Applied Surface Science 336 (2015) 396–400

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Characterization of hard coatings produced by laser cladding using laser-induced breakdown spectroscopy technique

J.A. Varela, J.M. Amado, M.J. Tobar, M.P. Mateo, A. Yañez, G. Nicolas*

Universidad de A Coruña, Dpto. Ingeniería Industrial II, Laser Applications Laboratory, C/Mendizabal s/n, 15403 Ferrol, Spain

ARTICLE INFO

Article history:
Received 15 July 2014
Received in revised form
16 December 2014
Accepted 5 January 2015
Available online 13 January 2015

Keywords:
Laser induced breakdown spectroscopy (LIBS)
Laser cladding
Chemical mapping
NiCrBSi-WC hardfacing alloys

ABSTRACT

Protective coatings with a high abrasive wear resistance can be obtained from powders by laser cladding technique, in order to extend the service life of some industrial components. In this work, laser clad layers of self-fluxing NiCrBSi alloy powder mixed with WC powder have been produced on stainless steel substrates of austenitic type (AISI 304) in a first step and then chemically characterized by laser-induced breakdown spectroscopy (LIBS) technique. With the suitable laser processing parameters (mainly output power, beam scan speed and flow rate) and powders mixture proportions between WC ceramics and NiCrBSi alloys, dense pore free layers have been obtained on single tracks and on large areas with overlapped tracks. The results achieved by LIBS technique and applied for the first time to the analysis of laser clads provided the chemical composition of the tungsten carbides in metal alloy matrix. Different measurement modes (multiple point analyses, depth profiles and chemical maps) have been employed, demonstrating the usefulness of LIBS technique for the characterization of laser clads based on hardfacing alloys. The behavior of hardness can be explained by LIBS maps which evidenced the partial dilution of some WC spheres in the coating.

1. Introduction

The materials engineering field requires, increasingly, new products with enhanced properties for cutting tools, biomedical implants or wear resistant coatings. In many cases, for this purpose, composites are employed for the production or synthesis of coatings often deposited on steel substrates. One way to obtain these new materials is the laser cladding technique which consists on the deposition of a melted and consolidated powder over the substrate during the irradiation process. The main features of this method includes a small heat affected area and a low dilution between clad and substrate. Common choices for the powder are titanium, CoMoCrSi alloys, tungsten carbides, aluminum, etc. [1–11] which provide the product with specific properties such as improved hardness or corrosion resistance. The cladding process depends on several experimental parameters that must be optimized to generate tracks of high quality. Therefore, the characterization of the produced clads is essential for process control. In this sense, laser induced breakdown spectroscopy (LIBS) is an analytical technique that allows to obtain the elemental composition of any kind of materials by performing different types of analysis: point analysis, depth profiles and chemical maps [12,13]. The last two measurement modes provide additional information compared to point analysis, such as evolution of elemental composition as a function of depth and spatial distribution of elemental concentrations along the surface, respectively.

Different kinds of materials can be analyzed with this technique and it is worth mentioning metals and ceramics which have been investigated in order to detect their main elements or impurities. In this last case, LIBS has demonstrated to be a versatile and a powerful technique for multi-elemental analysis of different ceramics such as powders [14,15], bio-ceramics [16], alumina-based titanium carbide composites [17] or archeological artifacts [18,19].

In the present work, the capability of LIBS technique to characterize laser produced clads of different composition and distribution, based on Ni matrix and tungsten carbide powders, has been tested for the first time through point analysis, profiling and chemical mapping in representative areas of the coating.

2. Experimental

The tungsten carbides in alloy matrix were produced using laser cladding method by blending NiCrBSi (Deloro 30) and tungsten carbide (WOKA 3303) powders, resulting in NiCrBSi-WC metal matrix

* Corresponding author. Tel.: +34 981337400x3274; fax: +34 981337410.
E-mail address: gines@udc.es (G. Nicolas).

http://dx.doi.org/10.1016/j.apsusc.2015.01.037
0169-4332/

composite. AISI 304 stainless steel was selected as base material, in virtue of its high thermal conductivity which is a common property of the steels used in abrasive environments. Laser cladding system consisted of a 2.2 kW continuous wave diode pumped Nd-YAG laser (Rofin DY022), equipped with a cladding head for coaxial powder delivering. Powder feeding was made with a Sulzer-Metco Twin 10C unit and cladding head was installed in a ABB IRB2400 six axis robot arm. Prior to the blending, the NiCrBSi and WC materials were stored in two different powder feeding hoppers, calibrated independently. The mixing of the two powders was performed during the flight and the parameters related to this process were automatically regulated by the robot controller. The obtained samples consisted of four clads with different tungsten carbide concentrations of 5%, 15%, 30% and 45% (percentage in weight of WC). Each sample was composed of a set of cladding tracks with an overlap of 40%. For the hardness and chemical analyses, samples were cut transversally, grounded and polished. Hardness was measured using a Vickers microindenter (Shimadzu) with loads of 2.96 N. Finally, the LIBS setup consisted of a Q-switched Nd:YAG laser (Quantel Brillant) operating at a wavelength of 532 nm with a pulse width of 5 ns, a repetition rate of 1 Hz, a pulse energy of 200 mJ and a beam diameter of 6 mm. The laser radiation was focused upon the sample surface by means of a focal 50 mm plano-convex quartz lens. The plasma emission was collected with an ICCD camera (Andor iStar) and guided by an optical fiber to an Echelle spectrograph (Andor Mechelle). The diameter of laser spot generated in the sample was 100 μm and the energy density was about 51 J/cm^2. For a precise control of positioning, samples were mounted on three motorized translation stages. The LIBS spectra were acquired using a delay time of 1 μs and an integration time of 10 μs. All irradiations were performed in air under atmospheric pressure.

3. Results and discussion

As it has been already mentioned, the specimens under study were obtained using deposition of a mixture of NiCrBSi and WC powders by the laser cladding method. The parametric study of this process led to the following values of 2000 W, 20 mm/s, 20 mg/mm, respectively for laser power, scanning speed and powder deposition per unit length. With these conditions, laser clads exhibited a good adhesion between deposited material and the substrate, almost free of pores and cracks over the surface and beneath it. The microstructure of the cladding tracks was composed of a metal matrix and spherical cemented carbides. Only a fraction of these carbides was diluted in the metal matrix while the other fraction remained undiluted as it can be observed in the optical micrographs of Fig. 1 which displays cross-sections of 5% and 30% tungsten carbide concentrations. This undiluted fraction of tungsten carbides continues maintaining the weight ratio relationship. The coating with a thickness of about 400–500 μm is easily distinguishable from the substrate and the carbide spheres can be clearly recognized within the metallic matrix for the four types of WC concentrations. As it was expected, the number of these spheres increases with the WC concentrations. This behavior can be confirmed by visual inspection of cross-sections of laser clads. Fig. 1 also shows a small transition zone with a constant width between the coating and stainless steel but where no defects were evidenced. It should be noted that the metallic matrix presented a dendritic structure and the carbide spheres were embedded and distributed more or less uniformly within it. For the observation of dendrites, a higher-magnification objective than that used in photographs of Fig. 1 is required. In some areas, isolated pores can be detected in the whole matrix. A more comprehensive study of the morphology of this kind of coatings can be found in Amado et al. [1]. The function of WC was the reinforcement of the NiCr

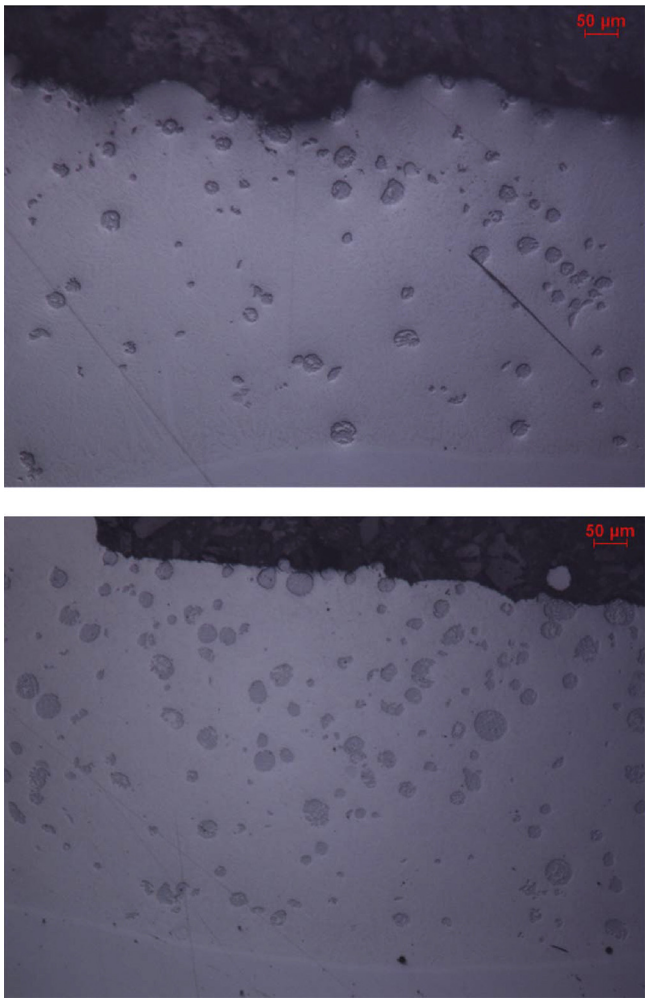

Fig. 1. Cross-sections of laser clads obtained for 5% (upper micrograph) and 30% (lower micrograph) tungsten carbide concentrations.

based matrix due to its high hardness. Hence, the lower dilution of WC particles the higher hardness of coating. Tungsten carbides selected for the coating are supplied as alloy powders consisting of binded-agglomerates of WC particles, providing particle hardness about 1500–2000 HV. The microhardness measurements were performed, for all concentrations, in a cross-section of the clad, starting at the most superficial part of the coating and finishing in the stainless steel. The mean hardness is maintained constant throughout the coating except in the region near the substrate where a slight decrease is observed. Noteworthy, hardness values depend on whether the measurements are made above carbide, where in such case a higher value is obtained. Metal matrix has a hardness about 300 HV and the insertion of WC particles can increase it, either slightly (350 HV) if the concentration is low (5%) or either highly (900 HV) if it is high (45%). The values given in Fig. 2 correspond to a mean of the different measurements made inside the clad and where the error bars take into account measurements in matrix and WC spheres. As it can be observed, the hardness followed a linear behavior with concentration in the explored range. Higher concentrations are not recommended even when higher hardness is expected because the binder effect of matrix would be lost and appearance of defects would not be negligible.

In order to evaluate if LIBS technique was suitable for characterization of the hardfacing alloys produced by laser cladding, several measurement modes were conducted. In the first place, point analyses were performed in the cross-section of the coatings for all

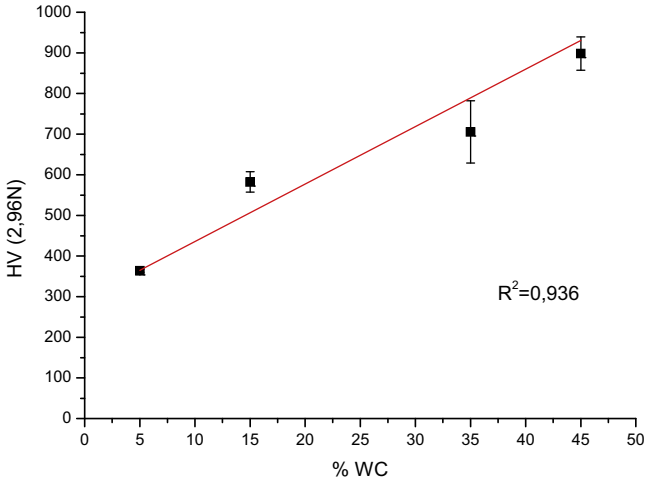

Fig. 2. Vickers hardness measurements for the different tungsten carbide concentrations, using a load of 2.96 N.

samples to identify spectral lines of the elements that compose it and to check if expected differences were detectable from characteristic areas of the clad (from the surface to the interface with the substrate). The spectral window for LIBS analysis was selected from 400 to 512 nm where the representative elements were tungsten and nickel with their main emission lines at 484.38 nm and 508.05 nm, respectively. Fig. 3 shows a typical spectrum of the coating where not only the mentioned elements were detected, but also lines of chromium, silicon and boron coming from the matrix and usual contaminants such as calcium. In the zooms of this figure, we can appreciate that the intensity of W and Ni peaks reaches quite high values which constitutes a satisfactory LIBS signal. Hence, depending on the location where the laser spot has been applied, whether it is above an area with a low or high carbide concentration, variations on W intensity have been observed. For example, above a carbide sphere, W intensity will augment while metal matrix contribution will drop, causing a dispersion in the results of point analyses. The choice of a laser spot with a diameter of 100 μm is an important factor because this area comprises spheres plus Ni based matrix. A higher diameter would be accompanied with a loss of spatial resolution for this kind of materials while a smaller one would be too reduced compared to the spheres size.

Once identified and selected the emission lines, profile mode was carried out from the outermost part of the coating to the substrate in order to determine the distribution of the elements. In addition, this analysis was intended to distinguish the location of the interface between the clad and the stainless steel. In Fig. 4, a LIBS profile is displayed showing intensity variations of the W and Ni lines from the steel substrate (left) to the top surface of the coating (right). The two goals are satisfied: on one hand, W profile indicates a non-uniform concentration of spheres along the clad while Ni signal increases when W one decreases as expected, and on the other

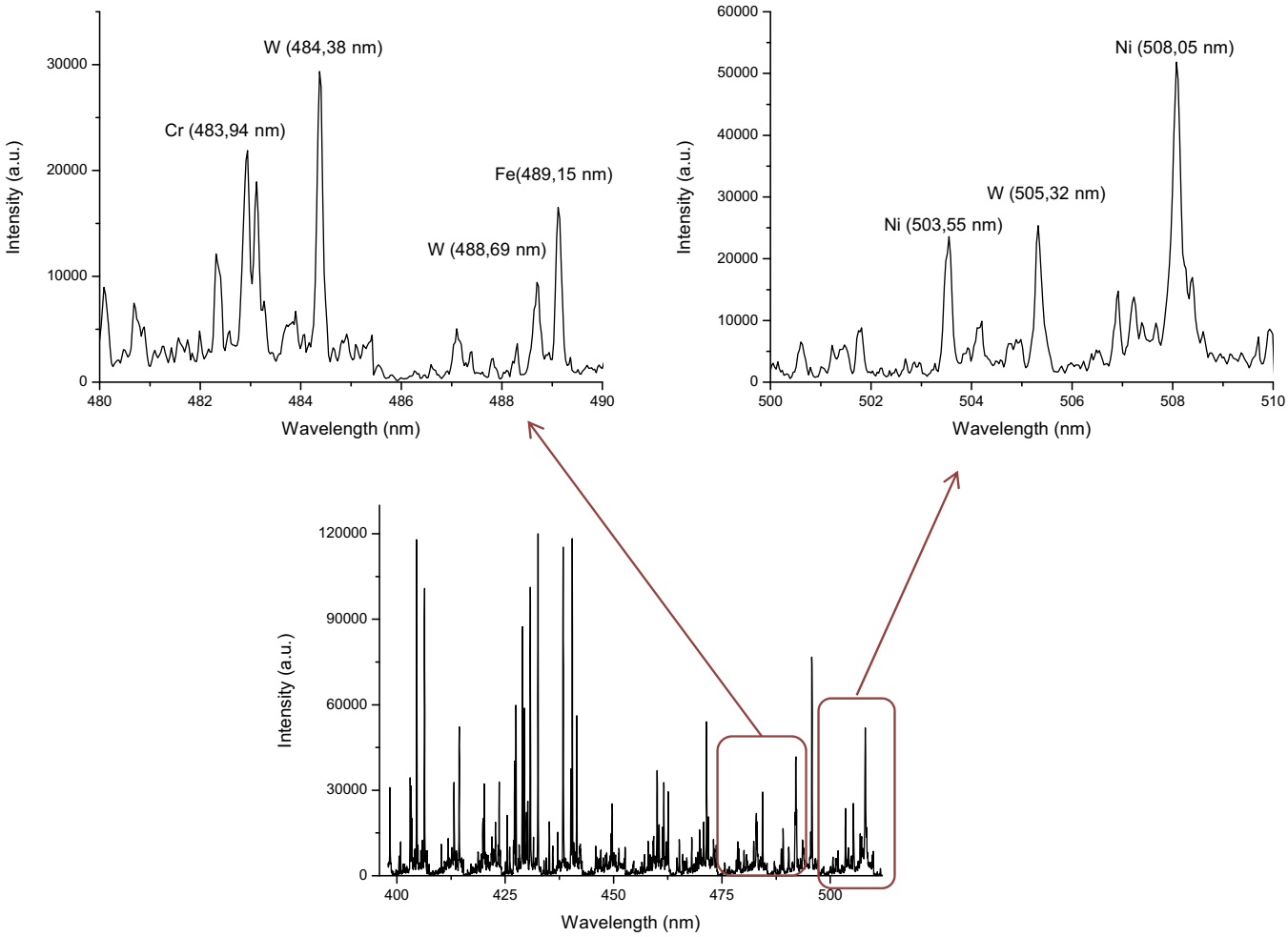

Fig. 3. Typical LIBS spectrum of NiCrBSi-WC metal matrix composite with W line at 484.38 nm (left zoom) and Ni line at 508.05 nm (right zoom), used for chemical profiles and maps.

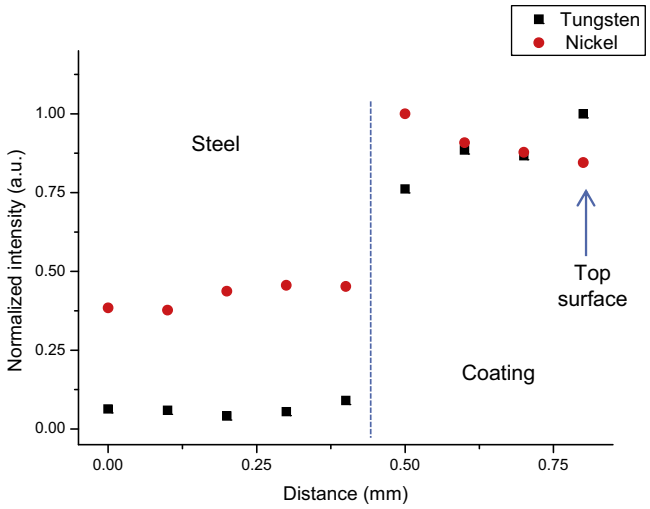

Fig. 4. LIBS profiles of representative elements (W and Ni) of the composite performed on a cross-section of the 45% WC laser clad, from the steel substrate to the top surface of the coating.

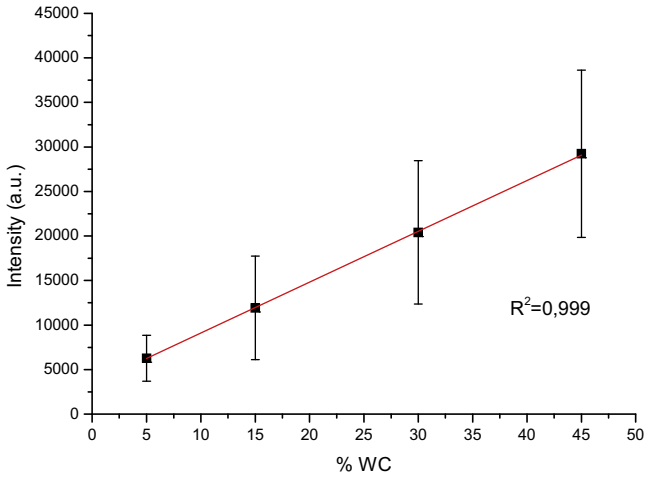

Fig. 5. LIBS signal of tungsten (484.38 nm) for different WC concentrations.

hand, this procedure can accurately differentiate, in the μm range, the clad from the steel substrate. Therefore coating thickness can be estimated from Fig. 4 to be about 350 μm, which match with measurements made by optical microscopy (Fig. 1). Moreover, as in the case of hardness and as expected, a higher amount of carbide spheres induced a higher LIBS signal of W.

As in the case of hardness, the influence of WC concentration has been studied through a series of shots in form of rectangular grid in the cross section of the coating with the purpose of obtaining a calibration curve. The data of Fig. 5 corresponds to an average value of LIBS intensities obtained in this grid where a linear relationship was observed between W intensity and WC concentration. The error bars have been calculated from standard deviation of average values. High standard deviation values were due to differences in intensity between the metal matrix and carbide spheres. Although an increase in the spot size would provide less standard deviation for all values, the number of spots that can be performed into the clad would also be less and could not properly characterize the hardfacing alloy.

Finally, the last mode of measurement employed by LIBS has been consisted on the elaboration of chemical maps for all studied concentrations which provided a more complete and detailed element distribution. In Fig. 6, W maps clearly show an increasing amount of carbides with WC concentration. In these representations, coating is displayed vertically which means that steel substrate is in the left part of the map and the top surface of the coating is in the right one near 1 mm in the *X* direction. For comparative purposes, the intensity scale is the same for the four maps, and even if for 5% WC it seems that W is not very well detected, a different scale with a lower intensity maximum would modify this display mode, revealing clearly its presence along the coating. The time required to perform these maps was about 10 min but it can be improved with faster motorized translation stages.

It can be mentioned also that not all representative elements can always provide a detailed description of the coating using profiles or maps. This is the case of Ni which exhibited small intensity variations at different positions in the clad and for the studied WC concentrations (more or less constant distribution of Ni), that does

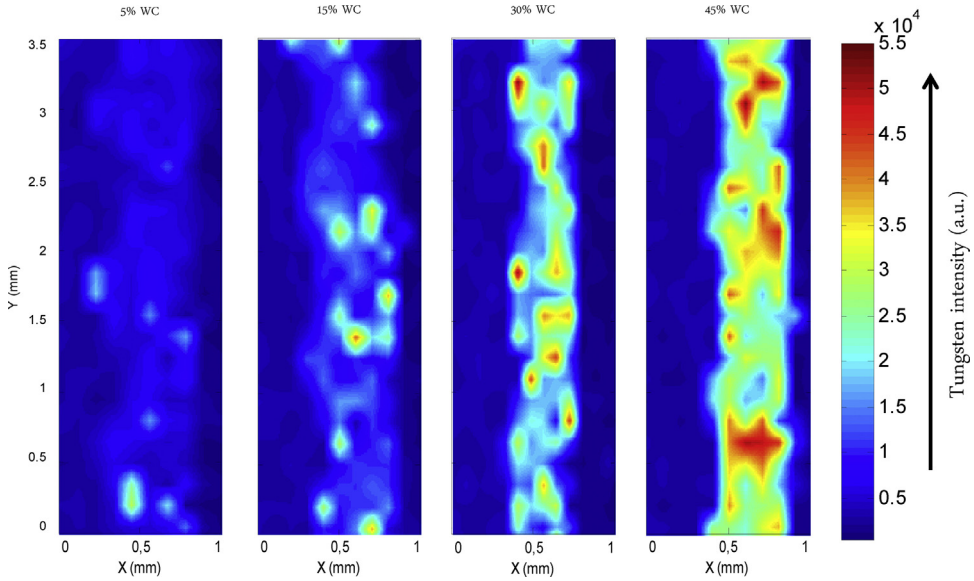

Fig. 6. LIBS chemical maps of tungsten (484.38 nm) for different WC concentrations where steel substrate is located on the left side and coating on the right side. The maps size is 3.5 mm × 1 mm and the step size is 0.146 mm for *Y* and 0.125 mm for *X*.

not permit to obtain data of the coating as useful as with W. However Ni signal can give information about features like thickness and interface location. In any case, the combination of the LIBS data allowed to characterize the spatial distribution of the constituents on these very hardfacing alloys. Similar data could be obtained with electrons techniques such electron dispersive X-ray spectroscopy concerning profiling and mapping but the electron beam size, much smaller than the laser beam size, would require a very long time to achieve a complete characterization and cannot be considered as a reliable method for coatings with thicknesses of several hundreds of micrometers.

Several factors can affect the generation of a chemical map by LIBS, such as surface topography [20], that is why the displayed maps and profiles have been obtained on polished surfaces. Hence, variations observed in signals intensity should be attributed mainly to differences in element distribution. A future work will consist of evaluating how the hardness can affect LIBS signals in these materials. Indeed, in the present study, hardness values and LIBS signals as a function of WC concentrations cannot be directly related because both measurements did not coincide accurately in the same spatial coordinates.

4. Conclusions and perspectives

LIBS has been proven to be a suitable tool for the characterization of NiCrBSi-WC coatings produced by laser cladding technique and therefore for similar materials which exhibits inhomogeneous distribution of elements. First, the laser spot size employed in LIBS analyses match well with features size found inside the coating such as carbide spheres and matrix areas, that allows to obtain representative chemical composition over the laser clad. Second, the non-uniform distribution of elements from the bottom to the edges of the coating can be easily determined by fast multiple points analyses. Third, depth profiles performed in cross-sections allows to measure coating thickness and to check elements migration inside the laser clad or from the steel substrate. If necessary, a more comprehensive study can be obtained through chemical maps which provides more detailed data over the whole area of the coating. Finally, the LIBS intensity of W, which confers the good mechanical behavior of the coating increases linearly with the WC concentration in the explored range (5–45%). This result is particularly interesting for future investigations where coatings with concentration gradients will be produced. As can be seen in this study, this non-uniform distribution of elements might not be the best choice for the laser clad because consequently the mechanical properties are not the same over the coating. In this sense, concentration gradients where powder deposition rate is varied during the laser cladding process could be a solution to produce more uniform clads. LIBS could be the right way for the compositional study of these gradients.

Acknowledgements

This work was supported by Ministerio de Ciencia e Innovación (Project: CTQ2009-14572) and Xunta de Galicia (Project: 08TMT010166PR).

References

[1] J.M. Amado, J. Montero, M.J. Tobar, A. Yáñez, Ni-based metal matrix composite functionally graded coatings, Phys. Procedia 39 (2012) 362–367.
[2] J.M. Amado, M.J. Tobar, J.C. Alvarez, J. Lamas, A. Yáñez, Laser cladding of tungsten carbides (Spherotene®) hardfacing alloys for the mining and mineral industry, Appl. Surf. Sci. 255 (2009) 5553–5556.
[3] K. Van Acker, D. Vanhoyweghen, R. Persoons, J. Vangrunderbeek, Influence of tungsten carbide particle size and distribution on the wear resistance of laser clad WC/Ni coatings, Wear 258 (2005) 194–202.
[4] E. Díaz, J.M. Amado, J. Montero, M.J. Tobar, A. Yáñez, Comparative study of Co-based alloys in repairing low Cr-Mo steel components by laser cladding, Phys. Procedia 39 (2012) 368–375.
[5] S. Huang, M. Samandi, M. Brandt, Abrasive wear performance and microstructure of laser clad WC/Ni layers, Wear 256 (2004) 1095–1105.
[6] S. Shang, D. Wellburn, Y.Z. Sun, S.Y. Wang, J. Cheng, J. Liang, et al., Laser beam profile modulation for microstructure control in laser cladding of an NiCrBSi alloy, Surf. Coat. Technol. 248 (2014) 46–53.
[7] M.J. Tobar, C. Álvarez, J.M. Amado, G. Rodríguez, A. Yáñez, Morphology and characterization of laser clad composite NiCrBSi–WC coatings on stainless steel, Surf. Coat. Technol. 200 (2006) 6313–6317.
[8] A. Suárez, M.J. Tobar, A. Yáñez, I. Pérez, J. Sampedro, V. Amigó, et al., Modelling of phase transformations of Ti6Al4V during laser metal deposition, Phys. Procedia 12 (2011) 666–673.
[9] F. Weng, C. Chen, H. Yu, Research status of laser cladding on titanium and its alloys: a review, Mater. Des. 58 (2014) 412–425.
[10] Y. Wang, G. Li, Z. Shi, M. Liu, X. Zhang, Y. Liu, Effects of graphite addition on the microstructure and properties of laser cladding Zr–Al–Ni–Cu amorphous coatings, J. Alloys Compd. 610 (2014) 713–717.
[11] M.J. Tobar, J.M. Amado, C. Álvarez, A. García, A. Varela, A. Yáñez, Characteristics of Tribaloy T-800 and T-900 coatings on steel substrates by laser cladding, Surf. Coat. Technol. 202 (2008) 2297–2301.
[12] V. Piñon, M.P. Mateo, G. Nicolas, Laser-induced breakdown spectroscopy for chemical mapping of materials, Appl. Spectrosc. Rev. 48 (2013) 357–383.
[13] J.M. Vadillo, J.J. Laserna, Laser-induced plasma spectrometry: truly a surface analytical tool, Spectrochim. Acta B: At. Spectrosc. 59 (2004) 147–161.
[14] T. Čtvrtníčková, L.M. Cabalín, J. Laserna, V. Kanický, Comparison of double-pulse and single-pulse laser-induced breakdown spectroscopy techniques in the analysis of powdered samples of silicate raw materials for the brick-and-tile industry, Spectrochim. Acta Part B: At. Spectrosc. 63 (2008) 42–50.
[15] T. Ctvrtnickova, L. Cabalin, J. Laserna, V. Kanicky, G. Nicolas, Laser ablation of powdered samples and analysis by means of laser-induced breakdown spectroscopy, Appl. Surf. Sci. 255 (2009) 5329–5333.
[16] J.S. Cowpe, R.D. Moorehead, D. Moser, J.S. Astin, S. Karthikeyan, S.H. Kilcoyne, et al., Hardness determination of bio-ceramics using laser-induced breakdown spectroscopy, Spectrochim. Acta B: At. Spectrosc. 66 (2011) 290–294.
[17] K. Ahmad, W. Tawfik, W.A. Farooq, J.P. Singh, Analysis of alumina-based titanium carbide composites by laser-induced breakdown spectroscopy, Appl. Phys. A (2014), http://dx.doi.org/10.1007/s00339-014-8544-7.
[18] K. Melessanaki, M. Mateo, S.C. Ferrence, P.P. Betancourt, D. Anglos, The application of LIBS for the analysis of archaeological ceramic and metal artifacts 198 (2002) 156–163.
[19] A.J. López, G. Nicolas, M.P. Mateo, V. Piñón, M.J. Tobar, A. Ramil, Compositional analysis of hispanic terra sigillata by laser-induced breakdown spectroscopy, Spectrochim. Acta B: At. Spectrosc. 60 (2005) 1149–1154.
[20] V. Piñon, M.P. Mateo, G. Nicolas, Effect of surface topography in the generation of chemical maps by laser-induced plasma spectroscopy, Appl. Surf. Sci. 258 (2012) 9432–9436.