Large area mapping of non-metallic inclusions in stainless steel by an automated system based on laser ablation

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Abstract

Large area compositional mapping (>6 mm²) using a fast and automated system based on laser-induced plasma spectrometry is presented. The second harmonic of a flat top Nd:YAG laser beam was used to generate a microline plasma on the sample surface. The emitted light from the microline plasma was imaged onto the entrance slit of an imaging spectrograph and was detected by an intensified charge-coupled device to generate a spatially and spectrally resolved data set. Individual LIPS images, each measuring roughly 2500x2500 μm with spatial resolution of 50 μm between adjacent craters and 4.8 μm along the microline are presented. These large area maps were acquired in less than 1 min. Steel samples containing MnS and TiN inclusions were chosen as the most adequate for this study. The results are presented for the characterization of inclusionary material in stainless steel products in terms of morphology, distribution and abundance.

Keywords: Laser-induced plasma spectrometry; Stainless steel; Materials characterization; Large area mapping

1. Introduction

Stainless steel plays an important role in all emerging technologies. However, steel melt usually contains insoluble components in form of particles which appear as inclusions in the solid material. The main part of these impurities in steel (oxides, sulfides and nitrides) are formed by reactions of elements dissolved in the steel (endogeneous inclusions) or by contamination of the steel by the slag or the refractory materials (exogeneous inclusions) and are the so-called non-metallic inclusions [1–3]. The dimension of these inclusions is within a range of 0.1–100 μm. Although the presence of inclusions with well defined composition (in machinable steels especially) can introduce beneficial effects [4], in general for most steel grades the presence of inclusions can cause surface defects or deteriorate the mechanical properties (castability, deformability and brittle fracture, hardness, corrosion, fatigue strength etc.) [5]. The detrimental effects of inclusions not only depend on their sizes, but also on their ductility and fracture behavior during the rolling process. Of all the inclusions, the hard and brittle inclusions produce the most harmful consequence on the properties of steels. For this reason, the characterization of non-metallic inclusions in steel in terms of number, size, shape, chemical composition and spatial distribution is an essential requirement on metallurgical process technology in order to determine their origin and to control their formation, and to produce a final product of high quality. Methodologies employed to assess steel cleanliness depend on the size of the impurities, the time available for assessment (on-line or off-line), the degree of detail needed and the state of the steel, e.g. liquid or solidified steel [6]. However, most of these techniques are time consuming, not proper for routine process control and have limited applicability for steel cleanliness assessment of large sample areas. Based on these requirements, the development of fast, reliable and accurate methods for the characterization of inclusions during the production process becomes a need.

At present, laser induced plasma spectrometry (LIPS) has become an important tool in the steel industry allowing solving a large number of analytical problems.
Rapid in situ analysis of steel products without sample preparation and micro and macromapping over several centimeters by scanning the optical system or moving the sample on a translation stage are interesting capabilities of LIPS. This technique has been applied successfully in bulk [7–11] and quantitative analysis [12–14], analysis of liquid [15,16] and high temperature steel [17], surface topography studies [18,19], depth profiling of coated steel [20–24], automation [25,26] and routine industrial applications for quality assessment [27] and remote analysis [17,28–31]. For these applications, numerous experimental approaches have been proposed to achieve better analytical performance and to improve surface sensitivity, lateral resolution, detection power, analysis time and precision in materials analysis.

Advancement in the investigations has resulted in the development of a new approach for fast generation of compositional maps from large areas. The basic idea relies on focusing the laser beam with a cylindrical lens to produce a long and narrow microline plasma in a direction parallel to the spectrometer entrance slit and to exploit both the multielemental and the spatial resolving capabilities of charge-coupled device (CCD) detectors. This focusing and acquisition method provides several advantages compared to conventional LIP spectrometry, including the improvement of data collection speed due to the reduction of laser pulse number necessary for generating LIPS chemical maps. This work discusses how large area compositional mapping using a fast and automated line-focused LIPS system can be successfully used to provide qualitative and quantitative information of elemental distribution of inclusionary material in stainless steel products. Two sampling procedures for obtaining chemical maps of good quality have been evaluated. Large area chemical maps of manganese and titanium in stainless steel products are presented.

2. Experimental

2.1. Instrumentation

The LIPS experimental set-up employed in this study has been previously reported [32–35] and therefore, only some details are given here. The second harmonic (532 nm) of a pulsed Q-Switched Nd:YAG laser with top hat energy profile (Spectron, model SL 284, pulse width 5 ns, beam diameter 4 mm) was used to ablate the sample in air at atmospheric pressure. The output energy of the laser beam was 52 mJ per pulse at a repetition rate of 2 Hz, which is the maximum allowed by the detector and the frame grabber used. The beam was three-fold expanded by an optical system consisting of two lenses, a 25-mm focal length concave lens and a 75-mm focal length convex lens. The beam was then focused to a line by a cylindrical lens with a focal length of 50 mm onto the sample surface. With this optical configuration, the dimensions of the obtained microline crater were of 1400 μm in length×48 μm in width, however, it should be noted that only 2500 μm of the cited length was analyzed. A planoconvex quartz lens with a focal length of 100 mm was used to image the microline plasma onto the entrance slit of a 0.5-m focal length Czerny–Turner imaging spectrograph (Chromex, model 500 IS, f/# 8, fitted with indexable gratings of 300, 1200 and 2400 grooves mm⁻¹). Spectral emission was detected by an intensified solid-state two-dimensional charge-coupled device (ICCD, Stanford Computer Optics, model 4Quik 05) with 768×512 pixels, each 7.8×8.7 μm². This configuration provides a spectral window of ~15 nm and a spectral resolution of 0.02 nm pixel⁻¹, using an entrance slit width of 20 μm and the grating of 2400 grooves mm⁻¹. The CCD active area was 6×4.4 mm². Operation of the detector was controlled by a personal computer with 4Spec software. For monitoring MnS and TiN inclusions in steel, spectral windows centered at 476.0 nm and 388.3 nm, respectively, were used. However, it was assumed that detection by LIPS of Mn or Ti indicated the presence of MnS or TiN inclusions in steel. Delay time of 500 ns and integration time of 1000 ns were employed in these experiments. For data acquisition, the CCD system was triggered by an output TTL pulse from the laser Q-switch system. The sample was placed on two crossed motorized stages (Physik Instrumente). The stages were computer controlled which allowed exact movement of the sample in both x and y directions. Laser trigger was controlled externally by a digital delay/pulse generator (Stanford Research System Model DG535). To automate acquisition of large chemical map data a laboratory software was developed which allowed the exact synchronization between the motorized stage movement and laser firing. Communication between devices was carried out by an IEEE 488 general purpose interface bus (GPIB). Stored data were treated by a lab developed software, which reduced the volume of acquired data to a XY matrix for each element of interest. For compositional mapping, these matrices were plotted by means of commercial imaging analysis data software. The area fraction occupied by inclusions regarding the total map area was calculated with a commercial image analysis software package (Visilog 5.2).

2.2. Samples

In order to study the effect of stainless steel manufacturing on the morphology, size and distribution of inclusionary material, three steel products (cold rolled sheet, bar and wire rod) containing each a single type of inclusion were prepared and provided by Acerinox, S.A. AISI 303, AISI 315 and AISI 319 steel classes have been chosen since they contain a unique kind of
Table 1
Chemical composition of AISI 303, AISI 315 and AISI 319 stainless steel materials

<table>
<thead>
<tr>
<th>Type of inclusion</th>
<th>Type of material</th>
<th>Chemical composition (wt.%)&lt;sup&gt;*&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Si</td>
</tr>
<tr>
<td>MnS</td>
<td>AISI 303</td>
<td>0.25</td>
</tr>
<tr>
<td>TiN</td>
<td>AISI 315</td>
<td>0.46</td>
</tr>
<tr>
<td>TiN</td>
<td>AISI 319</td>
<td>0.65</td>
</tr>
</tbody>
</table>

<sup>*</sup> These values were measured by X-ray fluorescence spectrometry in Acerinox S.A.

inclusion, manganese sulfide in the case of AISI 303, and titanium nitride in AISI 315 and AISI 319 steel. Samples were characterized by scanning electron microscopy with a microanalysis EDX system and by optical microscopy. The chemical composition of these stainless steel grades measured by X-ray fluorescence spectrometry is shown in Table 1.

To study the spatial distribution inclusionary material, steel cold rolled sheets 40 × 30 mm² with a thickness of 6 mm were analyzed. The procedure for obtaining steel bar and steel wire rod samples was almost similar in both cases. Samples of 30–40 mm length, with diameters of 17–24 mm for steel bars and 10 mm for steel wire rods, were cut by means of a mechanical sawing. Then, the steel pieces were embedded in resin in order to obtain a laboratory sample. In the case of bars before this last step the steel pieces were cut lengthwise. Finally, the steel samples were polished with a 1000 grit sandpaper to produce smoother surface, washed several times with tap water and dried and their metallurgical structures were developed.

According to their behavior during rolling, inclusions can be divided into two broad classes: non-deformable inclusions and deformable inclusions. The typical appearance of soft MnS inclusions in manufactured AISI 303 steels is presented in Fig. 1. As shown in steel cold rolled sheet the manganese sulfide inclusions are mainly globular. In contrast, the shape of these inclusions in bar and wire rod samples is narrower and longer than in cold rolled sheet since such inclusions exhibit high ductility at steel rolling temperature and deform and elongate as the steel is rolled. In the case of AISI 315 (for cold rolled sheet) and AISI 319 steel (for steel bar and steel wire rod), the distribution and aspect of TiN inclusions are similar for the three products and maintain their original shape as the steel is deformed. This fact joins to the hard and brittle nature of TiN species resulting in a breaking of inclusions during the manufacturing process and consequently the shape of TiN inclusions is non-uniform. Fig. 2 shows some details of this type of inclusions in AISI 315 and AISI 319 steels.

3. Results and discussion

3.1. Large area compositional LIPS maps

Large area microline LIPS maps (defined in this work as LIPS maps of area approx. 6 mm² in size) were performed to obtain the characterization and quantification of inclusionary material during processing of steel.
Fig. 2. Photographs of TiN inclusions in manufactured AISI 315 and AISI 319 steels (a) cold rolled sheet, (b) bar and (c) wire rod, obtained by optical microscopy.

The objective of making such large maps is to obtain whole information of the surface characteristics of the sample. As the distribution of inclusions in steel is heterogeneous, restricting the analysis to small areas could lead to results non-representative of the sample. For this reason, chemical images were constructed using the microline imaging arrangement described [32–35] which permits to obtain spectral and spatial information simultaneously of a large surface region from each laser pulse. With this focusing configuration, long and narrow craters were produced on the sample surface and each pixel of the CCD detector along the spatial direction corresponds to a particular position on the microline focus (the sampled area).

The greatest challenge in making large area microline LIPS maps is to obtain images with high lateral resolution and good quality. This can be achieved by combining the net intensity of an element along the microline plasma obtained from each adjacent position on the sample, with their spatial coordinates. With the purpose of generating large chemical images of good quality, a study of the influence of sampling procedure by using the microline LIPS approach was carried out with both steel bar and steel wire rod samples. The two sampling protocols described in Fig. 3 were evaluated. Chemical maps of manufactured AISI 303 steel were constructed by focusing the microline laser beam on the sample surface at perpendicular and parallel directions to the rolling of steel. Two large LIPS images of MnS inclusions corresponding to two different sample areas of the same size (2500×2500 μm²) obtained with both methods in a wire rod sample are compared in Fig. 4. Chemical maps were conducted with a single laser shot per position and were realized from 50 single laser shots with a lateral displacement of 50 μm between adjacent microline craters. The total analysis time for generating the chemical maps including time intervals for deceleration and acceleration of the X stage was 55 s. In this experiment, the stage was moved and stopped for each X position. The Y direction in the compositional maps corresponds to the spatial resolution along the microline, which depends on the number of pixels of CCD detector (512), the pixel size (8.7 μm), the optical magnification and plasma expansion. If all these parameters are taken in account, it was estimated that each pixel represents ≈4.8 μm of the microline length [35]. In the chemical images of Fig. 4, differences in elemental distribution are presented in binary code to remark the location of inclusions. The binary code was established by using an image processing software, which assigns the black color to any net intensity of Mn, which is three times higher than the net intensity of the element in the matrix. Thus, dark zones indicate the presence of MnS inclusions in steel, while white areas correspond to the steel matrix. This criterion was used for generating further chemical images. The results demonstrate that chemical images obtained by orientating the microline laser beam parallel to the rolling direction represent more accurately the dimension and shape of the MnS inclusions in AISI 303 steel than those obtained with the second sampling
Fig. 3. Description of sampling procedures evaluated for characterization of inclusionary material in steel. A detail of the microline craters generated in an AISI 303 steel bar (a) perpendicular to the rolling direction and (b) parallel to the rolling direction showing elongated MnS inclusions in steel is also presented.

Fig. 4. Comparison of two large LIPS maps of MnS inclusions in AISI 303 steel wire rod obtained by both sampling protocols: (a) microline plasma perpendicular to the rolling direction and (b) microline plasma parallel to the rolling direction. Plotted data correspond to intensity distribution of Mn (I) 482.352 nm emission line and were acquired by single laser shot on each position. The mapped area was 2500×2500 μm². Experimental conditions: laser pulse energy 52 mJ, delay time 500 ns and integration time 1000 ns.
Fig. 5. Microline LIPS images corresponding to the spatial distribution of MnS inclusions in manufactured AISI 303 steels: (a) cold rolled sheet, (b) steel bar and (c) wire rod shown in Fig. 1. Net intensity of the Mn (I) 482.352 nm line is presented in binary code. The mapped area was 2400×2500 μm². Other experimental conditions as in Fig. 4.

procedure (perpendicular to the rolling direction). This fact can be attributed to the better spatial resolution obtained along the microline crater (approx. 5 μm) than that obtained between consecutive microlines (50 μm).

The performance of the automated microline approach for large compositional mapping was tested by studying the deformation of inclusions in steel products during rolling. Two types of non-metallic inclusions found in manufactured steel including a soft one as MnS and hard one as TiN were characterized. These specimens were chosen due to present different deformability features.

A comparison of the large LIPS images corresponding to the distribution of MnS inclusions in AISI 303 and TiN inclusions in AISI 315 and AISI 319 steel products is plotted in Figs. 5 and 6, respectively. These distribution maps were accomplished from single laser shots per position after cleaning the surface with one laser shot. A total area of 2400×2500 μm² was sampled in a sequence of 49 positions separated by 50 μm. The
Fig. 6. LIPS maps of TiN inclusions in manufactured AISI 315 and AISI 319 steels: (a) cold rolled sheet, (b) steel bar and (c) wire rod shown in Fig. 2 using microline imaging approach. Plotted data correspond to net intensity of Ti (I) 395.821 nm emission line. The mapped area was 2400×2500 μm². Other experimental conditions as in Fig. 4.

Large maps required a total acquisition time of 54 s. These large area maps exhibit whole information of different behavior of inclusions in stainless steel products as manifested in the differences in shape and abundance of inclusionary material and indicate the good correspondence between the chemical maps obtained by LIPS and the results observed by optical microscopy. As shown in the case of AISI 303, the distribution and appearance of MnS inclusion change during the processing of the steel and these differences are more acute in bar and wire rod samples, where the inclusions present an elongated shape and are more abundant. However, large area composition maps of TiN inclusions in AISI 315 and AISI 319 steel samples demonstrated that the analyzed inclusions exhibit a similar distribution in the three steel products and their dispersion and aspect differ of MnS inclusions in AISI 303 steel. These maps indicate the different behavior of both inclusionary materials in steel during the manufacturing process and show clearly that the distribution of
Table 2
Percentage of MnS and TiN inclusions in steel product (cold rolled sheet, steel bar and wire rod)

<table>
<thead>
<tr>
<th>Type of inclusion</th>
<th>Type of material</th>
<th>Inclusionary material content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cold rolled sheet</td>
</tr>
<tr>
<td>MnS</td>
<td>AISI 303</td>
<td>1.4</td>
</tr>
<tr>
<td>TiN</td>
<td>AISI 315</td>
<td>1.3</td>
</tr>
<tr>
<td>TiN</td>
<td>AISI 319</td>
<td>–</td>
</tr>
</tbody>
</table>

Data were estimated from LIPS maps of Figs. 5 and 6, respectively. *The percentage represents the area fraction occupied by inclusions.

3.2. Quantification of MnS and TiN inclusions content (area fraction) in stainless steel

Image processing of the large area compositional maps enable extraction of quantitative information of inclusionary material. Each position in the map has its own compositional value defined by its binary code. The inclusion content present in the three steel products has been calculated. The resulting data expressed as the percentage area fraction occupied by MnS and TiN inclusions in the total area analyzed (2400×2500 μm²) from the large maps of Figs. 5 and 6 are summarized in Table 2. Similar values were obtained when other zones of the samples were analyzed. The percentage of inclusionary material in AISI 303 varied in the range of 1.0–1.4%, 17.6–25.0% and 9.8–11.6% for cold rolled sheet, bar and wire rod, respectively. In the case of AISI 315 and AISI 319 steels the content of TiN inclusions is similar for the three steel products and varied in the range of 1.1–1.3%, 0.6–1.4% and 1.1–2.3%, respectively. The results from Table 2 indicate that the abundance of MnS inclusions in surface varies considerably from sample-to-sample and reaches a maximum value of ca. 25% for the steel bar. However, only 11.6% and 1.4% of the sampled area contain inclusionary material for wire rod and for cold rolled sheet, respectively. In the case of AISI 315 and AISI 319 steels, the content of TiN inclusions is similar for the three steel products (ca. 1.2%), significantly lower than those observed for AISI 303 steel samples. However, it should be noted than the percentage area fraction occupied by the inclusionary material in steel products has been calculated assuming a lateral resolution of 50 μm, which is defined by the crater width. In this sense, the values in Table 2 could be over-estimated, mostly when inclusions much smaller than 50 μm are present in the analyzed surface.

4. Conclusions

Large area compositional mapping using an automated system based on laser ablation has been employed to characterize and quantify inclusionary material in process steel samples. High quality large area compositional LIPS maps with good lateral resolution (50 μm between adjacent microlines and 4.8 μm along the microline) of the steel products presenting two types of inclusions have been performed. The maps, which cover areas of approximately 6 mm², were acquired in less than 1 min and provide information on the morphology, and distribution of inclusions during rolling of stainless steel. By applying image processing techniques to the maps, the percentage of area occupied by a single inclusion type in steel can be determined. The results indicate that the automated microline imaging LIPS technique allows the steel manufacturers to obtain a complete overview of the quality of their products. This method applied to different steel grades provides crucial information on steel cleanliness. This fact is especially outstanding when the characterization of large areas is required.

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References


