Effect of Surface Topography in the Characterization of Stainless Steel Using Laser-induced Breakdown Spectrometry

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A pulsed Nd:YAG laser operating on the second harmonic wavelength at 532 nm was used in this work. The influence of sample surface topography on spectral emission of laser-produced plasmas was investigated. Stainless-steel samples with different grades of surface polishing (range 0.026–4.54 μm) were prepared and analysed using LIBS. The effect of surface roughness on analytical precision was found to be dependent on laser beam energy, with optimum results for beam irradiances in the range 28–57 GW cm⁻². The reproducibility of spectral emission for pre-ablated surfaces also has been investigated. Limits of detection of molybdenum in stainless steel at different sample finishes and for several laser irradiances are discussed.

Laser-induced breakdown spectrometry (LIBS) can be used as an alternative method for the direct analysis of stainless steel.13–14 This is a simple and fast technique based on laser ablation of the sample and direct spectral analysis of the microplasma produced.15,16 Rapid in situ analysis of worked material without sample preparation and micro- and macromapping over several centimetres by scanning the optical system or moving the sample on a translation stage are interesting capabilities of LIBS.17,18 The sulphur content in steel was determined by the LIBS method.19 The technique has been applied also for direct analysis of the carbon content in steel.20 With the use of time-resolved spectroscopy and the generation of plasma in nitrogen atmospheres, a precision of 1.6% and a limit of detection of 65 ppm have been reported.

For the analysis of solid samples, the grade of sample surface polishing may play an important role in the analytical results. Various finishes available from the stainless-steel producers include a brushed finish, a highly polished finish, a bright-annealed finish and intermediate polishing grades that depend on customer requirements. Also, as the grade of polishing increases, the sample preparation time and the cost per analysis increase. Recently, the influence of sample surface condition on the chemical analysis of a brass sample using laser ablation inductively coupled plasma atomic emission spectrometry has been published.21 In the present work, the effect of sample surface topography on the spectral emission of laser-induced plasmas from four elements of interest in stainless steel production has been studied. The precision of the signal for original surfaces with different grades of sample polishing and for pre-ablated surfaces has been evaluated. The influence of sample roughness on quantitative analysis of molybdenum as a function of laser irradiance is discussed.

INTRODUCTION

Stainless steel plays an important role in all emerging technologies and is used on a large scale in such everyday applications as furniture, electrical appliances, hospital and surgical equipment, petrochemical plants and the automobile industry. The compositions of stainless steels vary from a fairly simple alloy, essentially iron with 11% chromium, to complex alloys that include 30% chromium, great quantities of nickel and half a dozen other effective elements. Such compositions give stainless steel different mechanical properties, resistance to corrosion and applicability. However, the metallurgy of stainless steel is a dynamic, fertile technical field grown by continent demands of new alloys with better properties. This fact requires the improvement of existing instrumental analysis techniques and the development of new approaches for rapid, reliable and accurate analytical results, allowing real-time monitoring of steel production.2 Nowadays, spark ablation optical emission spectrometry3,4 and x-ray fluorescence spectrometry5,6 are the most extensively used techniques for real-time monitoring of steel production. The determination of major, minor and trace elements in stainless steel is also accomplished using a combination of analytical techniques, including inductively coupled plasma atomic emission spectrometry7,8 and atomic absorption spectrometry.9 Other techniques, such as glow discharge mass spectrometry and inductively coupled plasma mass spectrometry, also have been used.10–12

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Laser-induced breakdown spectrometry (LIBS) can be used as an alternative method for the direct analysis of stainless steel. This is a simple and fast technique based on laser ablation of the sample and direct spectral analysis of the microplasma produced. Rapid in situ analysis of worked material without sample preparation and micro- and macromapping over several centimetres by scanning the optical system or moving the sample on a translation stage are interesting capabilities of LIBS. The sulphur content in steel was determined by the LIBS method. The technique has been applied also for direct analysis of the carbon content in steel. With the use of time-resolved spectroscopy and the generation of plasma in nitrogen atmospheres, a precision of 1.6% and a limit of detection of 65 ppm have been reported.

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**EXPERIMENTAL**

**Instrumentation**

A Q-switched Nd:YAG laser (continuum, model Surelite SLI-20, pulse width = 5 ns) operating on the second harmonic at 532 nm was used. In order to obtain low laser irradiance, the laser flash lamp voltage was fixed at the minimum setting (0.90 kV) and then variation of beam energy was achieved using glass custom-bandpass filters. The laser pulse energy was measured with a pyroelectric joulemeter (Gentec, model ED-200, with a nominal sensitivity of 9.86 V J⁻¹) coupled with a digital oscilloscope. Samples were irradiated in air at atmospheric pressure. The beam was guided with a quartz prism and focused, at normal incidence, on the sample surface with a biconvex quartz lens of focal length 30 mm. The laser spot diameter was estimated to be 125 µm. Laser-ablated plasma emission was collected by a planoconvex quartz lens of focal length 100 mm into the entrance slit of a 0.5 m focal-length Czerny–Turner spectograph (Chromex, model 500 IS, with three indexable gratings). Light was dispersed using the 2400 grooves mm⁻¹ grating. The reciprocal linear dispersion was 2.5 nm mm⁻¹. The entrance slit was 20 µm wide and the height was 10 mm. The dispersed plasma light was detected using a two-dimensional charge-coupled device (CCD) detector (Stanford Computer Optics, model 4Quik 05) equipped with an intensifier system. The CCD consists of 768(h) × 512(v) elements. The photoactive area is 6 × 4.5 mm². In this configuration, each spectrum covers ~15 nm. Operation of the detector was controlled by 4 Spec 1.20 software. The emission signal was corrected by subtraction of the dark signal of the detector, which was measured separately for the same exposure time. Each pulse was stored as a file containing spectral and spatial information. Calibration of the detector system was carried out by using spectral lines emitted from a laser-induced plasma of titanium.

A sample holder was designed and manufactured in our laboratory. This sample holder accommodates different sample thicknesses, keeping its surface always at a fixed distance from the focusing lens. The sample holder was mounted on a manual X–Y–Z translation stage, which made it possible for sample manipulation as desired.

A stylus instrument Perthometer PRK (model RT-50 from MAHR) was used to determine the roughness parameters. This inductive pick-up device allows a lateral resolution of 0.2 µm, whereas the depth resolution was 0.01 µm.

**Samples**

Stainless steel samples of type AISI 304 (8.13% Ni, 18.44% Cr, 0.32% Mo, 1.41% Mn) and type AISI 316 (11.33% Ni, 17.10% Cr, 2.16% Mo, 1.20% Mn) were provided by Acerinox, S.A. Sample surfaces were polished using different grades of abrasive paper to result in variable surface finishes. The 1000 grit sandpaper produced the smoothest surface and the 40 grit sandpaper produced the roughest surface. The roughness parameters measured for each polished surface were the arithmetical mean deviation (R_a) and the maximum roughness depth (R_max). R_a is defined as the arithmetical mean of the areas of all profile values of the roughness profile and R_max is defined as the largest single roughness depth within the evaluation length. These values are summarized in Table 1 for the samples of interest. In this work, the R_a parameter will be employed.

**RESULTS AND DISCUSSION**

**Spectral analysis and surface topography**

Some preliminary spectral study was carried out in order to find an adequate spectral window for the simultaneous detection of four elements of interest in the analysis of stainless steel. Accordingly, in spite of the fact that many intense lines of Cr, Ni and Mo appeared in the ultraviolet region, the spectral window covering the range 540–554 nm was chosen due to the fact that the line emissions of the elements studied in that window are clearly distinguished and free from iron interference. Figure 1 shows laser induced breakdown (LIB) emission lines of Cr(I) 540.9 nm, Fe(I) 542.9 nm, Ni(I) 547.7 nm and Mo(I) 550.6 nm for an AISI 316 stainless steel. Acquisition conditions were fixed with an integration time of 1 µs and a 1.5 µs delay time.

Figure 2 shows the net emission signal of Cr from 10 consecutive laser shots, each on a fresh surface of target sample no. 60. Data were acquired at 0.2 mm intervals in a direction perpendicular to the direction of rolling. The laser beam irradiance was 16 GW cm⁻². The inset in Fig. 2 shows two scanning electron microscopy photographs corresponding to the 3rd, and the 8th, positions, which exhibited the lowest and the largest intensities, respectively. The photographs indicate that at low irradiance a single laser spot weakly erodes the sample surface and the original roughness remained without significant modifications. The variation of Cr intensity can be correlated clearly with the surface topography, which causes the laser beam drops in a ‘deep zone’ or in a ‘peak’ of the sample, as shown in the photographs corresponding to the 3rd and 8th laser shots, respectively. When the laser beam falls on a ‘deep zone’ there is a lower efficiency of material removal and, consequently, the signal intensity decreases.

| Table 1. Arithmetical mean deviation (R_a) and maximum roughness depth (R_max) of the stainless-steel samples used in this work. |
|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| No. | 40 | 60 | 120 | 180 | 320 | 600 | 1000 | Mirror |
| R_a (µm) | 4.540 | 4.220 | 0.167 | 0.183 | 0.111 | 0.030 | 0.048 | 0.026 |
| R_max (µm) | 34.260 | 39.840 | 3.314 | 2.407 | 1.104 | 0.349 | 0.552 | 0.174 |

Figure 1. Single-shot LIB spectrum of a type 316 stainless-steel sample showing emission lines of Cr(I), Fe(I), Ni(I) and Mo(I). The spectrum was obtained at a laser irradiance of 57 GW cm$^{-2}$, a delay time of 1.5 µs and an acquisition time of 1 µs.

Figure 2. Net emission signal of Cr from 10 consecutive laser shots each on a fresh surface of target sample no. 60. Data were acquired at 0.2 mm intervals in a direction perpendicular to the direction of rolling. The scanning electron microscopy photographs correspond to the 3rd laser shot (the lowest emission intensity) and the 8th laser shot (the largest emission intensity). In both cases, the laser beam irradiance was 16 GW cm$^{-2}$.
Influence of sample surface finish on emission intensity

The effect of sample surface preparation on the LIB emission intensity has been investigated. Eight samples with different grades of surface polishing (range 0.026–4.54 µm) were analysed. The samples were prepared as mentioned in the experimental section. Figure 3 shows net signal intensities for Fe, Cr, Ni and Mo versus superficial roughness at laser beam irradiances of 7, 16 and 28 GW cm$^{-2}$. Variation bars correspond to the signal range of 10 single laser shots, each on a fresh surface. For comparative purposes, diffuse reflectance values of the samples also have been included (Fig. 3(c)). As shown, at lower laser irradiances (7 and 16 GW cm$^{-2}$) variation of superficial sample characteristics notably affected the emission signal. In both cases, for instance, the Cr(I) emission intensity of sample no. 60 is lower than that corresponding to sample no. 1000 by a factor of $\sim$1.4. These results confirm the significant optical behaviour of the surface and the relationship between LIB intensity and the sample reflectance. When the superficial roughness is such that a minimum in diffuse reflectance is observed (higher degree of sample polishing), the spectral intensity reaches a maximum. On the contrary, as the diffuse reflectance increases, the intensity decreases. However, at 28 GW cm$^{-2}$, the LIB emission intensity for the four elements studied remained approximately constant, indicating that the surface finish had no significant effect on the signal measured. This fact can be attributed to the practical destruction of superficial topography with a single laser shot of higher irradiance.

Influence of sample surface finish on analytical figures of merit

The effect of surface topography on precision and quantitative analysis also has been investigated. Reproducibility of the LIB emission intensity of Cr(I) for a single laser pulse at four sample surface finishes ($R_a =$ 0.048–4.54 µm) was initially studied as a function of laser beam irradiance (Fig. 4). At 7 GW cm$^{-2}$, the results...
suggest that the polished surfaces gave better signal reproducibility. It should be noted that in all samples studied the relative standard deviation (RSD) values improved when the laser beam irradiance increased. For instance, for sample no. 40 at 57 GW cm\(^{-2}\) the precision improved by a factor of \(\sim 9\) compared to that obtained at 7 GW cm\(^{-2}\).

However, at larger laser energy (28 GW cm\(^{-2}\)) the measured precision for the four sample finishes was approximately constant. These results agree well with those obtained in Fig. 3 and confirm no dependence of precision with the surface morphology at higher irradiance.

The precision of the successive pulses on the target also has been evaluated. The results are summarized in Table 2, where RSD (%) measurements of the Cr(I) emission signal for the 1st, 5th, 25th, 50th and 100th, pulses at two superficial finishes (samples 60 and 1000) are given. In order to observe a noticeable roughness effect, the laser beam irradiance was adjusted to 7 GW cm\(^{-2}\). As shown, in both cases the shot-to-shot reproducibility was worse after 25 laser ablation pulses. This fact suggests that the original surface has been changed completely during the ablation process and an undefined surface has been generated. This pre-ablated surface may result in poorer reproducibility of measurements than the original superficial roughness. However, it should be noted that for the first pulses (<5th pulse) the RSD variability can be attributed mainly to the different roughness features in the samples surface.

According to the observations made above, it could be expected that different grades of surface polishing would affect the limits of detection (LODs). Limits of detection for Mo using the atomic line at 550.6 nm were calculated. A type 304 stainless-steel sample containing 0.32% Mo was used. Table 3 shows LOD values for samples 40, 60, 120 and 1000 using several laser beam irradiances. The LOD values were calculated by the method proposed by Boumans et al.\(^{27}\)

\[
LOD = \frac{(0.01)3(RSD)_{n}m}{S/B}
\]

where RSD\(_n\) is the relative standard deviation in the background, m is the concentration of the analyte used in the determination, a value of 3 is used to give a >99% confidential level and S/B is the signal-to-background ratio. As shown, limits of detection tend to improve for polished surfaces. The best LOD values were obtained with low roughness surfaces at the intermediate beam irradiances examined in this study (16–28 GW cm\(^{-2}\)). Lower irradiance results in a lower amount of ablated mass, where is a higher irradiance decreases plasma emission by reducing the amount of laser energy reaching the sample surface via plasma shielding effects.\(^{27}\) Both circumstances—low irradiance and plasma shielding—tend to deteriorate the LOD/s. It should be noticed that the LODs in Table 3 do not represent the best possible values for Mo in stainless steel using LIBS. These values could be regarded as two or three times greater than the optimum detection limits, which therefore can be estimated to be \(\sim 100\) ppm. Improvement of acquisition conditions in terms of integration time and accumulated signal should result in better signal-to-background ratios and lower RSD values, and consequently an improvement in the LODs should be achieved. Although the values shown above are far from typical values of LOD (0.1–1%) and LOD (1–10 ppm) provided by x-ray fluorescence spectrometry and optical emission spectrometry, for the purpose of this study the values given are consistent in terms of the detection wavelength and operating conditions used.

### Table 3. Limits of detection for Mo(I) in different sample surface finishes at several laser irradiances (a type 304 stainless-steel sample containing 0.32% Mo was used and the detection wavelength was 550.6 nm)

<table>
<thead>
<tr>
<th>Sample finish</th>
<th>7 GW cm(^{-2})</th>
<th>16 GW cm(^{-2})</th>
<th>26 GW cm(^{-2})</th>
<th>57 GW cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 40</td>
<td>1430</td>
<td>490</td>
<td>480</td>
<td>625</td>
</tr>
<tr>
<td>No. 60</td>
<td>1730</td>
<td>475</td>
<td>325</td>
<td>460</td>
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<tr>
<td>No. 120</td>
<td>860</td>
<td>225</td>
<td>385</td>
<td>460</td>
</tr>
<tr>
<td>No. 1000</td>
<td>980</td>
<td>324</td>
<td>344</td>
<td>426</td>
</tr>
</tbody>
</table>

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