Laser-induced breakdown spectrometry has been evaluated at high temperatures for stainless steel samples. A Q-switched Nd:YAG laser operating at 1064 nm was used to create a microplasma on an AISI 304L stainless steel sample placed inside a laboratory oven. The steel sample was 51.3 cm away from the focusing lens. The temperature of the samples ranged from 25 to 1200 °C. The plasma light was collected by means of a fiber optic bundle, spectrally resolved and then detected by a CCD camera. The effects of sample temperature in the formation of a laser-induced plasma have been studied in terms of its spectral features as well as the morphology of the ablated craters in air at atmospheric pressure. A noticeable dependence of signal emission intensity on sample temperature has been found. Depth profiling of stainless steel samples for several temperature conditions was performed. Results have revealed changes in the superficial composition at temperatures above 600 °C due to the formation of a slag layer of variable thickness, mainly composed of chromium, iron and manganese oxides.

Introduction
The need for increased productivity in many industrial areas drives the development of analytical methods capable of performing in-process measurements in real time. Although the possibility of obtaining analytical information able to provide feedback on a given process in real time is not a new concept, the increasing number of advanced instrument components results in new techniques, allowing the chemist to tackle traditionally unresolved problems or to design more adequate approaches for those previously solved. Production and transformation of steel comprise a high-value industry in which the in-process availability of analytical results is of critical importance. Of particular concern is the casting of steel, a process for which monitoring has been extensively sought. Difficulties arise both from the slag layer formed over the molten pool and from the high temperatures in the furnace and in the surroundings. In principle, any new technique should be able to perform non-contact measurements in the molten steel, generating results in a short period of time. Owing to technical limitations, this requirement has been traditionally satisfied by extracting a representative volume of molten material, which was subsequently left to cool down in order to be sent to the laboratory, where adequate techniques were then used to find the composition. Turn around times of 30 min are typical and induce notable delays in the overall production process.

Some methods of in situ analysis have been proposed with more or less success. Many of them are cited by Dulski.1 Attempts have been made by some researchers2,3 to generate an aerosol powder from a melt either using a probe containing an atomization die or using laser ablation to evaporate a sample from the molten metal. Thereafter, the removed material is transported by an inert gas line to an inductively-coupled plasma torch remote from the probe, where the metal powder is finally analyzed. However, the transport of the aerosol may induce subtle errors in the results due to selective evaporation of the volatile elements in the particles.

Laser induced breakdown spectrometry exhibits a great advantage over other surface techniques in the ability to perform analysis at a distance since the plasma is formed by optical radiation. This property confers on LIBS a capability for field-based and real-time analysis in industrial environments.4,5 Several papers in the literature deal with this topic. Rapid analysis of metals at a distance between 0.5 and 2.4 m from the focusing lens and light collection optics using a fiber optic cable to collect the laser plasma light has been reported.6 A portable instrument based on LIBS has been developed for the detection of metal contaminants on different surfaces.7 LIBS applications to the steel analysis have been also reported.8-10 Recently, the effects of stainless steel sample surface finishing on the emission intensity and on the analytical figures of merit have been studied.11 Saturation effects in the laser ablation of stainless steel in air at atmospheric pressure have been also described.12 Depth profiles of coated steel at a nanometric scale have been developed using laser ablation with a flat energy profile beam.13 Lorenzen et al.14 used LIBS directly on the liquid steel through a hole made in the wall of the furnace. Some experimental difficulties associated with this set-up involve the use of high-pressure Ar at 800 °C, used to avoid both the molten steel passing through the hole and the solidification of the steel due to the negative temperature gradient outwards. Moreover, the high temperatures in the neighborhood of the oven force the operator to use a water stream to protect the laser head.

In this paper, LIBS is evaluated for real-time measurements in solidified steel samples at high temperatures. The advantage of this approach is that it relies on the simplicity of the experimental arrangement, which can be similar to that used on standard LIBS experiments. Although the samples are still at high temperatures, laser focussing and collection of plasma light may safely be carried out by using relatively long optical paths. In order to establish the influence of temperature on laser-induced breakdown emission, studies have been carried out at temperatures ranging from 25 to 1200 °C. The effects of sample temperature on plasma formation have been studied in terms of its spectral features as well as the morphology of the ablated crater. Depth profiling of stainless steel samples under several temperature conditions has been performed in order to correlate the extension of the oxide layer to the temperature.
Experimental

A schematic diagram of the experimental set-up used for this study is shown in Fig. 1. Stainless steel samples were placed inside a laboratory oven set at different temperatures, ranging from 25 to 1200°C. After thermal equilibrium had been reached (15 min) for each temperature, the door of the oven was opened for the duration of the acquisition time (60 s). Samples were irradiated using a Q-switched Nd : YAG laser (Big Sky Laser, Bozeman, MO, USA, Model Ultra CFR, pulse width 8 ns) operating at 1064 nm. A specific optical arrangement had to be employed to make it possible to perform the LIBS experiments while avoiding the high temperatures in the surroundings of the sample receptacle. The beam was diverged by means of a planoconcave lens (BK7, diameter = 6 mm, f = −15 mm) and then focused at normal incidence on the sample surface with a biconvex lens (BK7, diameter = 38 mm, f = 12.5 mm). The spacing between both lenses was 15 cm, which resulted in an actual working distance of 51.5 cm. The frequency of pulsing was fixed at 5 Hz for the overall experiments and the pulse energy was measured with a pyroelectric joulemeter (Gentec, Quebec, Canada, Model ED-200, nominal sensitivity 9.86 V J⁻¹) coupled with a digital oscilloscope. A pulse energy of 20 mJ beyond the focusing lens was measured. The optical arrangement outlined, together the multimode transverse distribution of the laser beam, gave rise to spot diameters of the order of 400 μm. On the other hand, the customary need for a tight adjustment of the working distance was overcome to a great extent. Laser-ablated plasma emission was collected on a fiber optic bundle (19 fused silica fibers, 100 μm core diameter, round to in-line configuration, 3.5 m long) using a planoconvex lens (fused silica, diameter = 25.4 mm, f = 30 mm) placed 50 cm away from the sample. The output of the bundle (in-line arrangement) was coupled to the entrance slit of a spectrograph (Oriel, Stratford, CT, USA, Model MS125, f = 3.9, entrance slit = 50 μm, grating 3600 grooves mm⁻¹) using two planoconvex lenses (fused silica, diameter = 10 mm) matching the numerical apertures of both the bundle and the spectrograph. The dispersed light was detected using a two-dimensional charge-coupled device (CCD) detector (Andor Technology, Belfast, UK, model IS401, 1024 (h) × 128 (v) elements). In this configuration, each spectrum covers approximately 38 nm. Operation of the detector was controlled by Instaspec software (Andor Technology). Laser Q-switch synchro signal was used for the synchronisation between the incident laser beam and the camera read-out. Although our CCD does not allow delay generation, the constant delay between the laser shot and the acquisition due to the CCD electronics was estimated to be ~ 500 ns. The acquisition time was set to the minimum available (17 ms) for all the experiments. Signal emission was corrected by subtracting the dark signal of the detector, which was separately measured for the same exposure time and oven temperature. Each pulse was stored as a file containing spectral information. Calibration of the detector system was carried out by using spectral lines emitted from laser-induced plasma of reference titanium.

A sample holder made of stainless steel was designed and manufactured in our laboratory. This sample holder allowed simple exchange of the samples in the vicinity of the oven as well as repetitive positioning and refreshing at a fixed distance from the focusing lens. Stainless steel sheets, Type AISI 304L (8.12% Ni, 18.13% Cr, 0.31% Mo, 1.23% Mn), with a nominal thickness of 500 μm, were used. Samples were supplied by Acerinox S.A. (Los Barrios, Cadiz, Spain), with a rectangular shape of approximately 2.5 cm × 2 cm.

Results and discussion

Spectral analysis and emission intensity

To evaluate the applicability of the technique for spectral measurements in stainless steels at high temperature a spectral window centered at 355 nm was chosen because at that wavelength Fe, Ni, Cr and Mn emission lines could be measured simultaneously. Fig. 2 shows a LIBS spectrum of a stainless steel sample obtained by accumulating 25 laser shots in the same location at room temperature and atmospheric pressure.

Fig. 1 Schematic diagram of the laser ablation experiment.

Fig. 2 LIB emission spectrum of a 304L stainless steel sample obtained by accumulating 25 laser shots in the same location at room temperature and atmospheric pressure.
Table 1 List of the main emission lines identified in Fig. 2

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Wavelength/nm</th>
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<tbody>
<tr>
<td>A</td>
<td>Cr (II) 340.87</td>
</tr>
<tr>
<td>B</td>
<td>Ni (I) 341.47</td>
</tr>
<tr>
<td>C</td>
<td>Cr (II) 342.27</td>
</tr>
<tr>
<td>D</td>
<td>Ni (I) 343.35</td>
</tr>
<tr>
<td>E</td>
<td>Ni (I) 349.29</td>
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<tr>
<td>F</td>
<td>Ni (I) 352.45</td>
</tr>
<tr>
<td>G</td>
<td>Mn (I) 353.21</td>
</tr>
<tr>
<td>H</td>
<td>Mn (I) 354.78</td>
</tr>
<tr>
<td>I</td>
<td>Cr (I) 357.87</td>
</tr>
<tr>
<td>J</td>
<td>Fe (I) 358.12</td>
</tr>
<tr>
<td>K</td>
<td>Cr (I) 359.35</td>
</tr>
<tr>
<td>L</td>
<td>Fe (I) 363.14</td>
</tr>
<tr>
<td>M</td>
<td>Fe (I) 373.49</td>
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</tbody>
</table>

304L type stainless steel sample, where contributions for the major steel components are present. This spectrum was generated by accumulating 25 laser shots in the same sample position at room temperature. The relative standard deviation for the spectrum in Fig. 2 was calculated to be about 14% for major elements. The detection system used in the experiment did not provide the possibility of carrying out a time-resolved analysis. Spectra were recorded with a fixed delay time given by the CCD camera electronics of about 500 ns, which is insufficient to eliminate totally the intense continuum background produced by the plasma formation. Consequently, the spectrum appears with an intense background close to 25% of the full signal. The most important peaks were identified and are summarized in Table 1. The emission lines of Ni (I) at 341.47 nm, Cr (I) at 357.87 nm, Fe (I) at 373.49 nm and Mn (I) at 354.78 nm were selected for the overall spectral study.

The emission intensity, the crater size and the amount of sample ablated by the laser can be affected by the conditions to which the sample is subjected. In our case, the plasma was generated in air at atmospheric pressure and only the influence of sample temperature was investigated. The net signal intensity of the elements of interest as a function of sample temperature was calculated as shown in the text. Solid line corresponds to experimentally determined ablated mass and dotted line corresponds to the theoretically calculated ablated mass.

![Fig. 3 Effect of sample temperature on emission lines intensity of: (■) Ni (I) 341.47 nm; (●) Cr (I) 357.87 nm; (♦) Fe (I) 373.49 nm; and (▲) Mn 354.78 nm. Error bars correspond to the standard deviation of three averaged values.](Image 314x166 to 538x302)

![Fig. 4 Theoretical and experimental ablated mass after 300 accumulative laser shots versus sample temperature. These values were calculated as shown in the text. Solid line corresponds to experimentally determined ablated mass and dotted line corresponds to the theoretically calculated ablated mass.](Image 53x157 to 285x301)

Effect of sample temperature on emission lines intensity of: (■) Ni (I) 341.47 nm; (●) Cr (I) 357.87 nm; (♦) Fe (I) 373.49 nm; and (▲) Mn 354.78 nm. Error bars correspond to the standard deviation of three averaged values.

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contribute to a better laser beam–sample surface coupling and, therefore, to a greater removal of material in the ablation process and to a higher spectral intensity.

**Depth profiles**

The steel sample is analyzed inside the oven in air at atmospheric pressure. The presence of oxygen and other oxidizing gases cause the steel surface to oxidize at such high temperatures, with further carbon losses resulting in the formation of a thin layer composed of a mixture of iron, manganese and chromium oxides. This is known as a decarburization phenomenon and is well described elsewhere.19

Fig. 5 shows two spectra corresponding to the first laser shot on the sample surface and to the 200th laser shot inside the matrix. Both spectra were obtained at 1200 °C. As is shown, the emission lines corresponding to Cr (I) 357.87 nm and Mn (I) 354.78 nm are stronger in the surface layer and decrease when the laser penetrates into the bulk sample, while the Ni (I) 341.2121 nm emission signal is lower in the sample surface and higher for the inner pulses. This fact corroborates the formation of a superficial layer composed of a mixture of chromium and manganese oxides.

Oxidation processes in stainless steel occur at approximately 600 °C. A morphological study of the craters formed after 250 laser shots at (a) 25 °C, (b) 600 °C and (c) 1000 °C is shown in the SEM micrographs of Fig. 6. As can be observed, the crater formed at room temperature (a) shows a flat bottom and the absence of metallic oxides covering the surface. The crater formed at 600 °C shows a longer heat affected area and an incipient oxide layer covering the crater base. The crater formed at 1000 °C shows a crater totally covered by a rough oxide layer, which impedes observation of the bottom of the crater. Examination of craters formed at 1200 °C was not possible because of the slag layer formed on the sample surface. Notice that all of the craters have similar areas.

The composition and thickness of the oxide layer depends on multiple factors, such as the surrounding atmosphere during the heat exposure, the steel composition, the thermal history of the sample and the roughness of the surface. In order to study the extent of the oxide layer, normalized depth profiles for Cr, Ni and Mn were measured at 600 and 1200 °C. Fig. 7 shows the results. Depth profiles obtained at 600 °C show a weak increase of chromium signal during the first pulses, reaching almost immediately a constant signal level. On the other hand, the Ni signal shows the reverse behavior, decreasing initially and then reaching a stable level. Mn signal emission is constant in the oxide layer, which impedes observation of the bottom of the crater. Examination of craters formed at 1200 °C was not possible because of the slag layer formed on the sample surface. Notice that all of the craters have similar areas.

The morphological study of the craters formed after 250 laser shots at sample temperature of (a) room temperature, (b) 600 °C and (c) 1000 °C.

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**Fig. 5** LIB spectra corresponding to the first laser shot on the sample surface (top) and the 200th laser shot, obtained at a temperature of 1200 °C (bottom). The variations in the emission intensity of the main components indicate the compositional changes between the superficial layer and the stainless steel matrix.

**Fig. 6** SEM micrographs showing the morphological features of craters obtained after 250 laser shots at sample temperature of (a) room temperature, (b) 600 °C and (c) 1000 °C.

**Fig. 7** Depth profiles of Cr (I) 357.87 nm, Ni (I) 341.47 nm and Mn (I) 354.78 nm obtained at (a) 600 °C and (b) 1200 °C showing the extent of the mixed metallic oxides layer generated by the temperature effect on the sample surface. The signals were normalized to the addition of the intensities of the major constituents of the stainless steel (Fe+Cr).
sample depth range measured. The small compositional changes observed during the first pulses could be attributed to the passivation layer, which is composed of mixed oxides of chromium and iron. This layer contributes to giving the steel its mechanical properties such as brightness, hardness and corrosion resistance. However, the profiles obtained at 1200 °C show significant changes in the composition, with chromium and manganese enrichment in the superficial region and a lower nickel content. When the laser beam ablates the superficial oxidation layer and reaches the stainless steel matrix the emission signals become constant.

Conclusions
Laser-induced breakdown has been tested as a rapid method to observe the changes produced in stainless steel exposed to high temperatures at atmospheric pressure. The simplicity of the method allows a real-time analysis of blooms that have just finished and are about to leave the converters, which are in a temperature condition close to the melting point, without needing anything more than the use of an adequate optic and a laser system that is more or less portable. The possibility of performing a remote analysis confers on the LIBS technique the capability of being applied for quality control purposes on an industrial scale.

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