Characterisation of Inclusions in Clean Steels via Laser Ablation-ICP Mass Spectrometry

C. DUBUISSON, A. G. COX, C. W. MCLEOD, I. WHITESIDE,1) R. JOWITT1) and H. FALK2)

Centre for Analytical Sciences, Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK.
E-mail: c.w.mcleod@sheffield.ac.uk 1) CORUS, Teesside Technology Centre, Middlesborough, TS6 6 UB, UK.
2) Spectro Analytical Instruments GmbH. Borchstr. 10, D-47533 Kleve, Germany.

(Received on May 13, 2004; accepted in final form on August 11, 2004)

A new method for detection and assessment of inclusions in clean steels based on laser ablation and ICP mass spectrometry has been developed. Samples were subjected to UV laser ablation (Nd Yag) and ion intensities of elements of interest were monitored on a time-resolved basis. Lasers exhibiting both gaussian and flat-top intensity beam distributions were used. Analytical response for inclusion and matrix elements as a function of laser ablation parameters was studied and procedures were developed for rapid inclusion characterisation and elemental mapping. Main inclusion types identified in clean steels were Mn–S, Mg–Al and Mg–Al–Ca–Ti–Si. Results indicate the considerable analytical potential for the laser ablation technique in a production environment.

KEY WORDS: clean steels; inclusions; mapping laser ablation; ICP mass spectrometry.

1. Introduction

Steel cleanness is a critical property affecting the performance of steel in end use and is dependent on the type, the frequency and size distribution of non-metallic inclusions. Inclusion size can vary from sub to hundreds of μm where the larger particles tend to be agglomerates of small particles rather than single individual precipitates. The main types of inclusions are oxides, sulphides or nitrides in combination with elements such as Mg, Ca, Mn, Al, Ti.

At present, steel cleanness is normally assessed through determination of oxygen in the final product and by optical/electron microscopy. These techniques are labour intensive and time consuming and do not provide definitive chemical information, i.e. the identification of the elements present in the inclusions. Kawakami et al.2) have proposed image processing of micrographs to assess inclusion chemistry according to the shape of the inclusion. Mathematical models have been developed by Shi et al.3) to estimate the maximum inclusion size in a large volume of steel based on data from a small observation volume. However, such approaches need specific sample preparations and consequently the analysis time, in the context of production control, is excessive.

The opportunity exists to exploit new spectrochemical methods for cleanness assessment, the analytical challenge being to develop rapid, sensitive and objective methods that can be deployed at the site of production with minimal sample preparation. In this respect significant progress has been realised using the single spark emission (SSE) spectrometric technique.4) In this approach emission intensities are recorded on a time-resolved basis and, as a result of significant variations in pulse height for discharges adjacent to non-metallic inclusions it is possible to detect inclusions, and obtain information on composition and size distribution. Moreover, an elemental mapping capability has been developed by linking the source excitation stand to a sample translation stage. The current status and capabilities of the SSE method, with respect to assessment of steel cleanness are being addressed by several groups. Brown5) detected Ca-rich MnS inclusions and pure MnS inclusions in clean steels and also noted that frequency distribution charts for inclusions correlated well with the steel cleanness grade. Falk and Wintjens6) used the SSE technique to quantify soluble and insoluble Al in steel and in addition, through correlation analysis, characterised dominant inclusion species in terms of frequency of occurrence and size. Specific inclusion types studied included Ca–O, Al–Ca–O, Si–O, Al–O, Al–N, Ti–N, Ca–S and Mn–Ca–S. In the work of Meillard et al.7) compositional analysis of inclusions involved the simultaneous measurement of some 20 elements including Ca, Al, Na, O, N, Si and S. In addition to rapid confirmation of inclusion chemistry, the possibility for quantitation based on the use of specially produced inhouse reference standards was considered. Elemental mapping for a particular specimen (sample size 8×6 cm²) revealed the presence of a 300 μm defect containing Al, Ca and Na.

Laser spectrochemical methods would seem to offer considerable potential for characterisation of inclusions in clean steels. The laser beam is readily focused to small aperture sizes (~5–100 μm) and thus can offer an improved spatial measurement capability relative to spark-based measurement. Laser induced breakdown spectroscopy (LIBS) is
a versatile microanalytical technique and is analogous to the SSE method in that elemental analysis is based on direct spectral observation of the plasma discharge. LIBS has yet to be fully exploited for characterisation of inclusions in clean steels but the potential is considerable given its success as a microanalytical tool for spatially resolved measurement and depth profiling. Progress in the use of LIBS for inclusion measurement has recently been elaborated by Noll et al. and Laserna et al.

Laser ablation in combination with ICP emission or ICP mass spectrometry constitutes an important bulk and microanalysis tool as evidenced by an extensive literature. Relative to the LIBS approach a major advantage of the laser-ICP combination is the improved measurement sensitivity particularly for ICP-MS detection where the current state of the art is at the ng/g level. The high detection sensitivity combined with good spatial measurement capability has been exploited in geological investigations including the characterisation of fluid inclusions and for zonation studies in minerals.

The aim of this research was to evaluate the potential of the LA-ICP-MS method for steel cleanliness assessment. The effects of key parameters, i.e. laser energy, frequency, spot size, and rate of sample translation on signal response have been investigated using both gaussian and flat top beam intensity distribution profiles. The approach permits rapid identification of elements present in inclusions and gives new information related to the spatial distribution of inclusions in samples.

2. Experimental

2.1. Materials

A glass standard reference material (SRM 612, NIST, Gaithersburg, MD) was used for initial instrument set-up (daily basis) and in-house research materials previously characterised by optical metallography were used in method development.

2.2. Instrumentation

Laser ablation was performed using Nd Yag lasers (LSX-100 and LSX-200, frequency quadrupole; CETAC Technologies, Omaha) interfaced to an ICP mass spectrometer (Agilent Technologies, HP 4500). The main difference in the two laser systems was that the LSX-100 exhibits a gaussian beam intensity distribution whereas the LSX-200 has a flat top beam profile. Both ablation systems allowed viewing of the sample surface (typical magnification, ×8) through a CCD camera. The ablation cell (52 mm dia. × 50 mm high) was connected to the injector of the ICP torch via Teflon tubing (1 m × 6 mm id).

Sample was placed in the ablation cell and during laser firing was translated under stepper motor control at 40 μm/s. Ion intensities for 11B, 13C, 25Mg, 27Al, 31P, 32S, 34S, 40Ca, 47Ti, 55Mn and 57Fe were monitored in the time-resolved analysis mode. Unless stated otherwise, standard ICP-MS operating conditions and data acquisition parameters were utilised. For a single line raster, a laser track of typically 15 mm in length and 50–300 μm in width was created depending on laser operating parameters. A fresh area of sample was usually selected for the next run, thus in method development laser interrogations would result in a series of single laser tracks on the samples. For elemental mapping the scanning mode was utilised whereby successive line rasters were used to map the area of interest. The area sampled was typically 8 mm × 6 mm and the distance between adjacent laser tracks was ~125 μm. The data sets (ion-time response as a function of position) were exported to Excel in order to realise distribution maps for elements of interest.

3. Results and Discussion

3.1. Laser Operating Parameters

Initial experiments were concerned with identifying laser operating parameters that permitted discrimination of signals originating from inclusions and that associated with the bulk matrix. As shown in Fig. 1, laser interrogation of an in-house research sample resulted in sharp transient signals for Mn and S as distinct from the relatively smooth steady state response for Fe. Moreover the transient signal spikes for Mn and S were perfectly correlated confirming the presence of MnS inclusion in the sample. Inclusion stoichiometry in terms of Mn and S content was similar as indicated by the relative constancy of the Mn/S intensity ratios computed for the 10 prominent inclusions detected (see Fig. 1). As stated earlier, the analytical response is the sum of 2 contributions and it is clear that, on the basis of this single experiment, the LA-ICP-MS technique offers considerable scope for rapid micro and bulk analysis. For the sample in question it is seen from consideration of the respective ion-time responses that Mn is present in both the inclusions and the bulk matrix whereas S is primarily associated with the inclusion species. In order to gain further insight into measurement capability, particularly to clarify the extent to which sensitivity and spatial resolution are influenced by laser operating parameters, additional systematic
3.1. Sample Translation

Experiments were undertaken on a research sample previously characterised by optical metallography and known to contain 2 well defined inclusions (sizes ~162 µm and ~87 µm) separated by approximately 2 mm. Five successive line rasters, corresponding to different sample translation rates (20, 40, 80, 100, 200 µm/s), were repeated over the same single laser track that bisected the two inclusions. Thus it was possible to compare ion-time responses and hence assess the effect of sample translation rate on spatial resolution. As shown in Fig. 2 there is clear separation of inclusion signals for translation rates of 20 and 40 µm/s as distinct from that at 200 µm/s. Effective separation was also realised at 80 and 100 µm/s but signals are omitted from the diagram in the interests of clarity. Ion intensities did decrease for successive laser scans (Scan 1, 40 Hz; Scan 2, 20 Hz; Scan 3, 200 Hz, Scan 4, 80 Hz; Scan 5, 100 Hz) indicating inclusion integrity was not maintained for the duration of the study. Notwithstanding this limitation in experimental design, results confirm the powerful microanalytical capability of the focused laser beam for inclusion detection. Subsequent studies were performed at a sample translation rate of 40 µm/s.

3.1.2. Laser Energy

Figure 3 shows the ion-time response for Mn at three different power settings (3, 4, and 5 mJ/pulse) using the LSX-200 laser (spot size 200 µm, frequency 20 Hz, scan speed 40 µm/s). As expected, an increase in laser energy led to an increase in response for the bulk Mn signal consistent with an increase in ablation rate. The energy level was, however, less important with respect to inclusion detection and as shown, for the lowest setting (3 mJ/pulse), prominent transient peaks for inclusions were registered.

Ion-time responses (Mn/Fe) for ratioing to the Fe matrix signal are given in Fig. 4 and indicate unambiguous detection of inclusions for the 3 energy levels used. Ratio values might serve as a useful diagnostic tool since they give a clear indication of whether signals are due to detection of inclusions or are noise spikes. From an analysis standpoint, ratioing could also compensate for any variations in ablation efficiency. The intense signal at approx. 135 s
(3 mJ/pulse) is probably due to a large inclusion although attempts to correlate inclusion size with the analytical response function, would require separate studies involving reference samples that were well characterised in terms of particle size and size distribution.

3.1.3. Laser Frequency

Increase of the laser repetition rate (frequency) resulted in an increase in the signal for the host matrix (Fe) consistent with an increased ablation yield. Regarding signal intensities for Mn and S only a slight increase of peak area was observed between 5 and 10 Hz and there was no further increase beyond 10 Hz. In other words, a frequency of 10 Hz was sufficient to release/vaporise the MnS inclusions from the host matrix. Also, from intensity ratios presented in Fig. 5, it can be seen that low laser frequency is effective for sensitive detection of inclusions. The Mn/Fe ratio is a maximum at 5 Hz since at low frequency the contribution of the matrix signal (Fe) is also low. However, low frequency (5 Hz) led to a worsening of precision as a result of relatively noisy transient signals. With respect to spatial resolution, it was noted that the width of the transient signals did not vary for the three frequencies, indicating that the contribution of laser frequency (to spatial resolution) is unimportant for the scan speed (40 μm/s) and the spot size (200 μm) utilised in this experiment. Most likely the dominant factor governing the width of the transient signals is the transfer function that describes analyte transport from the ablation cell to the ICP-mass spectrometer (a single shot ablation with stationary target yielded a response time of 2 s).
aspect has been discussed at length by Arrowsmith in the context of bulk chemical analysis.

3.1.4. Laser Spot Size

Laser spot size is potentially important from the stand-points of both spatial resolution and sensitivity. These aspects were studied using both the LSX-100 and LSX-200 lasers. For the LSX-100 (gaussian beam profile) changes in laser focus influence both the diameter of the laser beam and the energy density at the sample surface for a given power setting. With the laser fully defocused, the $^{57}$Fe response was highest indicating the laser-sample interaction area was maximised hence maximum removal of the host matrix. The inclusion signals (Mn, S) were less affected by focus but the analyte/Fe ratio was a maximum for laser focusing since for this condition the amount of host matrix ablated was minimised. However, the high energy condition associated with the focused laser did give rise to a redeposition of matrix in finely divided form along and adjacent to the laser tracks. Such operating conditions would not be desirable in mapping studies where successive and closely spaced line rasters could re-mobilise this ejecta.

In the case of the LSX-200 (flat top beam profile) a uniform energy distribution was realised over the sample surface irrespective of spot size selected. For spot sizes less than 50 $\mu$m detection sensitivity was inadequate, particularly for S. In the range 100–350 $\mu$m the intensities for the inclusion signals showed less dependency on spot size indicating an efficient energy transfer/ablation beyond a critical beam size. In the case of the response for the Fe matrix, the Fe signal increased progressively with increase in laser spot size consistent with an increase in ablation rate.

3.2. Chemical Speciation and Mapping

Conventional approaches to inclusion assessment do not provide direct information on inclusion chemistry. Unless spectroscopic techniques are used the shape of the inclusion may provide the only indication of inclusion type. As already shown in the case of MnS inclusions (Fig. 1), LA-ICP-MS allows a rapid and objective determination of the nature of the elements present in the heterogeneity. A further example of measurement capability is given in Fig. 6. Ten samples previously characterised by optical methods to have inclusions with sizes less than 10 $\mu$m, were submitted to laser interrogation. It was found that some samples exhibited a high proportion of inclusions containing Mg and Al, (Fig. 6(a)), while others exhibited a high proportion of heterogeneities containing Mg, Al, Ti, Ca, and Si (Fig. 6(b)). The percentage of each inclusion type was calculated for each sample, and the results obtained were found to match an index determined from the metallographic data. The presence of non-deformable inclusions such as spinels or alumina in clean steels is detrimental but the problem may be overcome at the production stage by transforming non-deformable inclusions such as the Mg–Al type into deformable inclusions through changes in slag chemistry. Thus the quality of clean steels can be monitored and controlled via the LA-ICP-MS technique.

3.3. Spatially Resolved Measurement and Mapping

Inclusion assessment in a polished sample previously studied by optical microscopy was performed via LA-ICP-MS (LSX-100). Ten successive line rasters were performed on the same location, with an energy of 1.70 mJ/pulse, a frequency of 20 Hz, a sample translation rate of 40 $\mu$m/s, and a defocused condition (+7.5 mm). A photograph of the sample is shown in Fig. 7 and corresponding time resolved analyte signals ($^{24}$Mg, $^{27}$Al, and $^{57}$Fe) for a single line raster are presented in Fig. 8. It can be seen that the $^{24}$Mg and the $^{27}$Al signals are perfectly correlated, and the ratios against $^{57}$Fe clearly indicate detection of inclusions, in precisely the same locations as shown in the photograph (Fig. 7).

Spatially resolved studies were also performed (LSX-200), on two samples of differing levels of cleanness. A surface of about 8×6 mm was analysed by continuous fir-
ing of the laser using the scanning mode. An energy of 3 mJ/pulse and a frequency of 10 Hz were selected as a compromise between sensitivity and morphology of the crater, the aim being to avoid the re-mobilisation of previously ejected matter. A scan speed of 40 μm/s was used, as a compromise between lateral resolution and analysis time. A spot size of 120 μm was selected, and the distance between the centres of two adjacent rasters was fixed to 125 μm. The intensities for 8 elements were recorded, i.e. one data point was obtained every 0.586 s. The data set were

Fig. 6. Ion-time responses for samples with (a) Mg–Al inclusions, and (b) Mg–Al–Ca–Ti–Si inclusions. LSX-200. Energy, 3 mJ. Frequency, 10 Hz. Spot size, 120 μm.

Fig. 7. Photo (magnification, ×8) of laser track resulting from 10 successive scans on research sample. LSX 100. Energy, 1.7 mJ. Frequency 20 Hz. Sample translation, 40 μm/s. Focus condition, +7.5 mm.

Fig. 8. Ion-time responses corresponding to single line raster on research sample (experimental parameters as in Fig. 7).
then exported to Excel in order to obtain a 3D map for each element for the surface analysed. The mappings obtained for Al and Mg (Fig. 9) perfectly matched with the inclusion pattern observed on the photograph of the sample taken under magnification 8. Even if the number of data points used for mapping were reduced by a factor of five, the same elemental distribution pattern was observed. This indicates that the density of data points was high enough to detect all the inclusions and that the spatial resolution was acceptable. Moreover, results indicated that a higher scan speed, or alternatively enlarging the interrogation area, could be used, without loss of information. Regarding the ‘clean’ sample, inclusions were not directly visible from the photograph on account of the small size, but the perfect correlation of the mappings for Mg and Al clearly indicated the presence of small, well-distributed Mg–Al heterogeneities (Fig. 10). Thus LA-ICP-MS was able to provide a compositional map of the inclusion distribution for both samples. It should be further noted that such mappings can be realised for an unpolished sample, which is a distinct advantage compared to optical microscopy which requires a perfectly polished surface.

4. Conclusion

It has been shown that laser ablation coupled to ICP mass spectrometry provides a powerful new route for characterisation of inclusions in clean steels. The approach offers distinct advantages over current non-spectroscopic methods in terms of sensitivity, spatial information, speed of analysis and minimal requirement for sample preparation. Further work is needed to clarify the precise relationship between inclusion size and analytical response; the availability of reference materials well characterised in terms of particle size, size distribution and inclusion chemistry will aid such investigations. From a production control standpoint further work is needed to assess the relative merits of LA-ICP-MS with the competing SSE and LIBS techniques. These studies are planned for future work.

Acknowledgements

This work has been performed under E.C.S.C. project number 7210-PR-041 to which C.D. is grateful for financial support. Technical support of Agilent Technologies and Cetac Technologies is gratefully acknowledged.

REFERENCES

1) Proc. Clean Steel: Superclean Steel, ed. by J. Nutting and R. Viswanathan, Institute of Materials, London, (1996), 1965.
2) M. Kawakami, T. Nishimura, T. Takanaka and S. Yokoyama: ISIJ Int., 39 (1999), 164.
3) G. Shi, H. V Atkinson, C. M. Sellars and C. W. Anderson: Acta Mater., 47 (1999), 1455.
4) V. Muller, V. Tuset, B. D. Summerhill, R. Jowitt, G. Willoy and F. Meyer: Progress in Anal. Chem. in the Steel and Metals Industry, ed. by R. Nauche, EC, (1996), 444.
5) A. J. Brown: Progress in Anal. Chem. in the Steel and Metals Industry, ed. by R. Tommeline, EC, (1999), 405.
6) H. Falk and P. Wintjens: Progress in Anal. Chem. in the Steel and
7) R. Meilland, H. Hocquaux, C. Lonis, L. Pollino and F. Hoffert: Progress in Anal. Chem. in the Steel and Metals Industry, EC, (1999), 420.
8) Y. Talmi, H. P. Sieper and L. Moenke-Blakenburg: Anal. Chim. Acta, 127 (1981), 71.
9) J. M. Vadillo, I. Vadillo, F. Carrarco and J. J. Laserna: Fresenius’ J. Anal. Chem., 361 (1998), 119.
10) H. J. Hakkanen and J. E. I Korppi-Tommoka: Anal. Chem., 70 (1998), 4724.
11) P. Lucena, J. M. Vadillo and J. J. Laserna: Anal. Chem., 71 (1999), 4385.
12) C. J. Lorenjen, C. Carloff, U. Hahn and M. Jozued: J. Anal. Atom Spec., 7 (1992), 1029.
13) D. R. Anderson, C. W. McLeod, T. England and A. T. Smith: Appl. Spectrosc., 49 (1995), 691.
14) I. M. Vadillo and J. J. Laserna: J. Anal. At. Spectrom., 12 (1997), 859.
15) R. Noll, H. Bette, A. Brysch, M. Kraushaar, I. Monch, L. Peter and V. Sturm: Spectrochim. Acta B At. Spectrosc., 56B (2001), 637.
16) L. M. Cabalin, M.P. Mateo, J. J. Laserna: Spectrochim. Acta B At. Spectrosc., 53 (1998), 723.
17) S. A. Darke and J. F. Tyson: J. Anal. At. Spectrom., 8 (1993), 145.
18) E. R. Denoyer, K. J. Fredeen and J. W. Hazer: Anal. Chem., 63 (1991), 445A.
19) D. Günther, S. E. Jackson and H. P. Longerich: Spectrochim. Acta B At. Spectrosc., 54 (1999), 381.
20) A. Moissette, T. T. Shepherd and S. R. Chenery: J. Anal. At. Spectrom., 11 (1996), 177.
21) Å. M. Ghazi, T. E. McCandless, D. A. Vanko and J. Ruiz: J. Anal. At. Spectrom., 11 (1996), 667.
22) D. Günter, A. Audetat, R Frischknecht and C. A. Heinrich: J. Anal. At. Spectrom., 13 (1998), 263.
23) C. Fabre, M. C. Borron, J. Dubessy and A. Moissette: J. Anal. At. Spectrom., 14 (1999), 913.
24) S. E. Jackson, H. P. Longerich, G. R. Durnay and B. J. Fryer: Can. Miner., 30 (1992), 149.
25) W. T. Perkins and N. J. G. Pearce: Miner. Soc. Ser. 6 (Microprobe Techniques in the Earth Sciences), (1995), 291.
26) P. Arrowsmith and J. K. Hughes: Appl. Spectrosc., 42 (1988), 1231.