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Limit of detection and hardness evaluation of some steel alloys utilizing optical emission spectroscopic techniques

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ABSTRACT

Steel alloys are of the most useful materials utilized in the manufacture of various industrial components. In this work, Laser-induced breakdown spectroscopy (**LIBS**) and spark-induced breakdown spectroscopy (**SIBS**) techniques have been used as diagnostic tools for the elemental composition of steel alloys and determination of the limit of detection (**LOD**). Also, the surface hardness of these alloys was measured using the ratio between the Calcium ionic and neutral lines (Ca II/Ca I) as well as the well-known method of mechanical Vickers one. The self-absorption of silicon, copper and calcium lines under investigation was corrected via comparison of the electron densities. The densities have been measured from these lines to that calculated from the hydrogen Hα-line at 656.27 nm which are in the same spectra under the same condition. Calibration curves were achieved for Si and Cu with linear regression coefficients about 0.99 and limits of detection values were 147 and 89 ppm respectively. Also, high accuracy linear relations have been obtained between Vickers mechanical hardness, the ratio between the Calcium ionic and neutral lines (Ca II/Ca I) and the plasma temperature. These results proved the importance of correcting the spectral intensity line for the self-absorption effect before the LOD measurement. Also, they confirmed the correction importance before evaluation of the hardness in LIBS experiments.

1. Introduction

Elemental analysis via identification and quantification of elements can be used to determine elemental compounds, molecular species regarding the weight percent of each component, and their purity. This significance is due to the non-metallic elements influence the physical properties of metallic materials. For that, studying the manufactured metal parts is a target field that needs to be analyzed primarily [1,2]. In the field of spare parts and manufacturing of heavy industries, steel alloys represent the most suitable composites in the engineering field with specific properties. Structural, industrial and spare part manufacturing are among the applications in which these alloys have been implemented [3]. Classification of steel alloys is controversial especially in spare parts manufacturing to differentiate between different types [4]. Metal testing services help in identifying and evaluating the properties of metal parts to determine their safety, reliability, and integrity. Moreover, the chemical analytical techniques are commonly used to measure the chemical composition, material classifications then correlation all parameters with quality control [5].

LIBS technique is the most promising method used to collect high-quality information. It is a fast, semi-nondestructive, non-complicated and remote method. It is an analytical technique based on analysis of laser spectral line of different types of matter (solid, liquid, gas or aerosol) produced from plasma state formed by focused high power laser mater interaction [6–8]. Recently, it can be used to measure some physical properties of solid materials like surface hardness [9–14], and determine the limit of detection [15,16]. Along with the LIBS technique, SIBS was used as an effective method to enhance material classifications. It is a high-quality spectroscopic method enabled metal analysis for all metal industry process stages, from metal production through processing and recycling [17].

In the present work, LIBS and SIBS techniques were used as a method to enhance discrimination between different steel alloys used in spare parts manufacturing materials. Then, LOD, the surface hardness, and the plasma temperature were measured before and after correction from the self-absorption effect. Moreover, the surface hardness of the target materials was calculated and compared using mechanically surface Vickers method.

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1.1. Measurement of plasma parameters

The spectral emission of the plasma is not only affected by the concentration of the element in the sample, but also by the plasma properties, which sequentially depends on the properties of the excitation source. Plasma parameters as electron density and the plasma excitation temperature with time were determined to achieve a sensitive quantitative analysis. In the spectroscopic measurements, the electron density in the plasma can be determined via several methods such as calculation of the optical refractivity of the plasma, Stark profile of specific optically thin emission spectral lines, and the absolute emission coefficient of the spectral line. Among these methods proposed for electron density measurement, the broadening of emission lines due to the Stark effect has been commonly utilized. This method is based on the assumption that the Stark effect is the leading broadening mechanism, in comparison with the Doppler broadening and the other pressure broadening mechanisms, due to collisions with neutral atoms namely resonance and Van der Waals broadenings [18,19]. The hydrogen Hα-line always exists in the LIBS spectra acquired in the open air. It was proposed in [20,21] that the accurate electron density could be measured by using the Hα-line at the wavelength of 656.27 nm since it was confirmed to be optically thin [20]. The theoretical calculations of the expansion of hydrogen lines parameters have been described in several investigations [18,22–24]. For these elements, the stark broadening is linear which affects the Lorentzian full-width Δλ. The plasma electron density from this spectral broadening can be calculated using the following equation;

$$n_e(\mathrm{cm}^{-3}) = C(\lambda, T)(\Delta\lambda_{1/2})^{3/2} \tag{1}$$

whereas Δλ is the full measured width at the half maximum of the H_α line in A°, C(λ, T) is a coefficient which depends weakly on electron density and temperature, tabulated by Griem [22].

On the other hand, this stark broadening is quadratic in case of elements other than hydrogen which affects the Lorentzian full-width Δλ. The plasma electron density from the spectral expansion of these lines such as calcium lines can be calculated using the following equation [25];

$$n_e(\mathrm{cm}^{-3}) = \left(\frac{\Delta\lambda}{2\omega_s}\right)N_r \tag{2}$$

where Δλ is the measured full width at half maximum FWHM, ω is the half width at half maximum (HWHM) Stark broadening parameter caused by the electron density and N_r is the reference electron density which is equal to 10^{17} cm^{-3} for ionic atoms and 10^{16} cm^{-3} for neutral atoms.

On the other hand, plasma temperature is measured using a variety of advanced theories [26]. Most spectral temperature measurements are based on two primary methods, the primary one, is the successive isoelectronic ions; on line and continuum intensities ratio, on relative continuum intensities. The secondary one, the relative line intensities of either similar atom or ion, of neighboring ionization stages [22,25,27]. Our discussion rests on the assumption that the non-relativistic Doppler effects predominate over the other line broadening mechanisms [27]. The methods that are utilized to compute the plasma parameters (T_{ion}, T_{ex}, N_e, …, etc.) under the assumption that the laser-induced plasma is in local thermodynamic equilibrium (LTE). The primary method is well known as the Boltzmann plot. The electron temperature can be measured from the slope of the line described by the following expression [28];

$$\ln\left(\frac{I_{ij}}{A_{ij}g_i}\right) = \ln\left(\frac{n^s}{U_s(T)}\right) - \frac{E_i}{kT_e} \tag{3}$$

where I_{ij} is the spectral line intensity, g_i is the degeneration of the upper level, A_{ij} is the transition probability, and E_i is the energy of the upper level, U_s is the partition function, and n_s is the total number density of the species s in the plasma.

The secondary method is suggested to enhance the measurement accuracy of the temperature given that the plasma is in local thermodynamical equilibrium (LTE). This method is well known as Saha-Boltzmann plot. By applying the same equation to Eq. (3), the plasma temperature can be measured [28].

1.2. Self-absorption effect on the emitted spectral line

Some spectral line interferences are significant to take care to achieve the proper quantitative analysis of LIBS and enhance their data. The high active chemical interferences are matrix effect, self-absorption, and overlapping from spectral line interference or band interference. The self-absorption process appears when the cold atom absorbs emissions waves from hotter ones. For that, to avoid or decrease self-absorption phenomena, there are some rules must be taken into account [29,30]. When the plasma is homogenous, the temperature and electron density gradients which effect on line profiles are neglected.

The self-absorption coefficient SA is defined as the ratio of the measured peak height to the value of the line peak in the absence of self-absorption. SA is equal to one if the line is optically thin, while it decreases to zero as the line becomes optically thick. The exact relation between the observed (Δλ) and the corresponding non-self-absorbed ($\Delta\lambda_0$) widths can be parameterized as in the following equation [13,14,31];

$$SA = \frac{I(\lambda_o)}{I_o(\lambda_o)} = \left(\frac{\Delta\lambda_{sl}}{\Delta\lambda_{so}}\right)^{\frac{-1}{0.54}} = \left(\frac{n_e(line)}{n_{\boldsymbol{e}}(H_\alpha)}\right)^{\frac{-1}{0.54}} \tag{4}$$

where $I(\lambda_o)$ is the experimentally measured height of the same line in the presence of SA, $I_o(\lambda_o)$ is the spectral line intensity of negligible SA, $\Delta\lambda_{so}$ is the intrinsic FWHM of the Lorentzian component for the optically thin spectral line, and $\Delta\lambda_{sl}$ is the distorted Lorentzian component of the same line under the self- absorption effect.

2. Experimental work

2.1. Materials

Set of steel alloys samples used for spare parts manufacturing materials of Robot structure consist of four samples. One was the original, and the other three samples were laboratory manufactured for testing. The originated stainless-steel sample (SS304) was obtained from the company Avesta Sheffield Ltd with analysis certification, while the other samples were prepared in the National Commission for Military Production, Egypt. Each sample has a different mechanical property. The dimensions of all samples are 4 × 4 × 2 cm. The elemental composition of the samples under study measured by spark analysis technique is listed in Table 1.

2.2. Experimental LIBS setup

A typical experimental LIBS setup was shown in Fig. 1. In this setup, an Nd:YAG laser (Continuum laser, PRII 8000, Electro-optics, Inc., Wyandotte, MI, USA) of laser spot size was about 0.5 ± 0.1 mm of effective focused beam diameter that delivers 70 mJ/pulse energy at its fundamental wavelength of 1064 nm with 7 ns pulse duration and repetition rate of 10 Hz is focused on the sample by a plano-convex quartz lens of 10 cm focal length. All the measurements have been performed at atmospheric pressure. The light emitted from plasma plume was then collected through an optical fiber of diameter 0.6 mm at a distance 3 cm from the tar-

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