Novel Surface Topography and Microhardness Characterization of Laser Clad Layer on TC4 Titanium Alloy Using Laser-Induced Breakdown Spectroscopy and Machine Learning

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This study was performed to characterize surface topography and microhardness of 40 wt pct NiCrBSiC-60 wt pct WC hard coating on TC4 titanium after coaxial laser cladding via Laser Induced Breakdown Spectroscopy (LIBS) and machine learning. The high content of the hard WC particles is accomplished to enhance the abrasion wear resistance of such alloy. Various powder feeding rates were carried out during laser cladding process. The energy-dispersive X-ray analysis assured that W content in the metal matrix notably increased from 26.19 to 53.49 pct while the Ti content decreased from about 15.16 to 0.46 pct for the clad layer processed at 20 and 60 g min\(^{-1}\), respectively. The LIBS measurements successfully estimated such elements' concentration as well as the clad layers' topography indicating that the effect of material matrix is a crucial challenge. Therefore, canonical correlation analysis and Belsley collinearity diagnostics were established to identify the essential emission lines from the whole spectra. Then, an optimized adaptive boosted random forest classifier was developed for microhardness investigation, with accuracy, sensitivity, and F1 score values of 0.9667. The results, confirmed by the metallurgical study, clarified that most of the titanium and tungsten emission lines have a significant impact on the surface topography as well as the microhardness values. The misclassification was attributed to the matrix effect such that the samples processed at 40 and 60 g min\(^{-1}\) were comparable in microstructure and chemical characterization unlike the one processed at 20 g min\(^{-1}\). Vickers microhardness of the metal matrix coating increased with the increase in the powder feeding rate, which is assured by the quantitative classification model.

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I. INTRODUCTION

The TC4 is a common titanium alloy used in aerospace, weapons, marine, and many other industrial applications that require a high strength-to-weight ratio, high-temperature properties, and good corrosion resistance.\(^{[1,2]}\) However, because of the low hardness, poor tribological properties, and limited high-temperature oxidation resistance of titanium alloys, they are restricted in their applications under intense wear and friction conditions.\(^{[3,4]}\) Fortunately, laser material processing provides excellent approaches for providing surface protection and hence improving the surface performance of such components.\(^{[5,6]}\) Laser cladding is an ideal surface modification technology that has been used efficiently for depositing various coatings on substrates. By selecting appropriately deposited alloys, laser cladding can achieve the desired surface...
Laser cladding has the advantage of digitizing the deposited materials by mixing and/or switching among individual feedstocks in addition to lower dilution rate, narrow heat-affected zone, and consequently, good metallurgical bonding between coating and substrate.\[8,9\] Recent studies for the fabrication of the composite coating on the titanium alloy substrate have mainly focused on improving the hardness and wear resistance.\[10,11\] Generally, the cladding materials are developed from single-based alloys or/and ceramic to multiple alloys or ceramics. Alloys such as Co, Mo, Ni, and Fe-based alloys are predominant, particularly Ni-based alloys, to provide better high-temperature, corrosion, wear resistance, and ease of bonding with the titanium substrate due to the close of their properties.\[12\] Nickel-based alloys are prone to tribological attack due to their ductile matrix, accordingly, Inconel alloys,\[13\] and various ceramics\[14,15\] are widely used as feedstock materials. Lately, ceramics like carbides (TiC,\[16\] SiC\[17\]), nitrides (TiN,\[18\] BN\[19\]) and oxides\[20\] were deposited on titanium alloys. Deposition of WC and NiCrBSi coatings is quite common by thermal spray,\[21,22\] however, such process suffers from various restrictions. In the study of Ali et al.,\[23\] 60 pct WC + 40 pct NiCrBSi hard composite on a commercial Ti–6Al–4V (\(x + \beta\)) titanium alloy was performed by laser cladding. The results showed an increase by more than three folds in the microhardness values of the clad layers and an improvement in the wear resistance by values reaching 400 times. In addition, the new phases in the metal matrix coating (MMC) layers were found to be strongly dependent on the heat input amount. In the research of Elshazli et al.,\[24\] laser cladding was performed by applying different WC percentages with stellite-6 (Co-based alloy) to the surfaces of TC21 titanium alloy. The authors reported that the wear resistance of the deposited layer was significantly improved, as reflected by a decrease in the samples’ wear weight loss by 99 pct. Nevertheless, the published studies related to this cladding composite powder containing high content of the WC ceramic particles with high powder feeding rates on titanium alloys are scarce. Therefore, higher powder feeding rates were investigated in this study to reach an optimum condition that can achieve homogenous WC distributions on the substrate.

Laser Induce Breakdown Spectroscopy (LIBS) is an influential analytical technique that can detect and characterize multi-elemental analysis of different ceramics,\[25\] bio-ceramics,\[26\] and alumina-based titanium carbide composite qualitatively and quantitatively.\[27\] It is worth noting that the LIBS accuracy is influenced by the matrix effect which depends on the physical as
It was confirmed that LIBS is a proper tool for the characterization of NiCrBSi-WC coatings produced by the laser cladding process.\[32\] Whereas the heterogeneous distribution of elements along the cross-section of the coating was easily determined by multiple points analyses. In similar studies,\[33,34\] LIBS measurements could provide information on all elemental distribution in the hard coating powder including the light elements such as carbon and boron that couldn’t be detected by the energy dispersive X-ray (EDX) spectroscopy. As well, tungsten, nickel, and carbon concentrations were detected during the coating synthesis process.\[35\] Additionally, the different volume fraction of titanium carbide (TiC) in the alumina (Al₂O₃) was analyzed through the spectroscopic analysis of the plasma generated by LIBS irradiation.\[37\] The results suggested that LIBS can be utilized in the ceramic industry for estimating the composition just by calculating the plasma temperature. Moreover, all elements of a high-entropy alloy coated on the aluminum substrate by laser cladding process were detected by LIBS measurements through the calibration of the collected plasma.\[36\] Regarding the sample’s surface topography, its influence on the spectral emission of LIBS was investigated by analyzing stainless steel samples with different surface finishes (0.026 to 4.54 \( \mu m \)).\[37\] On the other hand, various carbon steels with different surface roughness range from 0.039 \( \mu m \) up to 0.535 \( \mu m \) were examined through LIBS at an ablation diameter of 10 \( \mu m \).\[38\] Likewise, the influence of the surface roughness on the acquired LIBS chemical maps of several stainless steel samples with different surface finishes was evaluated.\[39\] Such studies concluded that differences in the surface state yield change in the LIBS signals.

Interestingly, the LIBS technique has proved to be able to obtain the relation between the sample hardness and the plasma properties. Surface hardness is considered as a key indicator of mechanical properties. For example, the hardness of tungsten heavy alloy samples after plasma irradiation was investigated via the intensity ratio of atomic to ionic spectral lines of W.\[40\] Similarly, the ratio of ionic to atomic emission lines was utilized to measure the Vickers hardness of low-carbon spring steel.\[41\] In another study,\[26\] the authors reported that the plasma excitation temperature revealed a linear relation with the hardness values of bio-ceramic samples. The results indicated that the measured hardness based on these measurements poses better reproducibility than the Vickers hardness measurements. Furthermore, electron density, plasma temperature, multivariate statistical analysis of the LIBS spectra as well as the ratio of atomic to ionic spectral lines of Fe were applied to investigate the surface hardness of igneous and sedimentary rocks.\[42\] Additionally, the matrix effect could be utilized to characterize the mechanical properties of samples as well.\[43\] Accordingly, some researchers have focused on determining the surface hardness corresponding to the matrix effect.\[28,30\] It was found that the emission signals could be used to correct the interferences between elements in the sample matrix.\[44\]

To sum up, the measurements of the homogeneity and element distribution of MMC are substantial in engineering industries as the surface irregularity has a considerable impact on the quality and performance of the products such as their hardness and wear resistance. In this work, clad layers containing 60 pct WC + 40 pct NiCrBSiC with excellent wear resistance and high mechanical performance were deposited successfully via laser cladding technology using different powder-feeding rates on TC4 substrate. Afterward, the LIBS technique was performed in order to characterize the surface topographies of the formed hard composite coatings for the first time. Such results were validated by the experimental findings. In addition, the evaluation of the feasibility of the surface hardness estimation via the LIBS technique utilizing the matrix effect was investigated. Although most of the previous studies utilized univariate analysis to measure the surface hardness, these methods lack several important factors such as sample inhomogeneity and selecting the optimum specific lines from the raw LIBS spectrum data. Consequently, in this study a multivariate analysis method in which canonical correlation analysis (CCA) has been conducted to reduce variable dimensions by selecting significant variables from the raw LIBS spectrum followed by an optimized adaptive boosted random forest classifier for acquiring representative information to discriminate between the samples for quantitative microhardness estimation.

## II. MATERIALS AND METHODS

### A. Laser Cladding Process Setup and Materials Examination

The titanium alloy used in these experiments was grade 5 (TC4) alloy with nominal chemical composition (wt pct) of 6.62 pct Al, 3.89 pct V, and balance Ti. The TC4 sheets were cut into specimens with a size of 50 mm \( \times \) 30 mm \( \times \) 5 mm by a traditional wire cutting machine for the laser cladding process. Powder blends of 60 pct WC and 40 pct NiCrBSiC with the chemical composition listed in Table I were utilized as the cladding materials. The particle size ranges from 45 to 125 \( \mu m \). The laser cladding process was conducted on surfaces that were ground with emery papers and ultrasonically cleaned in acetone to obtain a good surface finish.\[23\] A high-power Yb:YAG disk laser manufactured by TRUMPF with a coaxial laser head system with an average output power of up to 3 kW in...
Table I. Chemical Compositions of the Cladding Powder (Weight Percent)

| Weight Percent (nominal) | Hard Phase 60 pct | Metal Matrix 40 pct |
|--------------------------|-------------------|---------------------|
| W                        | C                 | Ni                  | Cr | Si | B | C |
| Balance                  | 3.8               | Balance             | 8.0 | 3.5 | 1.6 | 0.3 |

Continuous wave (CW) mode was used in this study. The laser machine operates at a wavelength of 1030 nm, with a beam diameter of 3 mm and a coupled coaxial cladding nozzle. The laser beam with a Gaussian profile was used to scan the samples during the deposition process. Laser processing parameters shown in Table II were used for the fabrication of metal matrix composite coatings on the TC4 substrate.

The microstructure of the clad layer was investigated through a Sigma 500 VP – Zeiss – Gemini field emission scanning electron microscope, FE-SEM (Carl Zeiss, Germany) with energy dispersive X-ray analysis (SEM/EDAX). Electron high tension (EHT) voltage of 7 kV with secondary electrons (SE) imaging was used during the scanning of the clad layer surfaces. The phases present in the clad layer were determined by X-ray diffraction (XRD) (D8-Discover; Bruker, Karlsruhe, Germany) using CuKα radiation. Metallographic cross-sections were prepared by grinding, polishing, and etching in Kroll’s solution (98.2 mL H2O, 6 mL HNO3, and 4 mL HF).

The microhardness of the coatings was determined on metallographically prepared cross-sections by means of an HMV Vickers hardness tester (SHIMADZU, Kyoto, Japan) under a 980 mN testing load for 15 seconds. Readings were taken on the metal matrix cross-section at 100 μm away from the top surface. Fifteen readings were measured throughout the MMC excluding the hardness values through the WC particles as shown in the supplementary Figure S-1.

B. LIBS Setup

The LIBS experimental setup consists of the second harmonic Nd: YAG laser system (532 nm) from Spectra Physics (Quanta-Ray PRO 350) with 10 ns pulse duration and 10 Hz repetition rate as illustrated in Figure 1. The spatial profile of the laser beam is a Gaussian distribution with a TEM00 spatial mode with a maximum pulse energy of 1400 mJ with pulse-to-pulse stability for > 99 pct of pulses. The pulse energy was controlled by controlling the laser flashlamps discharge voltage. The laser beam shot-to-shot pointing stability < ± 50 μrad. The laser beam was guided by highly reflecting mirrors before being focused on the sample’s surface by a convex lens with a focal lens of 100 mm. The sample was mounted on three translation stages for precise positioning control. The laser spot produced in the sample was 100 μm in diameter and had an energy of about 4.5 mJ. The plasma emission was collected with VIS collimating lens (74-VIS) and guided by an optical premium fiber (QP600-2-SR) to Ocean Spectrometer (FLAME-S-XR1). The LIBS spectra were acquired using a delay time of 1 μs and an integration time of 10 μs. All irradiations were carried out in the open air at atmospheric pressure.

C. LIBS Analysis

1. Canonical correlation analysis

Canonical correlation is a multivariate statistical analysis, called a multiple–multiple correlation, that deals with the interdependence between two different sets of multi-dimensional variables. CCA can be seen as trying to find basis vectors for the two variable sets by maximizing the correlation between the projection of variables onto the basis vectors. Then, it maps the two variable sets into a pair of linear transformations, one for each set, known as canonical variables \((u = \{u_1, u_2, \ldots, u_p\} \text{ and } v = \{v_1, v_2, \ldots, v_p\})\) with a dimension of a new coordinate system that is consists of two pairs of canonical correlation coefficient vectors, \(\{a_1, a_2, \ldots, a_p\}\) and \(\{b_1, b_2, \ldots, b_p\}\). Consider \(x = \{x_1, x_2, \ldots, x_p\}\) represents one set of variables with \(p_1\) dimensional and \(y = \{y_1, y_2, \ldots, y_p\}\) is the other \(p_2\) dimensional set of variables, then the linear combination can be expressed as follows:

\[
u_i = a_i^T X, v_i = b_i^T Y
\]

where \(a_i\) and \(b_i\) are \(p_1\) and \(p_2\) dimensional vectors, respectively, and \(i\) is the canonical variable pair number. It must be declared that \(a_i\) and \(b_i\) maximize the correlation between \(u_i\) and \(v_i\) such that being uncorrelated to all previous canonical variables pairs whereas the process stops when a subsequent pair presents no significant correlation. Significantly, if there is a linear relationship between variables, i.e., linearly dependent, such a relationship may not be seen as a correlation. Consequently, it can be used for variable reduction by selecting the significant variables. Finally a matrix of canonical correlation coefficients implemented from a correlation between \(X\) and \(Y\) is the canonical variable pair number.

2. Adaptive Boosted random forest classifier

Random forest is a supervised machine learning classifier that makes predictions by combining multiple individual decision trees. Therefore, it eliminates the high misclassification risk that may arise from a single decision tree. The random forest algorithm first chooses the number of individual trees to grow and the variables that are needed to split each node. Then, combine the results from the different decision trees through one of the main ways of combination; bagging or boosting. In brief, bagging is the default algorithm used by random forest in which the decision trees are trained on randomly selected observations with replacement. Besides, every tree randomly selects variables for each decision split. Boosting works similarly, however, the observations are weighted for sampling. Then, the
Observations which are misclassified get higher weights and go sampling more and more. In this study, an adaptive boosted random forest classifier algorithm was implemented. The algorithm computes weighted pseudo-loss for k classes and N observations as follows:

$$e_t = \frac{1}{2} \sum_{m=1}^{N} \sum_{k \neq y_m} d_{n,k}^{(t)} (1 - h_t(x_n, y_m) + h_t(x_n, k))$$

where $x_n$ is a vector of variable values for an observation $n$, $d_{n,k}^{(t)}$ are the weights of observations at step $t$ for class $k$ and $h_t(x_n, k)$ is the prediction confidence at step $t$ into class $k$ whereas the sum is over all classes except the true class $y_m$.

Hyperparameters, such as the number of decision trees, the maximum number of decision splits, and the minimum number of observations per leaf, are the arguments that define how the training of random forest classifiers is done. Subsequently, this study aimed to discover and fine-tune the hyperparameters for optimum classification accuracy. At that point, Bayesian optimization was utilized. The Bayesian optimization seeks to find the minimum of an objective function $f(x)$ for $x$. Therefore, it builds a Gaussian process model for $f(x)$ and uses it to select hyperparameters to evaluate the objective function $f(x)$ and control the learning process.

### III. RESULTS

#### A. Clad Layer Characterization

With the application of the selected laser parameters, the samples were prepared under three different powder feeding rates 20, 40, and 60 g min$^{-1}$ during coaxial laser cladding to attain coatings with new microstructures that have hard reinforcement. All the clad layers exhibited good adhesion between deposited powder and the substrate with free cracks and pores over the surface and along with the whole layer. The presumed reason is that during the laser cladding process the deposited powder and a thin layer of the TC4 surface were melted together as a result of the high heating rate produced from the scanning laser beam. New clad phases were formed depending on the diffusion rates, chemical reactions, growth properties and nucleation between the reacting species as well as the thermophysical properties of the different elements. According to the literature, the quality and performance of the products such as their hardness and wear resistance are dependent on the element distribution of the coated surface and the homogeneity of the formed phases inside the matrix. The SEM micrograph presented in Figure 2 illustrates the whole clad layer of a sample processed at 20 g min$^{-1}$ that constitutes two zones, clad zone (CZ), and interface zone (IZ). The clad zone contains bulk WC particles with some new constituents embedded in the metal matrix of Ni-based alloy plus the Ti-based alloy from the substrate. The interface zone involves few WC particles with a dilution from the TC4 substrate alloy because of the thermal diffusion effect. Similar zones in the cross-section microstructure were observed...
for all powder feeding rates, however different distributions of the WC particles were detected.

The SEM photographs shown in Figure 3 present zoomed parts of the CZ with three different powder feeding rates. It can be observed that with further increase in the powder feeding rate, the microstructure characteristics of the hard coating tend to be uniform, and the WC particles increased with the rise of the powder feeding rate from 20 to 40 to 60 g min⁻¹. This could be related to the higher density of the WC particle (15.63 g.cm⁻³) than that of Ni-based alloy (8.9 g cm⁻³) which leads to a higher flow of WC particles than the Ni particles from the deposited powder. This behavior can confirm the increase in the powder flow rate and the concentration of the WC particles quantity in the melt pool of the deposited layers. Another observation is that the WC particles’ edges were fragmented and diffused into the solid solution of the metal matrix forming new phases. All new constituents observed in the clad zone were identified using XRD. The matrix phases mainly consist of β-Ti, W, WC, W₂C, and TiC with other reinforcements. This confirms the melting and the diffusion of the WC particles fragmentations into the matrix resulting in the formation of titanium carbides, and re-crystallized β-Ti. The XRD pattern is given in supplementary Figure S-2.

B. Impact of Surface Topography on LIBS Measurement

The effect of coating surface topography on LIBS spectral emission lines was investigated by ablated 83 different distinct areas from each clad layer of the titanium alloy samples after laser cladding with the powder feeding rates of 20, 40, and 60 g min⁻¹. Forty spectra were collected along a 4 × 10 two-dimensional spot array allowing elemental spatial distribution through the coating surface. While 8 spectra were investigated along a line within the clad depth for elemental depth investigation within the coating layer deeply to about 900 μm from the highest point of the coating surface. The spot-to-spot distance was kept at 110 μm to avoid overlapping between spots, whereas the laser spot diameter was about 100 μm. The other spectra were collected arbitrarily along the coating surface to enrich the analysis. Due to the heterogeneous structure of the coating surface, the LIBS measurements were treated as independent. In the whole samples’ spectra (from 187 to 1033 nm), the data before 280 nm and over
780 nm had no significant information, at the background level. Therefore, the spectra were preserved only from 280 to 780 nm to clearly present significant characteristic lines resulting in 1169 wavelengths (variables). Significantly, domination of titanium spectral lines was noticed in all measured data from the different

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Fig. 4—Intensities of LIBS spectra measured from the clad layer of TC4 alloy samples processed at powder feeding rates of 20, 40, and 60 g min\(^{-1}\). Each spectral line is an average of 83 spectral lines measured from one sample.

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Fig. 5—Intensity fluctuations of atomic emission lines of (a) W and (b) Ti for samples processed at 20 and 60 g min\(^{-1}\) from the LIBS spectra of forty adjacent areas of the coating surface arranged in a 4 × 10 two-dimensional spot array.
Fig. 6—Area EDAX analysis and two-dimensional EDAX elemental map, corresponding to the SEM images presented in Fig. 2(a) and (c), respectively, of the samples’ clad layer processed at (a) 20 g min$^{-1}$ and (b) 60 g min$^{-1}$.

| Element | Weight % |
|---------|----------|
| Ti      | 15.16    |
| W       | 26.19    |

| Element | Weight % |
|---------|----------|
| Ti      | 0.46     |
| W       | 53.49    |
areas of the clad layer which was processed at 20 g min\(^{-1}\), confirming the higher dilution from the titanium substrate alloy.

Figure 4 shows zoomed parts of the average of the 83 LIBS spectral lines measured from each clad layer of the TC4 alloy sample using the second harmonic wavelength 532 nm. The plots demonstrate that the emission lines mainly belong to the main matrix and alloy elements of both powder and substrate (tungsten, carbon, silicon, nickel, and titanium), which agreed with the phases determined by the XRD spectra in the supplementary Figure S-2. Besides, it is depicted that the emission intensities of tungsten, carbon, silicon, and nickel measured from the clad layer of the sample processed at the highest powder feeding rate (60 g min\(^{-1}\)) were observed to be the highest, due to the intensifying of the bulk WC particles in the melt pool, and vice versa. On contrary, the titanium peaks of the sample processed at 20 g min\(^{-1}\) are found to be significantly higher than those emitted from the other processed samples. As less laser heat input is needed for melting less clad powder when the powder feeding rate is 20 g min\(^{-1}\), the thermal interaction between the deposited powder and the titanium substrate is stronger compared with other thicker coating with higher powder feeding rates. As a result, numerous TiC phase has been crystalized due to the dilution from the titanium substrate. Then, the difference in the obtained spectra intensities was initiated by the matrix effect as a result of using various powder feeding rates.

The heterogeneity and irregularity of the clad layer were depicted in Figure 5 by investigating the intensity fluctuations of LIBS spectra collected from the forty adjacent areas. It is worth noting that the microstructure and the chemical characteristics of samples (i.e., the matrix effect) have a great influence on the plasma excitation, which affects the intensities of the emission lines from the clad layers.

To further verify the phase composition and recognize the thermal diffusion behavior, EDAX analysis was implemented for the lowest and the highest powder feeding rates. The analyses mainly focus on the cross-section, perpendicular to the clad direction to expose comprehensive details of clad layer characteristics. The variation trends of the EDAX signals for titanium, tungsten, carbon, and nickel along the selected area are shown in Figure 6. The difference in the obtained intensities from EDAX analysis was initiated by the matrix effect as a result of using various powder feeding rates. All samples had different degrees of microstructure due to the different amounts of the formed phases in the metal matrix. The perceived values of Ti peaks from the area EDAX analysis assured that the titanium content in the metal matrix notably decreased with the increase in the powder feeding rate. This could be explained as a large portion of the incident laser beam mostly consumed by the deposited powder in the case of using the highest powder feeding rate resulting in melting very small thickness from the TC4 substrate alloy. In addition, the EDAX characterization map of the clad zone shows an evenly homogeneous distribution of the titanium through the clad layer processed at 20 g min\(^{-1}\) (Recall Figure 6(a)). While by comparing the tungsten element distribution, it can be visualized that its percentage and concentration increase with the increase in the powder feeding rates. This is confirmed by the chemical composition of titanium and tungsten elements from the area EDAX analysis; Ti content decreased from about 15.16 pct to 0.46 pct however the W content increased from 26.19 pct to 53.49 pct for the clad layer processed at 20 g min\(^{-1}\) and 60 g min\(^{-1}\), respectively. The EDAX analysis demonstrates the same trend for the concentration of the elements measured by the LIBS technique which of course supports and validates such spectrochemical analytical results.

To conclude, the matrix effect is considered a challenge in this study for LIBS analysis to distinguish the samples according to their surface topography and mechanical properties, especially the hardness. Moreover, it is time-consuming to select the specific emission line for further quantitative analysis. Therefore, canonical correlation analysis and Belsley collinearity diagnostics were applied to identify the significant wavelength points from the row LIBS data. Afterward, a machine learning algorithm employing a classification tree was utilized to establish a calibration model with such selected wavelengths so as to discriminate between the various samples for quantitative investigation of microhardness.

C. Variable Selection

To acquire highly significant information from the LIBS data correlated with the microhardness, CCA was performed to select the important lines (wavelength points) from the spectrum, i.e., variables. The matrix of correlation coefficients in which each row contained the correlation coefficients of one variable was computed from the LIBS data that is represented by a matrix of 249 \(\times\) 1169 elements. Each column in the data matrix is an observation vector described from one variable after data pre-processing by mean centering. Recall that CCA tends to find a matrix of correlation coefficients that maximize the correlation between canonical variable pairs such that all the canonical variables pair are uncorrelated, the calculated coefficients represent the significance of the variables pair. Therefore, all emission lines which have zero correlation coefficients were removed from the LIBS spectrum and the data matrix was shortened to 249 \(\times\) 246. Zoomed part of the correlation coefficients matrix and the first column of the matrix identified by all wavelength points are plotted in Figure 7.

Since several variables might be highly correlated, multicollinearity issues that could decrease the prediction accuracy of the estimated microhardness might appear. Therefore, Belsley collinearity diagnostics, described in detail in References 49, 50, were applied to the shortened data matrix to measure the strength and sources of multicollinearity among the 246 variables. To do that, we computed the singular values and the variance decomposition proportions of the LIBS data matrix and identified a number of 19 dependent
variables associated with less significant canonical correlation coefficients of values less than $5 \times 10^{-5}$ (detailed in the supplementary file and supplementary Figure S-3). Therefore, the emission lines which have absolute correlation coefficients less than $5 \times 10^{-5}$ were unconcerned. Finally, the raw LIBS spectrum was modified into 227 wavelength points selected after removing all dependent emission lines as shown in Figure 8. The modified LIBS spectra demonstrate that most of the selected emission lines are peak lines and adjacent to peak lines belonging to tungsten and titanium elements. The results suggested that the differences between the clad layers processed at various powder feeding rates can be mainly distinguished from the emissions lines of tungsten and titanium elements which manifest the potential of the canonical correlation analysis and Belsley collinearity diagnostics for selecting the important independent emission lines without redundancy and removing the unrelated emission lines.

D. Microhardness Estimation

The above results reveal that due to the matrix effect which occurred from the different microstructures of the samples, it was not easy to exploit a model that can accurately estimate the microhardness which depends on the surface topography of the different samples’ clad layers. Subsequently, a machine learning algorithm by means of an optimized adaptive random forest classifier was established to provide the best model to discriminate between the various samples for quantitative investigation of the microhardness. Sixty spectral lines chosen arbitrarily from the modified LIBS dataset after CCA, 20 spectral lines for each sample, were assigned to test the accuracy of such a supervised learning model. Then, the other 189 spectra were used for training the model. Considering the dynamic range of the different variables, before establishing the model, every variable in the training and testing datasets was mapped to the interval $[-1,1]$. To minimize the misclassification rate...
and establish the optimal tree-complexity level, the model was automatically optimized to fine-tune the hyperparameters using Bayesian optimization. The hyperparameters as returned by the optimization model for 50 classification trees are presented in Supplementary Figure S-4 through 30 misclassification rate.

Fig. 8—Average intensities of LIBS spectra measured from the clad layer of TC4 alloy samples processed at powder feeding rates of 20, 40, and 60 g min⁻¹. (a) raw LIBS spectra with the selected emission lines are highlighted in red within the inset. (b) modified LIBS spectra of the selected emission lines.

Fig. 9—An estimate of the variable importance as returned by the adaptive boosted random forest classifier.
function evaluations with a total elapsed time of 209 seconds. It can be observed that the unique minimum objective was achieved with 37 for the maximum number of decision splits and 8 for the minimum leaf size. In addition, it was found that the adaptive boosted random forest achieves optimum classification accuracy whereas the in-sample misclassification rate, the loss calculated between the training data and prediction that the model makes, was zero. This outcome guarantees that the adaptive boosted random forest classifier model categorizes all the training data correctly and hence gives an estimate for high-quality classification for new data.

Regarding the impact of the variable selection on the classification model, an estimate of the importance of variables is shown in Figure 9. Such estimate was computed by dividing the sum of changes in risk produced from the best splits on each node for every variable by the number of splits. It can be observed that

Fig. 10—Confusion matrix constructed from the test dataset.

Fig. 11—SEM micrographs of the deposition zone at powder feeding rate of: (a) 20 g min\textsuperscript{-1}, (b) 40 g min\textsuperscript{-1} and (c) 60 g min\textsuperscript{-1}. 
most of the titanium emission lines, as well as tungsten emission lines, have a great influence on the decision. Therefore, coupling such selected variables by CCA and the adaptive boosted random forest classifier was a feasible multivariate method for estimating the microhardness. The performance evaluation measurement of the adaptive boosted random forest model was assessed by the test dataset and the confusion matrix as indicated in Figure 10. It is depicted that the model performed better with values for the accuracy, sensitivity, precision, and F1 score being 0.9667.

The effect of the metal matrix is one of the principal reasons for determining the surface hardness. The microhardness of the MMC was enhanced by the uniform distribution of the WC particles within the NiCrBSiC solid solution with a further increase in the powder feeding rate. This is in accord with the Perrin et al.[51], Zhou et al.[52], and Elshaer[53] studies. The average MMC microhardness values were 844, 1000, and 1400 HV$_{0.1}$, for powder feeding rates of 20, 40, and 60 g min$^{-1}$, respectively. The increase in hardness values is due to the localized increase in the WC particles’ content that is embedded in the Ni-matrix with the increase in powder feeding rate. For clad zone at 60 g min$^{-1}$, the highest powder feeding rate, the microhardness of the MMC reaches around 1400 HV$_{0.1}$, which is nearly 4 times that of the TC4 substrate alloy. This may be attributed to the volume fraction together with the size of the secondary carbides, formed by solid-state precipitation of W$_2$C and TiC.[14] The two misclassification results were attributed to the samples with microhardness values of 1000 HV$_{0.1}$ and 1400 HV$_{0.1}$, which related to the clad layers formed at powder feeding rates of 40 and 60 g min$^{-1}$, respectively. The explanation was gained from the SEM at higher magnification (Figure 11). It is noticeable that the metal matrix changed with the increase in the powder feeding rates such that at 20 g min$^{-1}$, the fragmentations from the bulk WC particles were dispersed as uneven granular clusters of the W$_2$C phase. While with further increase in the powder feeding rate to 40 and 60 g min$^{-1}$, these granular clusters transformed into typically rod-type W$_2$C and fulfilled the whole matrix in the clad layer. This particularly makes such two layers, processed at 40 and 60 g min$^{-1}$, comparable in results, unlike the one processed at 20 g min$^{-1}$.

**IV. CONCLUSION**

Laser-induced breakdown spectroscopy has been demonstrated to be a suitable technique for the characterization of hard coatings NiCrBSi-WC fabricated by a coaxial laser cladding process on a TC4 titanium substrate not only for elemental analysis but also for the evaluation of surface topography and microhardness of deposited layer. The matrix effect is considered a challenge in this study for LIBS analysis. Accordingly, we propose a novel multivariate analysis model for acquiring representative information for quantitative microhardness analysis.

The main outcomes are outlined below:

1. The whole clad layer of the processed sample is composed of two zones: clad zone and interface zone. CZ contains bulk WC particles with some new constituents embedded in the metal matrix while the IZ includes a few WC particles diluted by the TC4 substrate alloy due to the thermal diffusion. The WC particles increased with the further increase in the powder feeding rate from 20 to 40 to 60 g min$^{-1}$.

2. The WC particles’ edge fragmentations led to the formation of new phases in the metal matrix coating such as W, WC, W$_2$C, TiC, and other reinforcements.

3. LIBS spectral lines demonstrate that the emission lines mainly belong to the main matrix and alloy elements of powder and substrate alloy. Titanium peaks of the sample processed at 20 g min$^{-1}$ are found to be higher than those emitted from the other processed samples while the emission intensities of W, C, Si, and Ni measured from the clad layer of the sample processed at 60 g min$^{-1}$ were observed to be the highest, due to the intensifying of the bulk WC particles with the increase in the powder feed rate.

4. Microstructure and chemical characteristics of samples (i.e., the matrix effect) have a great influence on the plasma excitation, which affects the intensities of the LIBS emission spectra from different clad layers.

5. Visualization of the LIBS technique demonstrates the same trend for the concentration of the elements in the MMC measured by the EDAX analysis which of course supports and validates such spectrochemical analytical results.

6. Canonical correlation analysis and Belsley collinearity diagnostics have noticeable potential for selecting the important independent emission lines without redundancy. The results indicated that the differences between the clad layers processed at various powder feeding rates can be mainly distinguished from the emissions lines of tungsten and titanium elements.

7. A machine-learning algorithm employing an optimized adaptive boosted random forest classifier was performed on the selected LIBS emissions for quantitative analysis of the microhardness. Bayesian optimization was applied to fine-tune the hyperparameters for 50 classification trees through 30 misclassification rate function evaluations with a total elapsed time of 209 seconds. It can be observed that the unique minimum objective, with zero in-sample misclassification rate, was achieved with 37 for the maximum number of decision splits and 8 for the minimum leaf size. The proposed classification model has accuracy, sensitivity, precision, and F1 score of 0.9667.

8. The classification model clarifies that most of the titanium and tungsten emission lines have a significant effect to differentiate between samples with different microhardness values, which is confirmed by the metallurgical study point of view. The quantitative microhardness values obtained from
9. Vickers microhardness of the MMC increased to almost four times over that recorded for TC4 substrate alloy for samples processed at 60 g min⁻¹ due to the intensification of the local content of WC particles in the MMC. Moreover, the fragmentations from the bulk WC particles of the clad layer processed at 20 g min⁻¹ were dispersed as uneven granular clusters of the W₂C phase. While the ones processed at 40 and 60 g min⁻¹, the granular clusters transformed into typically rod-type W₂C and fulfilled the whole matrix in the clad layer, resulting in comparable results.

Finally, the results revealed the ability of LIBS to discriminate the processed samples corresponding to their surface topography and microhardness according to their different powder feeding rates during the coaxial laser cladding process.

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CONFLICT OF INTEREST
On behalf of all authors, the corresponding author states that there is no conflict of interest.

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SUPPLEMENTARY INFORMATION
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