Implementation of laser-induced breakdown spectroscopy technique for qualitative analysis of an austenitic steel

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Abstract. In this work was used laser induced breakdown spectroscopy to study and characterize a sample of austenitic, steel American Iron and Steel Institute nomenclature, 304 series, with the objective of identifying constituent elements in the material. The steel was chosen because it is an economic and multipurpose material, which due to its physical characteristics, it is of great interest in the construction industry, design of tools and mechanical equipment. The contributions of this research to the industrial and metallurgical sector is that the laser induced breakdown spectroscopy technique allows to reduce costs in the experimental execution for qualitative studies of steels. Plasma generation was performed by focusing the radiation laser on the surface of a sample of steel. Plasma radiation generated was conducted through an optical fiber to a Mechelle spectrograph attached to an Intensified charge coupled device camera. The information obtained through the spectra allowed the characterization of the plasma by means of the parameters electronic temperature and electronic density, as well as the elementary identification of constituents of the steel sample, allowing identify major elements such as chromium, nickel, manganese and silicon, being concordant with the composition of elements present in the austenitic steel.

1. Introduction

Stainless steels are currently important materials due to the high demand in areas such as industrial, technological, and expansion in urban cities. Stainless steel can be classified into five different families; austenite, ferrite, martensite, duplex (austenite plus ferrite) and precipitation hardened alloys [1]. These families of stainless steels, they have characteristics and properties that depend on their composition. Among these steels are austenitic stainless steels, which are classified by American Iron and Steel Institute (AISI), in the 200 series and 300 series. The AISI 300 series is the most extensive, contains from 16% to 30% of Chromium (Cr), it has a high content of Nickel (Ni) and up to 2% of Manganese (Mn), it can also contain Molybdenum (Mo), Copper (C), Silicon (Si), Aluminum (Al), Titanium (Ti) and Niobium (Nb), elements that they are added to confer certain characteristics [2]. Some of these characteristics allow improve the quality of the metal surface, its wear resistance, excellent formability and corrosion resistance [3]. Laser induced breakdown spectroscopy (LIBS), is a technique that involves focusing radiation on a certain sample of study, independent of the state of aggregation of the material, generating a detectable emission in plasma form [4]. LIBS implementation to determinate elements present in materials such as steel, is of great importance, because it allows classifying steels according to their composition within types or classes elementary, within the high number of alloys existing in the metal industry. Also allows to characterize the plasma by determining the parameters electronic temperature and density electronic. To study the physical processes of plasma electron density, they must
be understood the mechanisms or effects of broadening of the spectral lines. Everyone of the mechanisms has in particular influence on the spectral line, which can be represented by Gaussian profile and others by Lorentzian profile. The broadening source most significant in the spectral lines is due to the Stark effect, which occurs due to the interaction of the particles charged by the electric fields formed in the plasma as consequence of the displacements of ions and electrons. Therefore, the Stark broadening a well insulated line is a useful tool to estimate the electronic density, always that the Stark broadening coefficient is known either by measure or by calculation. Stark broadening (∆\(\lambda_{\text{Stark}}\)) of an emission line expressed as the full width at half maximum (FWHM), in nanometers [5], is given by Equation (1).

\[
\Delta \lambda_{\text{Stark}} = 2w \left( \frac{n_e}{10^{16}} \right) + 3.5 \cdot A \left( \frac{n_e}{10^{16}} \right)^{1/4} \left[ 1 - B \cdot N_D^{-1/3} \right] w \left( \frac{n_e}{10^{16}} \right).
\]  

(1)

In Equation (1), \(B\) is a coefficient equal to 1.2 or 0.75 for ionic or neutral lines, respectively, \(w\) is the electron impact parameter and \(A\) is the parameter of ion broadening. The first term on the right side comes from the interaction of the electron, while the second is generated by ionic interaction; \(n_e\) is the density of electrons in \(cm^{-3}\) and \(N_D\) is the amount of particles in the Debye sphere [5, 6]. For the typical conditions of LIBS, the contribution of ion broadening is insignificant, and the Equation (1), becomes Equation (2).

\[
\Delta \lambda_{\text{Stark}} = 2w \left( \frac{n_e}{10^{16}} \right).
\]  

(2)

The previous equation allows us determine the electron density of the plasma, knowing the value of the electronic impact parameter and the FWHM value of the emission line. The plasma electronic temperature can be determined in the same way from graphs Boltzmann plot type, given by Equation (3).

\[
\ln \left( \frac{I_\lambda}{g_k A_{ik}} \right) = -\frac{E_k}{k_B T} + C,
\]  

(3)

where \(\lambda\) is the wavelength measured in angstrom (Å), the intensity is represented by \(I\), \(A_{ik}\) are the coefficients of transition probability, \(g_k\) is the statistical weight of the upper level, \(E_k\) is the energy of the upper level associated with said emission line, \(k_B\) is the constant of Boltzmann and \(T\) is the temperature measured in Kelvin (K).

2. Experimental description

The experimental setup is shown in Figure 1, for the plasma generation we use a pulsed laser system Nd-YAG (Tempest 10, New Wave Research) [7], with a focusing system. Laser power source is synchronized with an intensified charge coupled device camera (ICCD), iStar DH334T, coupled to a spectrograph Echelle type (Mechelle 5000, Andor Technology). The system is controlled with a personal computer with Andor Solis software.

The laser has 80 mJ per pulse, with a wavelength of 532 nm and a pulse duration of the order of 4 ns to 5 ns. The laser beam is focused on the surface of the sample through a convex flat lens of 10 cm focal length, an attenuator optical in the output of the laser beam that allows the adjustment of the energy delivered by pulse. To guarantee the reproducibility of the data the study, sample was placed in a precision positioning system. The detection of plasma radiation was carried out through a collector-collimator (ME-OPT-0007). The detected radiation was conducted to the input of the spectrograph equipped with an Echelle diffraction network of 1200 lines/mm by means of an optical fiber (QP400-2-UV/VIS) with a transmission range of 200 nm to 900 nm. The spectra obtained were captured by using the ICCD camera, with a resolution typical spectral of 4000 (resolution power of the spectrograph = \(\lambda/\Delta\lambda\)). Andor Solis software was used to register and display the spectra. The management software allows simultaneously control the ICCD camera and the Mechelle spectrograph [8, 9]. The parameters
used were set for 10 accumulations per record taken, delay times of $1 \mu$s to $10 \mu$s, steps of $1 \mu$s for each record.

![Figure 1. Experimental setup LIBS.](image)

### 3. Results

The spectrum obtained experimentally for AISI 304 austenitic steel sample, in the range of 200 nm to 900 nm, contains emission lines that are interfered with by lines of Fe, for being the majority element of the alloy; producing overlap or interference with lines of interest present in the plasma. Therefore, the identification of interest emission lines such as Cr, Ni, Mn, Si, among others, was carried out using reference lines of greater intensity of each element to be determined, compiled in the base of data from the National Institute of Standard and Technology (NIST) [10] and are shown in Figure 2(a) for Mn-I and Cr-I lines in the range of 390 nm to 440 nm, and for Figure 2(b) Cr-I and Cr-II lines in the range of 420 nm to 540 nm.

The analysis of the change in the intensity of an atomic emission line was also compared with ionic emission line at different delay times. Calculation was made determining the area under the curve of the intensity corresponding emission lines. Espectral lines were chosen the atomic line (428.990 Cr I) and the ionic line (284.340 Cr II), which are persistent lines and are interfered with by other nearby lines. These lines have overlap with neighboring lines, therefore it was necessary to carry out a deconvolution method.

![Figure 2. Emission lines found for the elements chrome and manganese. 304 austenitic steel sample spectrum in the spectral range of (a) 390-440 nm, and (b) 420-540 nm.](image)

For each calculated area, lines were used spectral that satisfy a Lorentz distribution, associated with processes of spectral broadening caused by collisions between atoms in the plasma. For this reason, the Lorentzian adjustment was used for the deconvolution of the spectral lines. Figure 3 shows the temporal
evolution for an atomic and an ionic line, here we observe that the half life time for an ionic line is smaller compared to the atomic line.

Figure 3. Comparison of the exponential decay for the line (428.990 Cr I) and the line (284.340 Cr II) for delay times from 1 $\mu$s - 8 $\mu$s.

Plasma temperature characterization was done through spectrum selection for a delay time of 3 $\mu$s, which has a good signal/noise ratio. Five wavelengths were chosen for lines of Cr-I emission, corresponding to emission lines reported by the NIST. The calculated values of the areas corresponding to the values of higher energy levels ($E_k$), the intensity of each of the emission lines ($I$), the Einstein coefficients of transition probability ($A_{ik}$) and the statistical weight value ($g_k$) [11], were tabulated as seen in Table 1.

Table 1. Parameters for plasma temperature determination.

| Ion | Wavelength observed (nm) | Intensity calculated (a.u) | Energy $E_k$ (cm$^{-1}$) | $A_{ik} \cdot g_k$ (s$^{-1}$) | Ln( $I \lambda / g_k A_{ik}$) |
|-----|--------------------------|---------------------------|---------------------------|-----------------------------|-------------------|
| Cr I | 374.380                  | 5431.252                  | 47222.208                 | 9.890E+08                   | -3.884            |
| Cr I | 520.600                  | 12922.557                 | 26796.269                 | 2.570E+08                   | -1.340            |
| Cr I | 529.800                  | 3937.093                  | 42256.086                 | 2.100E+08                   | -2.309            |
| Cr I | 532.830                  | 6876.159                  | 42261.225                 | 6.800E+08                   | -2.921            |
| Cr I | 534.570                  | 6349.254                  | 26796.269                 | 2.400E+07                   | 0.346             |

Figure 4(a) shows the Boltzmann plot for temperature determination of plasma. The five points taken represent the values for the natural logarithm versus the energy of the upper levels for each of the parameters represented in Table 1. According to Equation (3), the plasma temperature was determined from the inverse of the slope of the line of Figure 4(a), multiplied by the Boltzmann constant $k_B = 0.695$ in units (cm$^{-1}$/K). The determined value represents a single value for a single case, it is say, for a single delay time. The calculated value was 9387 K for a time of 3 $\mu$s delay.

Electronic density was determined by calculating the full width at half maximum (FWHM) of the atomic line 482.300 nm of Si-I, observed in Figure 4(b). The value of electronic impact parameter ($w$) for line 482.300 nm of Si-I, is reported in the literature for temperatures of 5000 K, 10000 K, 20000 K, and 40000 K, respectively [12]. The polynomial equation associated with this figure was used to determine the value of the impact parameter by interpolation of the data, since the temperature found by means of the Boltzmann plot equivalent to 9387 K it was in the range of 5000 K to 10000 K of the reported temperatures. The value determined for the parameter of impact ($w$) was 1.279 Å. Once the impact parameter is found, the electronic density is determined for each of the delay times using Equation (2). Figure 4(a) shows the Boltzmann plot type graphics used to determine the temperature of
the plasmas. Figure 4(b) shows the temporal evolution of electronic density as a function of time. The data obtained from electronic density for each of the delay times were tabulated and are shown in Table 2.

![Figure 4](image)

**Figure 4.** Calculated electronic temperature and electronic density. (a) Boltzmann plot for a delay time of 3 $\mu$s. (b) Electronic density versus delay time.

| Delay time ($\mu$s) | FWHM (Å) | Temperature (K) | Impact parameter (Å) | Electronic density ($cm^{-3}$) |
|---------------------|-----------|-----------------|----------------------|--------------------------------|
| 1                   | 2.830     | 9387            | 1.279                | 1.107E+16                      |
| 2                   | 2.603     | 9387            | 1.279                | 1.018E+16                      |
| 3                   | 2.314     | 9387            | 1.279                | 9.050E+15                      |
| 4                   | 2.345     | 9387            | 1.279                | 9.168E+15                      |
| 5                   | 2.447     | 9387            | 1.279                | 9.568E+15                      |
| 6                   | 2.189     | 9387            | 1.279                | 8.558E+15                      |
| 7                   | 2.437     | 9387            | 1.279                | 9.530E+15                      |
| 8                   | 2.509     | 9387            | 1.279                | 9.811E+15                      |
| 9                   | 2.445     | 9387            | 1.279                | 9.561E+15                      |
| 10                  | 2.369     | 9387            | 1.279                | 9.263E+15                      |

For plasma characterization we assumed that it was in local thermodynamic equilibrium (LTE) [13]. One way to verify this is to make sure if the electronic plasma density meets the McWhirter criteria [14]. This criterion allows determine the minimum limit of electronic excitation density so that the plasma is in LTE. By replacing the values found for the plasma temperature (T) measured in Kelvin (K) and the difference in the energy transition ($\Delta E$) measured in electron volts (eV), for the equation that represents the McWhirter criterion, the expression shown in Equation (4) was obtained.

$$N_e \geq 1.6 \times 10^{12} (9387)^{\frac{1}{2}} (2.569)^3$$

(4)

The minimum value found, for experimentally calculated electronic densities, for delay times from 1 $\mu$s to 10 $\mu$s, was $8.558 \times 10^{15} cm^{-3}$. This value found is greater that obtained by the McWhirter criterion, with a value of $2.630 \times 10^{15} cm^{-3}$, so therefore, it was concluded that, the necessary criteria are met for the plasma to be found in LTE.
4. Conclusions
Elements present in the sample of AISI 304 austenitic steel, such as Cr, Ni, Mn and Si by qualitative analysis using the LIBS technique was determined. In addition to determining elements present in the steels, a analysis of the behavior of a pair of lines, ionic and atomic with respect to different delay times was performed, finding that ionic lines decrease more rapidly with respect to the atomic lines, because the half life times for neutral atoms are greater than those of ionic species. Were determined the electronic temperature parameters (Te) and electronic density (Ne), for a specific case, by means of plasma characterization. The electronic temperature calculation was performed using Boltzmann graphs, taking into account and assuming that the plasma was in LTE. The value obtained from electronic temperature for the plasma of the AISI 304 steel sample was 9387 K, for a certain time. Similarly, the electronic density for the plasma mentioned above, first considering that the parameter value of electronic impact for certain temperatures, was reported in the literature for the line of Si-I 482.300 nm. The value of the electronic impact parameter for the temperature found experimentally through the Boltzmann plot, it was interpolated by being among the range of 5000 K to 10000 K of the values reported in the theory. This parameter value of impact was used to determine the plasma electron density for the sample of austenitic steel AISI 304. It was also possible verify that the consideration that the plasma was in LTE, it is correct, because it was demonstrated that the electron density found experimentally, is greater than that defined by the criterion from McWhirter.

The results obtained in this research can be extended to study different types of steels present in the metallurgical industry, as well as any metal alloy. This makes the LIBS technique an important, versatile tool with the potential to be used in the study of a wide variety of materials, and in very diverse applications, such as real-time control in foundry processes or production lines, in the taking measurements in-situ in museums, art galleries, archaeological sites, mining exploration, as well as remote analysis in dangerous environments. This research provided relevant information in the study of elements present in AISI 304 steel, identifying major constituent elements, allowing to determine the type or family of steels to which belongs.

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