Inclusion Analysis / Steel Cleanliness Determination by Spark OES

Characterization of inclusions in steel by OES Pulse Discrimination Analysis (OES-PDA)
Inclusion Analysis / Steel Cleanliness Determination by Spark OES

Topics
- Demand & Goals
- Reference Methods for Inclusion Analysis
- Rapid Method for Inclusions & Oxygen
- Hardware - Instrument Features
- Single Spark Evaluation
- Determination of Inclusions
- Principles of the PDA/MCI Method
- Comparison of Methods
- Results of PDA/MCI
- Conclusion

Speakers

**Georg Schick**  
VP, Industrial Sales & Marketing  
Bruker Elemental  
Billerica, MA, USA

**Martin Tilleman**  
Product Manager, Stationary OES  
Bruker Elemental  
Germany
Demands & Goals

Increasing demand for higher cleanliness in steels by customers in the metal processing industries.

- Production of high purity steels
  - Process monitoring of production steps
  - Final inspection of outgoing material
- Optimization of the production process
  - Improving Slagging Practices
  - Fast determination of oxide and sulfide inclusions during the process
  - Calculation of oxygen content
- Processing of steel for high demands
  - Fast cleanliness check of incoming billets and outgoing components

→ Determination of parameters that define Steel Cleanliness
Reference Method for Inclusion Analysis: SEM/EDS with Bruker Quantax 400 EDS

Scanning electron microscope with energy dispersive X-ray spectroscopy

- Universal method: differentiation of carbides, oxides, nitrides, sulfides
- Large observation area
- Imaging method
- Highest accuracy
- Surface method, low penetration depth (~1 µm)
- Costly, long measurement time (~3-10 h)
- Highly educated operating staff
Melt extraction with carrier gas method for the determination of oxygen

- Accurate analysis of total oxygen
- Fast measurement (~80 s)
- High analysed sample mass (~1000 mg)
- Demanding sample preparation
- Limited to oxygen only
Inclusion characterization & oxygen determination by Optical Emission Spectrometry with Pulse Discrimination Analysis

- Complete elemental analysis
- Determination of various oxide and sulfide inclusions
- Calculation of total oxygen
- Simple sample preparation (grinding w/ SiC paper or milling)
- Fast measurement (~5 s/burn. multiple burns recommended. e.g. 5x)
- User-friendly software for “normal” OES operator
- Feasibility study advisable
Q8 MAGELLAN Spectrometer

- Single Spark Detection (SSD) with visualization
- Unlimited parameters
  - any frequency up to 1 kHZ
  - all channels available for SSD
  - free source curve design
- Highest spectral sensitivity, lowest detection limits
- Lowest dark current, Channel-Photo-Multipliers (CPM)
Example for single spark signals with the Q8 MAGELLAN
Determination of Inclusions

Al-histogram of net-intensity distribution
Sample RM2501

Median
Average
2.5*SD

No. of sparks

Intensities

Frequency
Gaussian distrib.
Application field:
• Low and high alloyed steels with aluminium desoxidation

Workflow calibration & measurement
• Development of inclusion method with definition of spark parameters
• Calibration of method
• Sparking samples / generating data files (CSV format)
• Import data into MCI software
• Execute MCI software
• Print out (PDF) and export (CSV) and transfer results to other databases
Principles of PDA/MCI Method

Calculation steps

- Exclusion of sparks in the instable starting phase
- Detect and remove unenergetic sparks
- SD-Calculation of normalized Gaussian distribution
- Selection of oxide outliers (e.g. >3 SD)
- Calculation of element concentrations
- Identification of Ca as CaS. removing from oxide examination
- Identification of different oxides (correlation of outliers, e.g. Al to Ca)
- Stoichiometric calculation of oxide and sulfide compounds
- Calculation of total oxygen
- Classification of inclusions and grain size distribution
## Comparison of Methods

<table>
<thead>
<tr>
<th></th>
<th>SEM/EDS</th>
<th>ON/(H)</th>
<th>OES-MCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital investment (approx. k€)</td>
<td>550</td>
<td>60</td>
<td>80</td>
</tr>
<tr>
<td>Operating costs</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Reference method / norm compliance</td>
<td>Yes</td>
<td>Partly</td>
<td>No</td>
</tr>
<tr>
<td>Penetration depth (of sample), approx.</td>
<td>1-3 µm</td>
<td>Complete</td>
<td>10 µm</td>
</tr>
<tr>
<td>Tested area (of sample), approx.</td>
<td>200 mm²</td>
<td>Complete</td>
<td>7 mm²</td>
</tr>
<tr>
<td>PDA/MCI-Measurement time, approx.</td>
<td>10 h</td>
<td>80 s</td>
<td>5 s</td>
</tr>
<tr>
<td>Ease-of-use (instrument)</td>
<td>Complex</td>
<td>Medium</td>
<td>Easy</td>
</tr>
<tr>
<td>Sample preparation</td>
<td>Medium</td>
<td>Complex</td>
<td>Easy</td>
</tr>
<tr>
<td>Analytical performance / value</td>
<td>High</td>
<td>Limited</td>
<td>Medium</td>
</tr>
</tbody>
</table>

*) values given for single reading, multiple measurements necessary
Validation of MCI-method by comparison with Gas Analysis
Application: low and mild alloyed steel
Validation of MCI-method by comparison with SEM/EDS
Application: low and mild alloyed steel

Comparison Oxygen OES / SEM (ppm)

R² = 0.81
Comparison of Methods

Assessment of oxide cleanliness degree
Example of calibration based on customer samples (acc. EN 10247-KOX)

![Graph showing the relationship between cleanliness factor (K1) and PDA Value with R² = 0.75](image-url)

### Cleanliness degree

<table>
<thead>
<tr>
<th>PDA-Value</th>
<th>Cleanliness factor (K1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(R² = 0.75)
# Results of PDA Method

## Reproducibility - Example ball bearing steel

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analyse No</th>
<th>O-total (ppm)</th>
<th>Al-total (ppm)</th>
<th>Al-insoluble (ppm)</th>
<th>app. K1 value (EN 10247)</th>
<th>PDA-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>72 - BBS</td>
<td>1</td>
<td>5.9</td>
<td>88</td>
<td>5.5</td>
<td>1.9</td>
<td>35100</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>6.4</td>
<td>88</td>
<td>6.1</td>
<td>2.0</td>
<td>37527</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>5.4</td>
<td>86</td>
<td>5.1</td>
<td>1.7</td>
<td>31491</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6.3</td>
<td>87</td>
<td>6.1</td>
<td>1.9</td>
<td>36122</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>7.9</td>
<td>89</td>
<td>7.6</td>
<td>2.5</td>
<td>45566</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>6.4</td>
<td>88</td>
<td>6.1</td>
<td>2.0</td>
<td>37161</td>
</tr>
<tr>
<td></td>
<td>SD or RSD (PDA)</td>
<td>0.9</td>
<td>1.1</td>
<td>0.9</td>
<td>0.3</td>
<td>14</td>
</tr>
<tr>
<td>N14 - BBS</td>
<td>1</td>
<td>13.1</td>
<td>54</td>
<td>13.3</td>
<td>4.2</td>
<td>77534</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>13.7</td>
<td>53</td>
<td>13.8</td>
<td>4.2</td>
<td>78343</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>10.3</td>
<td>50</td>
<td>10.2</td>
<td>3.2</td>
<td>60312</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>12.9</td>
<td>55</td>
<td>12.8</td>
<td>4.0</td>
<td>73774</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>13.5</td>
<td>57</td>
<td>13.4</td>
<td>4.2</td>
<td>77671</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>12.7</td>
<td>54</td>
<td>12.7</td>
<td>4.0</td>
<td>73527</td>
</tr>
<tr>
<td></td>
<td>SD or RSD (PDA)</td>
<td>1.4</td>
<td>2.6</td>
<td>1.4</td>
<td>0.4</td>
<td>10</td>
</tr>
</tbody>
</table>
Reproducibility - Example reference material, low alloy steel

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analyse No</th>
<th>O-total (ppm)</th>
<th>Al-total (ppm)</th>
<th>Al-insoluble (ppm)</th>
<th>app. K1 value (EN 10247)</th>
<th>PDA-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>RM - V1 *)</td>
<td>1</td>
<td>26.8</td>
<td>312</td>
<td>26.4</td>
<td>8.8</td>
<td>163033</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>17.7</td>
<td>311</td>
<td>15.3</td>
<td>5.7</td>
<td>106909</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>44.7</td>
<td>364</td>
<td>44.0</td>
<td>14.7</td>
<td>273353</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>46.0</td>
<td>349</td>
<td>45.3</td>
<td>15.1</td>
<td>280605</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>15.1</td>
<td>310</td>
<td>14.6</td>
<td>4.9</td>
<td>91548</td>
</tr>
<tr>
<td>Mean</td>
<td>30.1</td>
<td>329</td>
<td>29.1</td>
<td>9.8</td>
<td>183090</td>
<td></td>
</tr>
<tr>
<td>SD or RSD (PDA)</td>
<td>14.6</td>
<td>25.5</td>
<td>14.9</td>
<td>4.8</td>
<td>49</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analyse No</th>
<th>O-total (ppm)</th>
<th>Al-total (ppm)</th>
<th>Al-insoluble (ppm)</th>
<th>app. K1 value (EN 10247)</th>
<th>PDA-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>RM - V3</td>
<td>1</td>
<td>19.4</td>
<td>1059</td>
<td>21.1</td>
<td>6.1</td>
<td>113989</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>17.9</td>
<td>1062</td>
<td>19.6</td>
<td>5.6</td>
<td>103371</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>19.3</td>
<td>1043</td>
<td>19.3</td>
<td>6.0</td>
<td>111988</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>19.8</td>
<td>1061</td>
<td>21.3</td>
<td>6.2</td>
<td>114449</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>17.6</td>
<td>1052</td>
<td>19.1</td>
<td>5.5</td>
<td>102769</td>
</tr>
<tr>
<td>Mean</td>
<td>18.8</td>
<td>1055</td>
<td>20.1</td>
<td>5.9</td>
<td>109313</td>
<td></td>
</tr>
<tr>
<td>SD or RSD (PDA)</td>
<td>1.0</td>
<td>8.0</td>
<td>1.0</td>
<td>0.3</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

*) Inhomogeneous inclusion distribution!
Results of PDA Method Presentation in the MCI Software

- Statistics
- Grain size distribution
- Total oxygen
Results of PDA Method Presentation in the MCI Software

PDF print-out
Analysis of a ball bearing steel (Standard quality)

<table>
<thead>
<tr>
<th>Sample name</th>
<th>B140-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method name</td>
<td>Fe Inc</td>
</tr>
<tr>
<td>No. of Ignored sparks (Fe)</td>
<td>0</td>
</tr>
<tr>
<td>No. of Ignored CaS incl. for PDA-O</td>
<td>44</td>
</tr>
<tr>
<td>PDA code total</td>
<td>42881,3</td>
</tr>
<tr>
<td>PDA code &gt;1 µm</td>
<td>38554,6</td>
</tr>
<tr>
<td>No. of inclusions in spark area &gt; 1µm</td>
<td>383</td>
</tr>
<tr>
<td>No. of inclusion (per 1000mm²)</td>
<td>2272,7</td>
</tr>
<tr>
<td>Cleanliness degree</td>
<td>1,2</td>
</tr>
<tr>
<td>PDA Oxygen (ppm)</td>
<td>11,9</td>
</tr>
</tbody>
</table>

**Statistics**

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Mg</th>
<th>Ca</th>
<th>Zr</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>745</td>
<td>919</td>
<td>926</td>
<td>1719</td>
<td>25751</td>
<td>5785</td>
<td>1185</td>
<td>852</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>670</td>
<td>291</td>
<td>225</td>
<td>266</td>
<td>3041</td>
<td>594</td>
<td>722</td>
<td>553</td>
</tr>
<tr>
<td>Median</td>
<td>691</td>
<td>885</td>
<td>897</td>
<td>1702</td>
<td>25642</td>
<td>5764</td>
<td>1059</td>
<td>732</td>
</tr>
<tr>
<td>Median std. deviation</td>
<td>77</td>
<td>207</td>
<td>136</td>
<td>248</td>
<td>2774</td>
<td>563</td>
<td>116</td>
<td>118</td>
</tr>
<tr>
<td>Outlier</td>
<td>168</td>
<td>84</td>
<td>91</td>
<td>35</td>
<td>20</td>
<td>34</td>
<td>261</td>
<td>435</td>
</tr>
</tbody>
</table>

**Concentrations (ppm)**

<table>
<thead>
<tr>
<th></th>
<th>AI</th>
<th>CaO</th>
<th>MgO</th>
<th>CaAlO</th>
<th>MgAlO</th>
<th>MgCaAlO</th>
<th>ZrO</th>
<th>TiO</th>
<th>SiO</th>
<th>MnO</th>
<th>TiAlO</th>
<th>MnSiO</th>
<th>CaSiAlO</th>
<th>CaS</th>
<th>MnS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outlier</td>
<td>174</td>
<td>61</td>
<td>61</td>
<td>10</td>
<td>33</td>
<td>0</td>
<td>35</td>
<td>148</td>
<td>32</td>
<td>18</td>
<td>20</td>
<td>2</td>
<td>24</td>
<td>20</td>
<td>14</td>
</tr>
<tr>
<td>Approximate total</td>
<td>13,1</td>
<td>0,7</td>
<td>1,0</td>
<td>0,4</td>
<td>5,2</td>
<td>0,7</td>
<td>3,7</td>
<td>20,7</td>
<td>15,7</td>
<td>5,9</td>
<td>2,7</td>
<td>6,9</td>
<td>2,5</td>
<td>14,8</td>
<td></td>
</tr>
</tbody>
</table>

**Grain size**

<table>
<thead>
<tr>
<th>Class</th>
<th>No.</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 1</td>
<td>31</td>
<td>42</td>
</tr>
<tr>
<td>Class 2</td>
<td>124</td>
<td>9</td>
</tr>
<tr>
<td>Class 3</td>
<td>19</td>
<td>1</td>
</tr>
<tr>
<td>Class 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Class 5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Results of PDA Method
Presentation in the MCI Software

Classification & Presentation in Ternary Diagrams
Conclusion

- OES-MCI reduces effort and costs, exceptionally in comparison to other methods
- Quick complementary method for material inspection
- Allows process control
- Final product assessment for steelworks and processing plants
- Easy extension of typical OES element/bulk analysis
New Application Report

Steel Cleanliness Analysis by OES-PDA

Abstract

The present production of steels shows demanding requirements for quality, especially the levels of cleanliness and nonmetallic inclusions. The key for premium steel products is the cleanliness degree and lowest levels of oxygen.

The classic way to determine non-metallic inclusions is usually done with metallographic microscopy and scanning electron microscope with EDX analysis (SEM-EDX). These methods are slow and cost-intensive applications. Using optical emission spectroscopy with pulse discrimination analysis (OES-PDA) means fast and efficient determination of the cleanliness degree and oxygen level. During the melting process, these quality indicators are available and allow the process control in real-time. In addition, a fast quality check of the final product is one of the main advantages of this method.

For this purpose, Bruker Elemental has developed the software package MCI. “Metal-Cleanliness-Inspection”. The MCI-Software evaluates on a statistical basis the sparks, which are caused by nonmetallic inclusions.

The main features are the determination of:

- Total oxygen content,
- Oxide and sulfide inclusions,
- Grain size distribution of different oxide types (e.g., alumina, Ca-aluminate, Mg-spinel),
- Cleanliness degree in correlation to reference methods (e.g., EN 10247, ASTM E45)
Visit us at AISTech 2013, booth #2035
Pittsburgh, PA, USA on May 6-9
Q & A

Any questions?
Please type any questions you may have for our speakers in the Q&A panel and click Send.

How did we do?
When you exit the webinar, please fill out our evaluation survey to let us know. We appreciate your feedback.

Thank you!

Georg Schick
VP, Industrial Sales & Marketing
Bruker Elemental
Billerica. MA. USA

Martin Tilleman
Product Manager, Stationary OES
Bruker Elemental
Germany
OES and CS/ONH Webinars
Live and On-Demand

Available at
Like what you learned in this webinar?

Subscribe to Bruker’s FIRST Newsletter to get webinar announcements, fascinating articles, and elemental analysis news delivered right to your inbox!

Subscribe at:
