps can be used for predicting composite material properties or/and improving technology.

For example, wear resistant coating synthesis by laser cladding technique is highly required in mining industry and machinery. Typical wear resistant coatings are based on nickel alloy matrix reinforced with tungsten carbide particles. Coating hardness can be improved by increasing tungsten carbide particles concentration but this will also triggers crack formation and tungsten carbide particles dissolution. Typically, composite material is studied by electron microscope equipped with energy dispersive X-ray (EDX) spectrometer [1]. EDX technique provided lateral resolution of 1-3 microns (depends on matrix) but suffered for low sensitivity in case of light elements (carbon, boron, etc.)
analysis. It should be noted, that carbon is a key element for tungsten carbide coating quality due to the possible chemical interaction with binding matrix elements and formation of complex carbides. These carbides can dramatically change the coating microstructure and, consequently, coating hardness. Elemental mapping of carbon is of primary interest for tungsten carbide coatings due to strong influence of WC grains dissolution and secondary carbides formation [3].

Recently, laser induced breakdown spectroscopy (LIBS) was recognized as a powerful tool for elemental mapping of laser clad coatings [4,5]. LIBS is a laser based analytical technique capable to quantitatively analyse and obtain elemental maps for most of the elements including light elements like hydrogen, boron, carbon, etc. [6,7]. In recent years many research groups have utilized LIBS for elemental mapping of analytes in numerous applications. For example, Laserna and co-workers [8,9] performed a systematic study for three dimensional mapping of heavy metals in automobile catalytic converters. Though spatial resolution was low (0.2-1 mm) but a ~100 cm² areas were mapped by LIBS for layers cut from samples. Gornushkin et al. [10,11] developed a compact microscopic LIBS system for rapid identification of solids and particles with spatial resolution of 20 µm.

In this study we carried out three dimensional LIBS elemental mapping for composite tungsten carbide wear resistant coatings produced by laser cladding technique. To the best of our knowledge three dimensional LIBS mapping haven’t been carried out so far for depth beyond few microns in case of metals. Depth profiling for metal matrix is more challenging compared to ceramics [12] or polymer samples 3D LIBS profiling [Russo] due to laser crater influence on laser ablation. Additionally, composite materials with metal binding matrix have not been studied with 3D LIBS mapping. In the first part of the paper we compared two dimensional elemental maps obtained by LIBS and EDX techniques. Then we optimize three dimensional LIBS profiling for depth beyond tenths of microns. In the final part we obtained 3D LIBS elemental maps for single clads of tungsten carbide in nickel alloy.

2. Experimental

Individuals clads of tungsten carbide wear resistant coatings was produced by coaxial laser cladding technique [3]. Laser beam of continuous wave ytterbium doped fiber laser (1070 nm, 2kW, YLS-2 by IPG Photonics) was focused to a 2 mm spot in the coaxial cladding nozzle in argon atmosphere. Nickel alloy and tungsten carbide powders (see Table 1) were mixed in the feeder (PF-2/2, GTV) and then flushed by argon gas to the coaxial laser cladding head (YC-50, Precitec) which was installed on industrial six-axis robot arm (IRB-2400, ABB) capable to manipulate with 100 µm precision.

Individual clads was deposited on low alloy steel (Fe37-3FN) substrate at 1 kW laser power, flow 6 (nickel alloy) + 1 (WC) g/sec and cladding head movement speed of 7 mm/sec. Clads were cut, glued in epoxy resign and then polished to a 1 µm finish in order to reveal its cross-section. Scanning electron microscopy (SEM) was carried out using a TESCA VEGA LMH microscope equipped with an energy dispersive X-ray (EDX) microanalysis system (AZtecEnergy, Oxford Instruments). The EDX detector was calibrated using standard samples of Ni (99.99%), Mn (99.99%) and Fe (99.99%).

Table 1. Chemical composition of the steel substrate and powders used for laser cladding.

| Element | Fe | Ni | Co | C | Cr | Mn | Si | B | W |
|---------|----|----|----|---|----|----|----|---|---|
| NiCrBSiFe | 3.65 | base | - | 0.69 | 14.07 | - | 4.42 | 3.2 | - |
| WC/Co | - | - | 12.1 | 5.4 | - | - | - | - | base |
| StFe37-3FN | base | - | - | 0.14 | - | 0.45 | 0.2 | - | - |

Elemental mapping by laser induced breakdown spectroscopy was carried out at experimental setup described previously described in details [13,14]. Briefly, laser beam of pulsed Nd:YAG laser (1064 nm, 10 ns, M2=5, 10 mJ/pulse, 5 Hz) was vertically focused onto the sample surface by microscope objective (x10, focal length 8 mm). Estimated focal spot diameter at 1/e² level was 10 µm but 110 µm diameter crater was produced by 10 mJ pulses ablation. To improve spatial resolution for LIBS mapping we decreased laser pulse energy to 0.5 mJ/pulse thus 60 µm diameter craters were produced.
The peak fluence at sample surface equals 10 J/cm$^2$ so plasma emission was bright enough for acquiring spectra with good signal-to-noise ratio. In case of smaller pulse energies (0.2 mJ) the crater diameter was 30 µm providing better spatial resolution. However, in last case we failed to reliably quantify carbon line C I 193.09 in the spectrum. Individual clads were placed in sample holder providing constant lens-to-sample distance. Sample holder was installed on two-coordinate motorized stage (8MT173, Standa LTD) which can be moved with 0.5 µm precision step. Laser plasma emission was collected by quartz lens (F=50 mm) and transferred to the spectrometer entrance slit with 1:1 magnification. Spectrometer (2400-grove/mm, $\lambda/\delta\lambda = 3500$, Shamrock 303i, Andor Inc.) was equipped with intensified CCD camera (iStar, Andor Inc.) for time resolved measurements. The motorized stage provided synchronization pulses which started the laser and the gated camera acquisition. The surface scanning was performed by recording plasma emission spectrum for each sampling spot. Overall control and data handling was carried out by custom software developed in LabVIEW environment. All the LIBS measurements were carried out in air at ambient pressure and temperature.

3. Results and Discussion

3.1. EDX elemental maps

Elemental mapping was carried out by Electron energy X-ray dispersive spectroscopy before any LIBS measurements and results are presented in figure 1. A semispherical clad profile was formed with good quality weld junction to the substrate. Tungsten carbide grains distribution was rather uniform. Some of tungsten carbide particles had irregular shape which indicated a partial tungsten carbide particle dissolution was taking the place. Heavy elements for matrix alloy (Ni, Cr, Fe) and tungsten carbide particles (W, Co) were clearly observed on the maps. However, carbon was not quantified by EDX spectrometer due to low intensity and spectral interference. Silicon map was obtained by EDX spectrometer but brightest areas corresponded to tungsten carbide (WC) particles. Spectral interference of silicon and tungsten peaks resulted in false silicon elemental map.

![Figure 1 SEM image and EDX elemental maps for substrate (Fe), nickel alloy (Ni, Cr, Si and Fe) reinforced with tungsten carbide particles (W, C, Co)](image)

3.2. LIBS spectra

The optimal choice of LIBS spectral lines depends on a number of factors including detector sensitivity, line intensity and spectral interference. In this study we were focused on light elements...
mapping by LIBS including carbon, silicon and boron. The choice of spectral line for carbon analysis in iron contained materials is challenged due to strongly spectral interference. For example, carbon lines in UV (C I 247.86) and near IR (C I 833.51) spectral regions are strongly interfered with iron and tungsten lines [7,15]. Carbon line C I 193.09 is seems to be an optimal choice since this spectral region is moderately absorbed by air while our detector was sensitive down to 185 nm. An example of laser plasma spectrum in 185-210 nm range is presented in figure 2. Atomic line for silicon (Si I 190.13) had low intensity but can be reliably quantified in the spectrum. All other atomic/ionic lines for nickel (Ni I 197.69) chromium (Cr I 199.99), iron (Fe I 193.45), tungsten (W II 207.91) and cobalt (Co II 194.13) were chosen to be free of spectral interference and sufficiently high intensity in the spectrum.

![Figure 2](image_url)

**Figure 2** Laser plasma spectra for matrix Ni-Cr-Fe-B-Si (black color) and tungsten carbide particle (red color). Spectra were acquired with 1 µs gate and delay 0.1 µs. Atomic/ionic lines selected for LIBS mapping are marked underlined.

### 3.3. 2D elemental mapping by LIBS

Typically, LIBS mapping is performed with spot-by-spot sampling without any overlapping of spots. In our case 5 laser pulses resulted in 50 µm crater diameter (figure 3). For lower energy pulses crater diameter was 20 µm but plasma emission was weak and we cannot quantify plasma spectra in 190-210 nm range with meaningful signal-to-noise ratio. The typical diameter of tungsten carbide particle was 70-100 µm so we acquire elemental map with 40 mm step between locations that resulted in 10 % overlapping of sampling spots.
Figure 3 Laser craters profiles with step of 100 µm (a) and 40 µm (c) and corresponding crater track cross-sections (b). The cross-section for craters with 100 µm steps is shifted in (b) by 4 µm for better view.

LIBS mapping was performed by point-to-point scanning with every spot sampled by 5 laser pulses to improve repeatability. Laser crater diameter was 50 µm thus sample was moved with 40 µm step between different spots. Comparing contour maps, it is clearly seen that the locations of tungsten carbide particles can be easily identified with carbon, tungsten and cobalt emission maximums. Nickel and chromium are correlated with each other and inversely correlated with carbon and tungsten. Summarizing figure 4, LIBS mapping provided results for light elements mapping like carbon and silicon which was not possible to quantify by EDX spectrometer.

Figure 4 Single laser clad elemental map for iron, nickel, chromium, silicon, cobalt tungsten, and carbon as revealed by LIBS.
3.4. Optimizing 3D LIBS elemental mapping

Three dimensional LIBS elemental mapping for non-metal samples was carried out in numerous studies with layer by layer ablation [16]. However deep depth profiling for metal alloy samples is a challenge due to laser crater formation which influenced on laser ablation and plasma emission. Three dimensional LIBS mapping for depth exceeding tenth of microns needs optimizing of sampling strategy. For example, multiple scanning through the same sampling spots will result in preferential ablation of the same spot thus plasma will be influenced by crater walls geometry. It is well known, that deep and narrow crater impacted the effective laser beam irradiance on crater surface thus plasma temperature and electron density are also affected resulting in depth dependence of atomic/ionic lines intensities. Additionally, crater wall material will be ablated or evaporated by expanding plasma thus depth resolution became poorer for deeper craters. We quantified laser craters profiles with white light interferometry microscope.

Generally, 2D LIBS mapping is performed by sampling of laser spots as close as possible to each other but without overlapping in order to prevent influence of previous spot crater. However, this is not a good choice for three dimensional elemental mapping by LIBS due to influence of crater formation. In order to estimate such influence we produce a series of 300x600 µm rectangular by successive scanning with 1 shot sampling and 0% laser spots overlapping. We specifically choose areas of Ni-alloy which were free from tungsten carbide particles in order to ablate homogeneous material. The results of surface profiling for areas after 1, 5, 10 and 30 scans by 1-shot sampling are shown in figure 5. Cavity bottom surface had the specific pattern with well resolved locations of laser craters. Moreover, huge re-solidified rims formed during ablation (see 5th and 10th scans in figure 5) resulted in mixing of layers from different depths that can strongly affect the 3D mapping results. The large curvature of the cavity area bottom decreased precision of depth profiling to 7 µm. The ablation rate defined as cavity area depth per single laser pulse was estimated as 0.8 µm/pulse.

![Figure 5](image)

In order to improve depth resolution and suppress influence of “surface cratering” we changed sampling strategy and produce a several 300x600 µm rectangular with 30 µm step (step equals to crater radius). Greater spots overlapping (38% per area) significantly improved the ablated area roughness (figure 6). The number of ablating pulses squared but ablated volume increased only two times with estimated ablating rate of 1.7 µm/pulse. Lower roughness of ablated area bottom (<4 µm) resulted in 2-fold improved absolute accuracy (4-fold relative of depth estimation.)
Figure 6 Ni alloy ablated areas (300x600 µm) with 1, 5, 10 and 30 scans (a) and corresponding cross-section (b) for sampling scheme with 38% spot overlapping (30 µm step) (c). Depth as a function of ablating pulses was fitted by quadratic function (d).

Finally, 3D profiles elemental maps were acquired for tungsten carbide composite coatings with 38% laser spot overlapping (30 µm step) according to previously discussed 3D mapping optimization. Layer-by-layer contour maps for nickel, tungsten and carbon in composite coating sample is presented in figure 7. Each layer represents an 900x900 µm area.

Figure 7 Layer-by-layer contour elemental maps for nickel (green), tungsten (red) and carbon (magenta). Violet circle indicates example of tungsten carbide particle (100 µm in diameter) appearance during layer-by-layer LIBS mapping.
4. Conclusions

Three dimensional multielemental mapping of composite wear resistant by laser induced breakdown spectroscopy has been demonstrated for the first time. Individual clads of nickel alloy reinforced with tungsten carbide were synthesized by co-axial laser cladding technique. Electron energy X-ray dispersive spectroscopy revealed elemental maps for major elements (W, Ni, Co, Cr, Fe, Si) but failed to measure carbon. Laser induced breakdown spectroscopy was utilized for elemental mapping of carbon and all other elements under interest. It was demonstrated that for depths beyond few microns three dimensional elemental profiling requires substantial laser spot overlapping in order to achieve ±2 µm accuracy of depth measurements. Elemental maps for nickel, tungsten and carbon were quantified for 900x900x45 µm volume with 30 µm lateral and 2 µm depth resolution in case of tungsten carbide particles in nickel alloy.

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**Acknowledgments**

The authors gratefully acknowledge the financial support of the Russian Science Foundation (agreement № 16-19-10656).