Synthetic Samples Preparation to Identify Al₂O₃ Particles in Steel by Laser Ablation ICP Mass Spectrometry

Aurora G. COEDO, Teresa DORADO, Isabel PADILLA and Ruben USERO

Centro Nacional de Investigaciones Metalúrgicas (CSIC), Gregorio del Amo 8, 28040 Madrid, Spain.
E-mail: coedo@cenim.csic.es

(Received on October 24, 2007; accepted on December 17, 2007)

The analytical technique based on laser ablation of the sample followed by Argon plasma excitation and mass spectrometry detection (LA-ICP-MS), was used to identify Al₂O₃ inclusions size and distribution on surface in iron samples. The main aim of the work is to evaluate different approaches for synthetic iron matrix samples preparation. Samples were made in four formats, from pure Fe powder (<25 μm) and Aluminum oxide with different ranges of particle size up to 100 μm: 1) metal samples, by melting in an induction furnace; 2) compressed pellets, by pressing at 50 ton cm⁻²; 3) sintered compact samples, by sintering (1050°C) and rolling (950°C) the compressed pellets; 4) beads (glass samples), by alkaline melting with lithium metaborate and sodium carbonate. The study includes the optimization of operating parameters; the evaluation of differences in ablation yield, by comparing the Fe signal intensities; and, the identification of Al₂O₃ particles in heterogeneous zones, by monitoring the Al time resolved signals. The optimized laser operating parameters were: laser pulse energy of 2.5 mJ pulse⁻¹, repetition rate of 10 Hz, and scanning speed of 3 μm s⁻¹. A good correlation between Al intensity peaks and mean size of particles was found for all types of produced samples, allowing estimate the size and the distribution of the Al₂O₃ particles in the sample surface.

KEY WORDS: laser ablation inductively coupled plasma mass spectrometry; Al₂O₃ inclusions; synthetic iron matrix samples.

1. Introduction

There is a clear need for microanalysis techniques with high sensitivity and good spatial resolution, since trace elements present in the form of segregates may be of considerable importance for material properties. Non-metallic inclusions of many different types are normally undesired components in steels, caused by the production process which unfortunately does not quantitative extract them with the slag. The mechanical properties of steels are controlled to a large degree by the volume fraction, size, distribution, composition and morphology of inclusions and precipitates, which act as stress raisers. Focusing on Low Carbon Al-Killed steel (LCAK steel), Al₂O₃ inclusions can generate many defects in the steel product.¹ The mentioned segregations will change in size from nanometers up to millimeters. Reliable reference samples will be of paramount importance for the characterization of segregations, giving the size and distribution.

LA-ICP-MS was widely adopted in a variety of research areas of materials science.² It was successfully applied to the direct analysis of steel composition³–⁶ and to the depth profile of different coatings on steel substrate.⁷–¹⁰ The real advantage, however, is the ability of the technique to provide information on spatial distribution in all three dimensions, dealing with inhomogeneous samples. The changing transient signals can provide information about the presence of heterogeneities, although the time delay in the sample transport system (including the sample cell volume) is a limiting factor, causing signal mixing during the transportation of the ablated material, and preventing accurate identification of the exact origin of every signal. An evaluation of the principles and capabilities of the most common spatially resolved analytical technique (XPS, AES, SIMS, SNMS, GD-ÖES, GD-MS, SEM-EDX, LA-ICP-MS) was reviewed by Bleiner et al.¹¹ Some of them (XPS, AES, SIMS, SNMS) offer nanometers depth resolution, but no more than qualitative trends in the chemical features of a sample. In recent years there have been an increasing number of applications of Laser Ablation-ICP-MS in the field of the spatial distribution of trace elements in the bulk material. Its high detection sensitivity combined with good spatial measurement capability has been exploited in geological research, including the characterization of fluid inclusions.¹²,¹³ Dubuisson et al.¹⁴ have estimated the potential of the technique for steel cleanliness assessment through the analytical response for inclusion as a function of laser ablation parameters, by using both Gaussian and flat top beam intensities distribution profiles. Plotnikov et al.¹⁵ used the evolution of the parameters of single-shot response to reveal the true concentration profile of spatially inhomogeneous samples. Pisonero et al.¹⁰ have investigated the dis-
tribution of element impurities and their relationship to the different segregations coefficients in metallurgical-grade silicon. Nafisi et al.\textsuperscript{17} present a line scanning method, as a helpful tool to control segregations of \( \alpha \)-Al particles formed during solidification of hypo-eutectic Al–Si alloys; the results show a good agreement with those obtained from electron probe micro-analysis (EPMA). Karasev et al.\textsuperscript{18} have evaluated the potential of the technique with respect to the size measurement of one component and multi-component inclusions in metal and other materials; a new method of making samples with particles is described and results are compared with those by SEM and single-particle-optical sensing (SPOS) methods. In a previous report\textsuperscript{19} they found that LA-ICP-MS can be successfully applied to the analysis of total and insoluble contents of elements and composition of inclusions in metals in the range of particle diameter from 1–100 \( \mu \)m.

Nevertheless limitations of LA-ICP-MS are well known, namely elemental fractionation and a lack of certified reference materials for many types of samples. Calibration samples preparation is an essential stage in the analysis process. External calibration utilizing matrix matching is the most common method for LA-ICP-MS. Certified reference materials are commercially available for some types of solids matrices (glass, ceramic, cement, metals); unfortunately, such standards are often not available for a particular sample of interest, as it is the case for inclusions. “In-house” solid synthetic samples are often prepared to allow external calibration utilizing matrix matching in terms of sample composition because the ablation rate (quantity of mass ablated per laser pulse) varies with the sample matrix. Preparation of pelletized solids\textsuperscript{20,21} or fused beads\textsuperscript{22,23} are two common approaches to the generation of solid standards; nevertheless, these procedures are primarily for bulk analysis, as they usually eliminate the spatial integrity of the sample.

In the present work, different procedures to prepare iron samples with controlled \( \text{Al}_2\text{O}_3 \) particle sizes, in different ranges up to 100 \( \mu \)m, have been evaluated for the identification of \( \text{Al}_2\text{O}_3 \) inclusions in steel. The samples were prepared in four formats: 1) metal samples, by melting in an induction furnace; 2) pellets, by pressing at 50 ton cm\(^{-2}\); 2) sintered compacts samples, by sintering at 1050°C and rolling at 950°C, after pressing; 4) beads (glass samples), by alkaline melting with lithium metaborate and sodium carbonate. After optimization of the operating parameters, an evaluation of differences in ablation yield was made by comparing the Fe signal intensities; and, the identification of the \( \text{Al}_2\text{O}_3 \) particles in heterogeneous zones was carried out by monitoring the Al time resolved signals. The possibilities of the different sample preparation procedures were evaluated and compared.

2. Experimental
2.1. Instrumentation

Experiments were performed with a commercially available quadrupled (266 nm) nanosecond Nd:YAG laser with Q-switch (LSX-100, CETAC Technologies, Omaha, Nebraska, USA) coupled to an ICP quadrupole mass spectrometer (ELAN 6000, Perkin Elmer, Sciex, Ontario, Canada). The sampling cell of the laser module is mounted on an X–Y–Z translation stage under computer control; the translation stage provides X–Y positioning control for laser targeting on the sample and the Z-axis is used to focus the laser beam. The CCD camera microscope viewing system provides a mean of visual laser focusing and also for identification of the sample areas of interest. A built-in crosshair generator origins a gunsight-style cross, giving the user a visual indication for sample positioning at the laser impact point. Laser pulse energy was measured with a laser power/energy meter model EM 400 from Molectron Detector, Inc. (USA) (EM 400, Molectron Detector, Inc, USA) and the morphology of the craters were observed by scanning electron microscopy, SEM (DSM 400, Zeiss, Germany).

The operating conditions of both the laser ablation and the ICP-MS instruments are listed in Table 1. Instrument conditions were optimized for best time-resolved data acquisition.

2.2. Procedure

Experiments were performed using the following laser sampling modes: single point (laser is fired repetitively over a single position of the sample), line scan (the sample is moving horizontally at a constant speed) and area scan (several scan lines are performed, with a specific distance

<table>
<thead>
<tr>
<th>Table 1. LA-ICPMS operating conditions.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Parameter</strong></td>
</tr>
<tr>
<td><strong>LA (CETAC, LSX-100)</strong></td>
</tr>
<tr>
<td>Laser type</td>
</tr>
<tr>
<td>Laser mode</td>
</tr>
<tr>
<td>Beam profile</td>
</tr>
<tr>
<td>Beam diameter</td>
</tr>
<tr>
<td>Wavelength</td>
</tr>
<tr>
<td>Pulse width</td>
</tr>
<tr>
<td>Transverse mode</td>
</tr>
<tr>
<td>Pulse energy output</td>
</tr>
<tr>
<td>Pulse repetition rate</td>
</tr>
<tr>
<td>Sample movement speed</td>
</tr>
<tr>
<td>Ablation chamber volume</td>
</tr>
<tr>
<td>Transport from ablation cell to MS</td>
</tr>
</tbody>
</table>

**ICP-MS (PERKIN ELMER SCIEX, ELAN 6000)**

<table>
<thead>
<tr>
<th><strong>Parameter</strong></th>
<th><strong>Value</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>RF forward power</td>
<td>1100 W</td>
</tr>
<tr>
<td>Ar plasma flow rate</td>
<td>14 l min(^{-1})</td>
</tr>
<tr>
<td>Ar carrier flow rate</td>
<td>0.65 l min(^{-1})</td>
</tr>
<tr>
<td>ICP frequency</td>
<td>40.86 MHz (free-running)</td>
</tr>
<tr>
<td>Detector</td>
<td>Dual mode</td>
</tr>
<tr>
<td>Analytes</td>
<td>( ^{27}\text{Al}, ^{56}\text{Fe}, ^{56}\text{Fe} )</td>
</tr>
<tr>
<td>Dwell time</td>
<td>10 ms</td>
</tr>
<tr>
<td>Sweeps/reading</td>
<td>4</td>
</tr>
<tr>
<td>Estimated reading time</td>
<td>156 ms</td>
</tr>
<tr>
<td>Readings/replicate</td>
<td>As many as provide enough replicate time</td>
</tr>
<tr>
<td>Data acquisition</td>
<td>Peak hopping, one point per peak and time resolved mode</td>
</tr>
</tbody>
</table>
between lines). Analyte signals were acquired and visually examined as a function of time. The monitoring of the signals in “real-time” allowed to change the operating parameters during the analysis, and to select the best parameters setting regarding both sensitivity and stability.

The laser pulse energy was tested in the range from 0.6 to 4.5 mJ pulse\(^{-1}\). As a good spatial resolution requires small spot size, the laser beam was always focused at the sample surface, in order to work with the smallest crater diameter attainable. A pulse repetition rate of 10 Hz was applied and a scanning speed of 3 \(\text{mm s}^{-1}\) was used for scanning test. The alumina particles were studied on cross sections of the melted and sintered samples and on the surface of the pellets and the glass samples.

\subsection{2.3. Samples Preparation}

Four series of five samples each were prepared from pure iron powder (particle size \(<25 \mu m\)) adding \(\text{Al}_2\text{O}_3\) powder with particles in the following \(\mu m\) size intervals: a) \(0 \text{ (blank)}\); b) \(<25 \mu m\); c) \(>25\sim50 \mu m\); d) \(>50\sim75 \mu m\) and e) \(>75\sim100 \mu m\).

1) Metal Samples

Obtained by melting 40 g of iron with 0.05 g of \(\text{Al}_2\text{O}_3\) in a refractory crucible in an induction furnace with a controlled Ar atmosphere. The melting process did not result in the dissolution of the Al in the Fe matrix. The \(\text{Al}_2\text{O}_3\) melting temperature (1200°C) is higher than Fe (1535°C). The molten metal was centrifuged and casting in an appropriate mould. The collector receiving the molten metal was formed of a “muzzle”, made of the same heat-resistant material as the crucible, and a “chill mould” consisting of two adjustable parts made from an alloy of 94% Cu and 6% Be. The samples obtained were mushroom-shaped, with a cylindrical head of about 30 mm diameter and 8 mm thick, and a stem about 12 mm in diameter and 6 mm high.

2) Pellets

Prepared by mixing 20 g of iron with 0.02 g of \(\text{Al}_2\text{O}_3\). The mixture was placed in an aluminium capsule, and a 50 ton \(\text{cm}^{-2}\) load was applied for 60 s in a hydraulic press.

3) Sintered

Pellet samples prepared in accordance with the above pelleting process were heated at 1050°C for 4 h in a horizontal tubular furnace with a controlled N\(_2\sim10\%\text{H}_2\) atmosphere. After the sintering process samples were rolled at 950°C three consecutive times, in order to obtain full dense samples.

4) Beads

The process was performed manually, using a muffle furnace. A mixture of 0.357 g \(\text{Fe}_2\text{O}_3\) (\(<0.25\ g\ \text{Fe}\)+7 g \(\text{Li}_2\text{B}_2\text{O}_3\)+1.5 g \(\text{Na}_2\text{CO}_3\)+0.02 g \(\text{NaI}\) was placed in a platinum crucible and fused at 1500°C. The molten alkaline mass was poured onto a platinum plate, preheated to dull red and dusted with the \(\text{Al}_2\text{O}_3\) particles. During the cooling process, the \(\text{Al}_2\text{O}_3\) particles dusted in the plate are adhered to the surface of the alkaline mixture in contact with the plate.

\section{3. Results}

\subsection{3.1. Influence of Power Density}

Processes of ablation, and consequently, behaviour and features of the analytical signal in LA-ICP-MS depend on the irradiance (power density, \(\text{GW cm}^{-2}\)) of the laser beam on the target surface. In turn, irradiance depends on laser pulse energy, laser pulse duration and laser spot size. By maintaining laser source and focusing conditions constant, the spot size (for a Gaussian laser beam profile) depends on the laser pulse energy and consequently it represents a critical parameter directly governing the irradiance and hence the ablation process. It is logical to suppose that this influence is especially important for the ablation of pressed powders, provided that in principle, pellets would have to be less resistant to laser radiation than the melted, sintered or fussed samples. For this reason the effect of laser irradiance on the analyte signal response was evaluated on a pellet sample. Samples were prepared without binders, after proving that the use of them didn’t improve the pellets characteristics. The two binders tested were: \(\text{N}-\text{butyl-methacrylate}\) (Ervacite, from ICI Acrylis, The Netherlands) and a mixture of cellulose and paraffin (Spectroblend, from Chemplex Industries, USA).

Laser pulse energies of 0.6, 1.5, 2.5, 3.3 and 4.5 mJ pulse\(^{-1}\), were tested. The laser beam was focused at the sample surface, in order to work with the smallest crater diameter, and 100 pulses were fired at a pulse repetition rate of 10 Hz. \textbf{Figure 1} shows the normalized iron signal response (expressed as the sum of the 64 signal intensities values measured while the 100 laser pulses were fired) for the different pulse energy values. The error bars represent standard deviation values based on 4 replicates.

A compromise has to be found between the sensitivity, which increases with energy, and precision, which is conditioned among others by the mechanical strength, the grain size or binding pressure.

A pulse energy of 2.5 mJ was selected, since a higher pulse energy could cause the pellets to crumble into large particles, which would deteriorate the signal stability. With this pulse energy the resulting crater diameter was of 48\pm2 \(\mu m\), and the corresponding irradiance value was \(17 \text{ GW/cm}^2\).

The blanks of the rest of the types of prepared samples (melted metal, sintered, and fussed glass) and a pure Fe sample (CRM 098-1, from Bundesanstalt für Materialforschung und -prüfung), were ablated using the same oper-

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{Normalized Fe signal at different pulse energy values.}
\end{figure}
ating parameters. Figure 2 shows the electron microscopy image of the ablated craters and Fig. 3 the corresponding Fe time resolved signals.

The crater diameters were of $48 \pm 5 \mu m$. The glass and pellet ablation yielded craters with a smooth surface and minimum deposits. The ablation craters in melted and sintered samples, the same as for the CRM 098-1, were characterized by deposits of solidified melt on the bottom and the crater walls.

3.2. Fe Signals Intensity

Due to the irregular crater shape, it was difficult to quantify the mass/volume ablation rate. Differences in the ablation yield (differences in the ablated sample mass with respect to the sample preparation system, i.e. ablation efficiency), were evaluated from the Fe signal intensities. To quantify the ablation differences, the blank samples were scanning along 1000 $\mu m$ scan lines at a speed scan of $3 \mu m/s$. Figure 4 shows the normalized Fe signal average.

As can be observed the averaged Fe signal from the melted samples was comparable to the CRM-098 pure iron signal. Pellets and sintered samples yielded signals roughly 9% and 13% higher, respectively. Nevertheless, all values were within the standard deviation of the CRM-098 pure iron signal. The stability and non-fragility of the pellets was verified and the acceptable similarity between the Fe signal from the pellet and the metal samples indicated its good cohesion.

Direct comparison of the fused glass sample signals was not possible due to its Fe content of only 2.2%. In order to match the Fe signals from glass to those from metal samples, bearing in mind the large linear dynamic range of the ICP-MS technique, the Fe signal value corresponding to the 2.2% Fe was extrapolated to the value that should correspond to 100% Fe. The calculated value was roughly 3 times higher than the Fe signal for the rest of the samples. From the above tests it can be conclude that the ablation rate is comparable for metal, melted, pressed and sintered samples and three times higher for glass samples when the Fe signal is extrapolated to 100% Fe content.

3.3. $Al_2O_3$ Particles Size Identification

Following visual identification with the laser system CCD camera microscope, the $Al_2O_3$ particles were examined in each sample type. The alumina particles were studied in cross-sections of the melted and sintered samples and on the surface of the pellets and the glass samples. Figure 5 shows an example of pellet samples containing $Al_2O_3$ particles with the different size intervals, together with the time resolved $^{27}Al$ and $^{57}Fe$ signals, when scanning surface lines traversing any of these alumina particles.

As expected, the intensity peak area increases with the ablated particle size. A similar pattern was observed for the time resolved $Al$ and $Fe$ signals in all the other sample types. Figure 6 shows the intensity peaks of $Al_2O_3$ particles with different sizes from the four sample preparation systems.

The correlation between area of $Al$ intensity peaks (expressed as the sum of ICP-MS intensity values measured in the peak interval) and particle size interval is presented in Fig. 7. An acceptable correlation and a comparable behaviour for all the sample preparation systems can be observed.

From the values of the intensity $Al$ peak areas it can be observed, the same as it was concluded from the Fe intensity values, a comparable ablation efficiency for melted, sintered and pellets and about three times higher for glass
In a complementary test a heterogeneous zone of a sintered sample, prepared with Al$_2$O$_3$ particles size in the range from 25 to 100 $\mu$m, was monitored. The selected area of 0.09 mm$^2$ was scanned at a scanning speed of 3 $\mu$m s$^{-1}$ and with a distance between lines of 50 $\mu$m. Figure 8 shows a diagram of the particles observed in the area and the corresponding time resolved $^{27}$Al signals.

The Al intensity values in the first and the last scans are below 5 $\times$ 10$^2$, which may be regarded as Al background values. In scans 2, 3 and 5, three Al$_2$O$_3$ particles between 50 and 100 $\mu$m were ablated and in scan 4, two particles of roughly 25 $\mu$m were sampled.

Fig. 5. Pellets surfaces with different sizes of Al$_2$O$_3$ particles, and typical $^{27}$Al and $^{57}$Fe time resolved signals when traversing, in scanning mode, one of these particles (3 $\mu$m s$^{-1}$ scanning speed).

Fig. 6. Intensity peaks of Al$_2$O$_3$ particles with different sizes (in the four sample preparation systems): a) <25 $\mu$m; b) >25<50 $\mu$m; c) >50<75 $\mu$m; d) >75<100 $\mu$m.

Fig. 7. Correlation between area of Al peaks (expressed as the sum of ICP-MS intensity values measured in the peak interval) and particle size interval.

Fig. 8. Al$_2$O$_3$ particles position and Al time resolved signals corresponding to a heterogeneous area of 0.09 mm$^2$ (3 $\mu$m s$^{-1}$ of scanning speed and 50 $\mu$m of distance between lines) of a sintered sample prepared with Al$_2$O$_3$ particles size in the range from 25 to 100 $\mu$m.
4. Conclusion

From the above tests it can be concluded that the ablation rate of the CRM-098 (pure iron sample) is similar to that of the prepared metal samples and comparable with those from pellets and sinter samples. The fussed glass samples, after extrapolating the Fe signal to the value that should correspond to a 100% of Fe, present a three higher ablation rate. Among the tested sample preparation procedures the simplest and more rapid system is undoubtedly that of pressed pellets. On the other hand the stability and not fragility of the pellets has been verified and the acceptable similarity between the Fe signal from the pellet and the metal samples shows its good cohesion. The availability of the produced in-house synthetic samples well characterized, in terms of particle size, provides an important help to clarify the precise relationship between particle size and ion signal response. A good correlation between area of ion intensity peak and mean size of particles has been found, confirming that LA-ICP-MS has the perspective to be used to look at heterogeneous element distributions and size measurement of inclusions in metals and other materials.

Acknowledgements

This work was carried out with financial support from the Comisión Interministerial de Ciencia y Tecnología (CICYT) of Spain under Project MAT2005-00348.

REFERENCES

5) Y. Ishibashi: ISIJ Int., 42 (2002), S137.