INCLUSION DETECTION IN LIQUID ALUMINUM VIA LASER-INDUCED BREAKDOWN SPECTROSCOPY

by

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Abstract

Aluminum alloy castings are becoming commonplace for critical applications in the automotive and aerospace industries where materials failure is not an option. In order to meet such property demands, tight control over the cleanliness of the melt (mitigation of solid particle inclusions) and microstructure must be achieved. In order to control cleanliness, it must first be well defined and measured. Very few techniques exist in industry that can quantitatively measure inclusion levels in-situ. Laser-induced breakdown spectroscopy (LIBS) is presented as a promising technique to quantify solid particles, desired or undesired, in aluminum melts. By performing LIBS with subsequent statistical analysis on liquid aluminum with varying concentrations of Al₂O₃, AlB₂, TiB₂ and SiC particles, calibration curves relating particle concentration and elemental intensity were drawn. Through metallography and automated electron microscopy, it was found that inclusions less than 10 μm in size could be detected with LIBS. Concentrations down to at least one part-per-million could be quantified. During experiments, it was found that dissolved hydrogen could be detected and accurately measured, allowing for LIBS to be used as a tool for complete, real-time melt cognition.

Thesis Supervisor: Diran Apelian
Title: Alcoa-Howmet Professor of Engineering
Acknowledgements

This dissertation would not have been possible without support from many people. I am humbly thankful for this opportunity given to me by my advisor, Diran Apelian. His guidance and support has helped me through all the problems that arose along the way. Special thanks go to Bob De Saro and Joe Craparo of the Energy Research Company, who supported this project from day one in supplying their equipment, time, and expertise. Many thanks also go to my thesis committee members, Brajendra Mishra, Kevin Anderson, Lin Zhang, and Rick Sisson, members of the Advanced Materials and Processes consortium, as well as my project focus group within the Advanced Casting Research Center for their service, advice, and constructive discussions. I also thank the MPI operations managers and secretaries, Carol Garofoli, Renee Brodeur, and Maureen Plunkett for their help in running the centers. In addition, I thank the following students and post docs at WPI for all their help and camaraderie – Cecilia Borgonovo, Luke Bassett, Baillie McNally, Danielle Cote, Aaron Birt, Mikaela DeRousseau, Sean Kelly, Theo Koutsoukis, Carl Soderhjelm, Inigo Anza, Ben Secino, Caitlin Walde, Anthony Spangenberger, Yuwei Zhai, and Jeff Porzio. I also thank all the friends I made in the WPI Pep Band, who made my time here so much more memorable.

Most importantly, I thank my fiancée, Laura Murray, for all her love and support in this adventure!
Guide to the Reader

This thesis consists of two sections. Part one is an executive summary intended to give the reader a sufficient background on aluminum cleanliness metrics and the use of laser-induced breakdown spectroscopy on molten metal. The section summarizes the results and conclusions from the project as well as outlines future work to be performed. Part two contains the results of the work as a collection of peer reviewed journal articles and conference proceedings that were published and submitted throughout the duration of the project. Articles that are included in this thesis are presented as they appear in the corresponding journal. Those that were not published before the binding of this thesis are presented in the format they were submitted. The following papers are included:

Appendix A
Inclusion Detection in Molten Aluminum – Current Art and New Avenues for In-situ Analysis
Hudson, S.W., Apelian, D., International Journal of Metalcasting, Published online March 25, 2016.

Appendix B
Applications of LIBS in Molten Metal Processing

Appendix C
Clean Aluminum Processing: New Avenues for Measurement and Analysis
Appendix D
Boride Particle Detection in Al Melts via Laser-Induced Breakdown Spectroscopy

Appendix E
SiC Particle Detection in Liquid Aluminum via Laser-Induced Breakdown Spectroscopy

Appendix F
TiB₂ Particle Detection in Liquid Aluminum via Laser-Induced Breakdown Spectroscopy

Appendix G
Inclusion Detection in Cast and Wrought Aluminum Alloys via Laser-Induced Breakdown Spectroscopy

Results were presented at the following professional conferences and seminars:


1. Motivation

Over the past 40 years, various technologies have been developed to detect inclusions – typically oxide phases and particles – in molten metal. As detailed in Appendix A: “Inclusion Detection in Molten Aluminum – Current Art and New Avenues for In-situ Analysis,” published in the International Journal of Metalcasting, inclusion rich metal results in: lower metal fluidity and feeding capability during casting, lower mechanical properties (static and dynamic), increased scrap rate, reduced machinability, and poor surface finish. This inhibits cast metals, such as aluminum, from use as materials for structural applications for the automotive, aerospace, and defense industries. In order for aluminum to be used in critical applications, proper control of impurities in the melt prior to casting is essential.

Many laboratory and shop floor techniques exist to assess inclusion content in aluminum and its alloys. They range from traditional optical metallography to filtration (PoDFA, Prefil), coulter counters (LiMCA) and X-ray techniques. The study in Appendix A found that no existing techniques can measure the three facets of inclusions: composition (MgO, TiB₂, etc.), concentration (e.g. 100 vs 0.1 ppm), and size distribution. And as shown in Figure 1, many methods fall short in several areas. Many techniques are lab based, lengthy, and sample only a small amount of metal. All that can perform measurements in liquid metal have a very limited sensing range and are unable to detect particles less than 20 µm in size. In addition, they cannot determine inclusion composition. The field is in need for a quantitative, in-situ, and quick evaluation of liquid metal quality.
Figure 1 – Qualitative comparison of inclusion detection methods with respect to inspection time and detectable range of inclusions.
2. LIBS as a Technique for Cleanliness Assessment

There has been significant interest in the use of laser induced breakdown spectroscopy (LIBS) as a tool for bulk composition measurement. Similar to conventional spark optical emission spectroscopy (OES), LIBS uses a short laser pulse to form a plasma on the metal surface. The elements present in the plasma emit characteristic EM radiation, which is collected and processed by a spectrograph. Its advantages over other atomic emission techniques include: 1) LIBS can be applied to both conducting and non-conducting materials, 2) sample preparation is not necessary, 3) only an optical line of sight is required for measurement, and 4) measurements are performed in seconds. Because only a direct line of sight is needed, LIBS is attractive for interrogating materials in extreme environments, including liquid metal. A detailed review on this area of research is compiled in Appendix B: “Applications of Laser Induced Breakdown Spectroscopy (LIBS) in Molten Metal Processing,” submitted to Metallurgical and Material Transactions B. LIBS has been successfully used in monitoring dissolved elements in molten steel and aluminum. Much of the technology has been developed by R. De Saro and colleagues at the Energy Research Company, a member of the Center for Resource, Recovery, and Recycling at WPI and collaborator in this project. A schematic of their LIBS system is shown in Figure 2. A refractory probe is submerged below the metal surface and is purged with an inert gas. The gas forms a bubble that creates a constant, fresh view of the metal for LIBS to interrogate. Both the laser pulse and the emitted plasma light are transmitted through a fiber optic cable.
In addition to determining melt composition, it was postulated that LIBS could be used as a means of detecting inclusions. Because of the small size of inclusions and the presence of convection in resistance and induction furnaces, particles are constantly moving throughout the melt. If an inclusion is present where the metal was vaporized, the spectra will reveal its presence and composition. As illustrated in Figure 3, by focusing on oxygen signal in the spectra, it will vary depending on whether an inclusion is present within the sampling volume. The concentrated amount of oxygen atoms within the particle will create a spike in oxygen signal observed by the spectrometer. In addition, if an MgO particle is ablated by the laser pulse, both a spike in Mg and O signal will be observed, allowing for differentiation between inclusions of different compositions. In principle, the size
of the elemental intensity spike from a particle “hit” is proportional to the size of
the particle. A large oxide inclusion would emit a higher oxygen signal than a
small inclusion. A clean metal will have few inclusions, which would correspond
to few spikes in elemental intensity. A dirty metal, rich in inclusions, would have
many spikes. Therefore, the average elemental intensity and number of hits varies
with the concentration of inclusions present.

Figure 3 – Example of LIBS acquisition for oxide particles in molten metal.
Inclusion concentration, $X$, can be calculated, through the relationship:

$$X = \left(\frac{\text{Average equivalent concentration for hits}}{\text{sampling frequency of hits}}\right)$$

Because oxygen is insoluable in aluminum, concentration (referring to dissolved elements) is not used in the calculation. Fortunately elemental intensity can be substituted as it is directly proportional to elemental concentration. Provided the same number of shots are taken every sampling run, frequency can be substituted by the number of particle hits. For the case of sensing oxide inclusions in molten metal, an equivalent relationship, relating the product of average particle hit intensity and number of hits, can be established.

$$X \propto \left(\frac{I_O}{I_{Al}}\right) \times N_{Hits}$$

Where $\left(\frac{I_O}{I_{Al}}\right)$ is the average oxide hit intensity (normalized by aluminum intensity) and $N_{Hits}$ is the number of hits in the measurement run. As a result, the overall measurement is reduced to the product of two statistical samples. The use of particle hit average, instead of the average over all measurements, has been shown to increase the signal-to-noise ratio and sensitivity. This is further explained in Appendix B.

A strict procedure must be taken to not mistake an errant spike in background noise as an elemental peak. In a time series, where measurements are taken at a given rate, a particle hit would appear as an outlier in the resultant data set. Unlike most experiments with LIBS, the goal of particle analysis is to investigate outliers in signal. The Nalimov test, a statistical test for determining if a data point is an outlier, was used in the analysis. A flowchart of the signal processing procedures is shown in Figure 4, and is detailed in Appendix C.
Figure 4 – Flow chart of spectrum processing operations to extract LIBS data on inclusions.
3. Experiments

3.1 Experiments with Pure Aluminum and Aluminum Alloys

The possibility of using LIBS to sense inclusions was examined with proof-of-concept experiments on pure aluminum. An overview of these tests is shown in Table 3. For details, refer to Appendices C-F which are conference publications in the conferences for The Minerals, Metals, and Materials Society (TMS) and Materials Science and Technology (MS&T).

<table>
<thead>
<tr>
<th>Metal + Particles</th>
<th>Method of Addition</th>
<th>Appendix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (99.99%) + Al₂O₃</td>
<td>Bubble with air</td>
<td>C</td>
</tr>
<tr>
<td>Al (99.99%) + AlB₂</td>
<td>Al-5B master alloy addition</td>
<td>D</td>
</tr>
<tr>
<td>Al (99.7%) + SiC</td>
<td>Duralcan (SiC) addition</td>
<td>E</td>
</tr>
<tr>
<td>Al (99.99%) + TiB₂</td>
<td>Al-XTi-YB master alloy addition</td>
<td>F</td>
</tr>
</tbody>
</table>

A schematic of the experimental apparatus, designed by the Energy Research Company, for this and subsequent studies on pure aluminum is shown in Figure 5. Initial experiments (Appendix C) consisted of pure aluminum with varying amounts of oxide inclusions, introduced by bubbling air. To build upon the results found in this first experiment, synthetic inclusions were added to pure aluminum in the form of master alloys or metal matrix composites and then interrogated with LIBS. These particles included AlB₂ (Appendix D), SiC (Appendix E), and TiB₂ (Appendix F). Specifics on the equipment, software, and materials used are disclosed in the appendices.
Figure 5 – Schematic of LIBS apparatus for experiments on pure aluminum.
With sufficient data gathered from experiments with pure aluminum, tests on industrial alloys were performed with a modified probe. These experiments are detailed in Appendix G: “Inclusion Detection in Cast and Wrought Aluminum Alloys via Laser-Induced Breakdown Spectroscopy,” submitted to Metallurgical and Material Transactions B. A schematic of the apparatus is displayed in Figure 6. Alloys tested included common compositions for cast products (A356, A380, A206) and wrought products (3104, 5182, 7050). Al₂O₃ inclusions were introduced through 5 g metal-matrix composite (MMC) additions. The size of the melt was 13.6 kg (30 lbs). Repeatability and depth trials were also performed on A356 with 15 g of MMC added.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Method of Addition</th>
<th>Appendix</th>
</tr>
</thead>
<tbody>
<tr>
<td>A206 + Al₂O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A356 + Al₂O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A380 + Al₂O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3104 + Al₂O₃</td>
<td>Duralcan (Al₂O₃) addition</td>
<td>G</td>
</tr>
<tr>
<td>5182 + Al₂O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7050 + Al₂O₃</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A – Inert Gas Tank  
B – Flowmeter  
C – Copper Tubing  
D – Probe (BN Coated)  
E – Induction Furnace  
F – Graphite Crucible (BN Coated)  
G – Manual Forklift  
H – Coolant Line  
J – Power Supply Line  
K – Fiber Optic Cable

Figure 6 – Schematic of LIBS apparatus for experiments on aluminum alloys.
3.2 Summary of Findings

3.2.1 Feasibility Tests
Three different melts of pure aluminum (2.5 kg) were prepared with varying cleanliness. Oxide inclusions were introduced by bubbling dry air directly in the melt. Initial experiments showed that LIBS could differentiate between relatively dirty and clean aluminum by monitoring oxygen signal and how it varied over the course of many laser pulses. As shown in Figure 7, the frequency of oxygen signal (normalized by aluminum signal) increased as the metal became more and more inclusion rich. This was compared to and verified by direct observation of inclusions through X-ray radiography.

![Figure 7](image)

**Figure 7** – Normalized oxygen peak intensity vs. laser shot number for a) Base Al; b) 50% Diluted Dirty Al; c) Dirty Al
3.2.2 AlB₂ Tests
By performing LIBS on melts with 0.01, 0.05 and 1.0 wt% B, it was found that LIBS could detect fine AlB₂ particles in a pure Al matrix. This demonstrated that, in certain scenarios, the ability for LIBS to detect particles is limited on by the thermodynamics and kinetics of the system. In addition, the particles observed through metallography were all less than 5 μm in size. Such particles would not be observed with current in situ technologies.

3.2.3 SiC Tests
Synthetic inclusions, in the form of SiC particles, were added to molten aluminum through dilution of an Al+SiC metal matrix composite. Volume fractions ranging from 0 to 50 ppm were analyzed with LIBS and compared to solidified samples through metallography. It was found that over the course of many laser measurements, LIBS was able to detect SiC particles by monitoring Si signal. A linear relationship between the hit number-hit intensity product and volume fraction was observed. All SiC particles observed were less than 20 μm in size, further showing that LIBS may be more capable than current technology in sensing particles less than 20 μm.

![Figure 8](image)

**Figure 8** – a) SiC particle size distribution determined from metallography; b) calibration curve relating SiC volume fraction and LIBS data
3.2.3 TiB$_2$ Tests

TiB$_2$ particles, through the addition of Al-Ti-B master alloys, were introduced to molten aluminum and probed with LIBS. Using the same procedures as the experiments involving AlB$_2$ particles, observance of the B emission line indicated that a boron containing particle was ablated by the laser. A concurrent spike in Ti intensity meant that a TiB$_2$ particle was observed. The Nalimov test was used to determine if a spike in Ti was indeed from a particle or an errant fluctuation. Calibration curves were developed for Ti and B with the compositional ranges for grain refinement (Figure 9). Nearly all TiB$_2$ particles found through microanalysis were less than 6 µm in size. These tests show that LIBS can be used for detecting particles that are intentionally added to the melt and, again, LIBS can detect particles in a size range that current technology cannot detect.

![Figure 9 – Calibration curves relating TiB$_2$ volume fraction to LIBS data for Ti and B.](image-url)
3.2.4 Al₂O₃ Tests with Cast and Wrought Alloys

Al₂O₃ particles were introduced to common cast and wrought alloys through dilution of an Al-Al₂O₃ metal matrix composite. For all alloys tested, a linear relationship was observed between volume fraction of oxide particles, found through microanalysis, and oxygen intensity, determined from LIBS. An example of the spectral signature from an oxide hit is shown in Figure 10. More than 90% of inclusions were found to be less than ten micrometers in size and volume fraction ranged from 0.5-10 parts-per-million – typical values encountered in cast alloys. Depth and repeatability performed on A356 gave results that were found to be, with 95% confidence, not statistically significantly different. This is attributable to the fact that an induction furnace was used. Electromagnetic stirring within a relatively small melt promoted particle mixing homogeneity.

Figure 10 – LIBS spectra of molten 7050 with a) no oxide hit and b) with an oxide hit.
3.2.5 Sensing Volume Estimations

During experiments, it was clear that the size of the sampling volume during each laser spark significantly influences what inclusions can and cannot be measured. With liquids, it is difficult or impossible to measure by direct observation. However, it can be approximated through an energy balance relating the energy contributing to ablation to the enthalpy in heating to the material to the plasma temperature. The derivations and assumptions made can be found Appendix B and C. It was determined that the sampling volume is heavily influenced by laser energy (Figure 11) and almost unaffected by composition (Table 5).

![Figure 11 – First order estimation of sampling volume diameter as a function of laser energy for pure, liquid aluminum at 800°C.](image)

**Table 5: Estimated sampling volume and equivalent spherical diameter for pure aluminum and alloys tested under a 330 mJ laser pulse energy.**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Sampling Volume ((10^6 , \mu m^3))</th>
<th>Equivalent Spherical Diameter ((\mu m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al</td>
<td>1.46</td>
<td>140.7</td>
</tr>
<tr>
<td>A356</td>
<td>1.47</td>
<td>140.9</td>
</tr>
<tr>
<td>A380</td>
<td>1.51</td>
<td>142.3</td>
</tr>
<tr>
<td>A206</td>
<td>1.50</td>
<td>141.9</td>
</tr>
<tr>
<td>3104</td>
<td>1.47</td>
<td>141.0</td>
</tr>
<tr>
<td>5182</td>
<td>1.46</td>
<td>140.6</td>
</tr>
<tr>
<td>7050</td>
<td>1.54</td>
<td>143.2</td>
</tr>
</tbody>
</table>
4. Conclusions from Articles

Current laboratory and shop floor techniques that exist to assess inclusion content cannot measure the three facets of inclusions: composition, concentration, and size distribution. The field is in need for a quantitative, in-situ, and quick evaluation of liquid metal quality. The presented work has introduced the use of laser-induced breakdown spectroscopy (LIBS) as an inclusion measurement technique.

Molten aluminum and aluminum alloys with varying amounts of added inclusions were analyzed using in-situ LIBS. It has been shown that LIBS can detect particles of different compositions (Al₂O₃, SiC, TiB₂, etc.) by monitoring the emission lines of elements of interest over many measurements. A conditional analysis, employing the Nalimov test for outliers, was developed to identify and collect laser shots that hit an inclusion. By direct observation of the inclusions through metallography and automated particle analysis, calibration curves were developed that related inclusion volume fraction and the average hit intensity multiplied by the number of hits. Volume fractions observed were within the ranges typically found in foundries. In addition, LIBS was able to detect particles less than 20 µm in size. This cannot be matched by current coulter-counter (LiMCA) and ultrasonic (MetalVision) technologies.

The ability for LIBS to monitor melt cleanliness as well as composition opens the door for metal producers and foundries to more accurately control the quality of their products. With more precise control of the metal that goes into cast and wrought components, producers can expect:

- Better grain refinement control and liquid metal feeding capability
- Lower scatter in tensile, fatigue, and other damage properties
- Faster response time if the melt is out of specification
• Lower frequency of reject castings

These benefits save money and time for metal producers and a more reliable product for end users. The presented work pushes light metals forward to be a better substitute for ferrous materials in the automotive and aerospace industries. Detailed in section 6, this work has opened several venues of investigation and provides opportunities for additional research and development.

5. Recommendations for Future Work

The work has involved laboratory-scale experiments in a controlled environment. It must be validated in an industrial environment to find out where it has optimum utility. As of the writing of this thesis, beta trials at ACRC members have been performed. Data analysis and microanalysis are ongoing as well as transfer of the technology to the Energy Research Company for further development.

To understand the capabilities of LIBS, additional research must also be carried out on additional particle concentrations and size distributions. The calibration curves drawn from this work should be further expanded to fully understand the limits of detection. The ability to detect dissolved hydrogen (another important quality detractor) in molten aluminum should also be explored.

In principle, LIBS may able be able to directly measure inclusion size. Derived by D. Hahn and colleagues, a relationship between the equivalent concentration and particle size can be expressed as:

\[ D_i = \left( \frac{6 C_i V_p}{\pi \rho_i} \right)^{1/3} \]

where \( D_i \) is the equivalent spherical diameter of one particle, \( C_i \) is the equivalent mass concentration of the particle, and \( \rho_i \) is the particle’s density. Because
elemental intensity is proportional to concentration, inclusion size is proportional to the cube root of intensity.

\[ 3 \sqrt[3]{I_i^\lambda} \propto D_i \]  \hspace{1cm} (4)

Whether this relationship holds in practice must also be confirmed.

Another area of future research is an in-depth investigation of sampling volume. Because the sampling volume is essential in determining the overall sensing capabilities of LIBS, the presented work provided a first order approximation with respect to laser pulse energy. Further experiments ought to be performed to verify and refine the model. It would also be of academic and industrial interest for additional research on the effect of alloying elements, temperature, and environment on sampling volume.
Journal Manuscripts & Conference Publications

**Appendix A**
Inclusion Detection in Molten Aluminum – Current Art and New Avenues for In-situ Analysis

**Appendix B**
Applications of LIBS in Molten Metal Processing

**Appendix C**
Clean Aluminum Processing: New Avenues for Measurement and Analysis

**Appendix D**
Boride Particle Detection in Al Melts via Laser-Induced Breakdown Spectroscopy

**Appendix E**
SiC Particle Detection in Liquid Aluminum via Laser-Induced Breakdown Spectroscopy

**Appendix F**
TiB$_2$ Particle Detection in Liquid Aluminum via Laser-Induced Breakdown Spectroscopy

**Appendix G**
Inclusion Detection in Cast and Wrought Aluminum Alloys via Laser-Induced Breakdown Spectroscopy
Appendix A

*Inclusion Detection in Molten Aluminum – Current Art and New Avenues for In Situ Analysis*

INCLUSION DETECTION IN MOLTEN ALUMINUM: CURRENT ART AND NEW AVENUES FOR IN SITU ANALYSIS

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DOI 10.1007/s40962-016-0030-x

Abstract

In order for light metals to meet the demands for critical applications in the automotive and aerospace industries, tight control over the composition and cleanliness of the metal must be achieved before casting. Melt cleanliness manifests primarily in the amount of inclusions present. A review of the state of the art in detecting and quantifying solid particle inclusions is given. Quick analysis of melt composition and quality, carried out in situ, is of great value in casting operations. Such quick measurements in the liquid alleviate analyzing samples in the solid state and thus increase productivity. The use of laser-induced breakdown spectroscopy as a new tool for quantifying melt cleanliness in situ is discussed.

Keywords: inclusions, cleanliness, oxides, quality

Introduction

Light metals, aluminum and its alloys in particular, have been the source of significant interest as materials for structural applications for the automotive, aerospace, and defense industries. The appeal of aluminum comes from its high specific strength, thermal conductivity, and corrosion resistance, which translate to reduction in vehicle weight and fuel consumption. In order for light metals to continue to replace ferrous metals for such applications, proper preparation of the molten alloy prior to casting or extrusion is essential. This entails control over the chemical composition and, more importantly, its cleanliness.

In general, the cleanliness of aluminum alloys primarily refers to the concentration of solid particle inclusions (exogenous and intrinsic), dissolved hydrogen, and residual elements to a lesser extent. When the quantity of any of these detractors exceeds a certain threshold limit, dictated by the intended use of the product, they will lead to unacceptable performance and early failure. Inclusions have a significant influence on the properties of aluminum. It has been shown that inclusion-rich metal results in lower metal fluidity and feeding capability during casting, lower mechanical properties, increased scrap rate, decreased machinability, and poor surface finish. There are several sources of these impurities, including the electrolysis process during primary aluminum production, surface turbulence, pouring atmosphere, and the interactions between the molten metal with alloying elements and refractory materials. Melt quality can be controlled by the removal of these elements and particles. Therefore, various technologies have been developed over the past 40 years to measure and remove these impurities.

The application of inclusion reduction techniques during casting can help limit the size and amount of inclusions remaining in the molten metal and its products. Such advances include rotary degassing and fluxing as well as ceramic foam and deep bed filtration. Advances in counter-gravity casting and modeling have allowed for optimized casting processes with minimal surface turbulence. Nonetheless, the difficulty of quantifying cleanliness, differentiating “clean” from “really clean” metal, has still not been fully realized. Chemistry, concentration, and size distribution of inclusions are particularly important to producers of clean metal. Depending on the application, an inclusion of 5–10 microns may be insignificant or the root cause of a rejected casting.

This paper will review and compare current techniques and methods of detecting and quantifying solid particle inclusions. It will also discuss experimental techniques that could be used to achieve the goal of in situ monitoring of inclusion content.
Inclusion Sources

Inclusions are defined as any exogenous solid- or liquid-phase particles present above the liquidus temperature of the molten metal matrix. Many kinds of inclusions can be present in the melt, including furnace dross, salts, and unmelted elements. The amount of unwanted particles in molten metal can be substantial. As can be seen in Figure 1, a small concentration of inclusions can yield a high number count. For example, 1 ppm of 40-micron inclusions results in 4000 particles in one kilogram of metal. Such particles can be exogenous or form in situ as seen in Table 1. They can be further characterized by their composition, size distribution, morphology, and phase (Figure 2). The number of inclusions present depends on a number of factors, including initial melt composition, solidification rate, and pouring atmosphere.4–9

The most common inclusions in aluminum are oxide particles and films. They are most commonly formed by direct oxidation in air or by reaction with water vapor:

\[
\begin{align*}
2\text{Al} + \frac{3}{2}\text{O}_2 & \rightarrow \text{Al}_2\text{O}_3 \\
2\text{Al} + 3\text{H}_2\text{O} & \rightarrow 3\text{H}_2 + \text{Al}_2\text{O}_3
\end{align*}
\]

Equations 1 and 2

Oxides can also form via alumino-thermic reactions with oxides of other metals, such as iron or silicon, contained in tools and refractories. Aluminum and its alloys oxidize readily in both the solid and molten states to provide a continuous self-limiting film. The rate of oxidation increases with temperature and is substantially greater in molten than in solid aluminum. The reactive elements contained in aluminum alloys such as magnesium, strontium, sodium, calcium, beryllium, and titanium are also factors in oxide formation. In both the molten and solid states, the oxide formed at the surface offers benefits in self-limitation of further oxide growth. It also acts as a barrier to hydrogen diffusion, another melt quality detractor. However, the low viscosity of liquid aluminum allows for induced turbulence either by handling or pouring. Surface turbulence results in the entrainment of oxide particles and films.\(^5\) \(\text{Al}_2\text{O}_3\) films can also include oxides such as SiO\(_2\), MgAl\(_2\)O\(_4\), MgO, and others depending on the alloy.\(^11\) Although oxide inclusions can sink, they often rise too and remain at the melt surface.\(^9\) The high surface-to-volume ratio and poor wettability of oxide films in Al act as driving forces for inclusions to remain close to a free surface as well as cause their agglomeration.\(^12\)

Spinel inclusions arise from melting scrap as well as the addition of magnesium to the holding furnace. MgO, due to its lower free energy of formation compared to \(\text{Al}_2\text{O}_3\), tends to form preferentially in alloys with more than 0.5 wt% Mg. In addition, adding low purity Mg can create spinels and non-metals such as MgS and MgF\(_2\).\(^13\)

Silicates can originate from the erosion of ceramic materials (used in the melting operation) as well as dissolved Si reacting with the atmosphere. Refractory particles can agglomerate and form complex oxides like \(\text{Al}_2\text{O}_3\)-SiO\(_2\)-CaO.\(^14\) Carbides such as SiC and Al\(_4\)C\(_3\) often come from pyrolyzed hydrocarbons in recycled aluminum melts as well as residual coolants and oils in recycled machining chips and pot cells primary in Al smelting.\(^9\) Nitrides can come from overly degassing with nitrogen gas as well as the addition of magnesium as an alloying element. Mg\(_3\)N\(_2\) inclusions in the magnesium can react with the aluminum to form AlN. Other particles such as MgF\(_2\) and MgS can appear in Al from sub-par magnesium.\(^15\)

Intermetallic compounds can arise from a variety of sources including residual elements (from smelting, melting and remelting), alloying, and grain refining. For example, grain refiners like TiB\(_2\) and dissolved elements, such as Fe and Ni, can create unwanted aluminides and borides. Precipitation of such phases is often only found in die casting, where processing temperatures are lower than the melting points of many intermetallics.\(^8,16,17\)

Liquid-phase inclusions can also form in molten aluminum due to fluxing or chlorinating. They are often in the form of molten salts (CaCl\(_2\), NaCl, MgCl\(_2\), and KCl) and can also contain fine fluoride particles (NaF, AlF\(_3\), and CaF\(_2\)).\(^18,19\)

Effect of Inclusions on Properties

Solid inclusions remaining in the metal can result in a plethora of product defects. Inclusions reduce mechanical properties by acting as stress concentrators and allow for cracks to form at their interfaces. This can lead to rapid crack propagation, large crack paths, and ultimately early failure. Properties such as elongation, yield stress, and fracture toughness have been observed to decrease when a

![Figure 1. Relationship between inclusion concentration (number/kg) and particle diameter for varying concentrations.]
high percentage of inclusions is observed on the fracture surface. An inclusion contributing to 1% of the fracture area can cut elongation in half.\textsuperscript{20–22} Fatigue properties are also severely affected by the presence of inclusions. Because they tend to act as crack initiators, fatigue life curves typically decrease as inclusion content increases. In addition, small inclusions, too small to act as crack initiators, will contribute to fatigue crack propagation.\textsuperscript{23} In addition to being crack initiation sites, oxide inclusions can act as heterogeneous nucleation sites for hydrogen pores. This promotes voids and hydrogen porosity, further reducing static and dynamic properties.\textsuperscript{24,25} With regard to other properties, it has been well documented that inclusions can negatively influence melt fluidity,\textsuperscript{26,27} as well as the machinability and surface finish of castings. In production of aluminum sheet and foil, inclusions have been known to cause holes and tears.\textsuperscript{28}

### Cleanliness Measurement Methods

#### Metallography

Traditional metallography involves the physical examination of ingot slices to determine the presence and type of inclusions. The sample is cut, polished, and microscopically examined. The prepared surface can then be analyzed in a variety of ways. Published standard comparisons exist, but typically only for steels.\textsuperscript{29} This is mainly due to the extremely low volume fraction of inclusions in aluminum preventing the ability to differentiate between clean and very clean metal. Charts also, at most, provide a semi-quantitative measure of melt cleanliness.

The use of software-based image analysis systems makes it possible to obtain quantitative analyses of inclusions. Provided the image processor has a high enough resolution, image analysis can quantify spatial distribution and clustering of inclusions in addition to size distribution and area fraction.\textsuperscript{30} There is a variety of statistical analyses that can be performed to characterize features of inclusions.

Once scanned, the number of inclusions per unit area can be counted. The degree of clustering of the particles can be described by the standard deviation:

\[
\sigma = \sqrt{\frac{1}{n} \sum (N_A - \bar{N}_A)^2}
\]

\textbf{Eqn. 3}

---

\begin{table}
\centering
\caption{Inclusions Observed in Aluminum Alloys\textsuperscript{1,4,6–8,14,16–19}}
\begin{tabular}{|l|l|l|l|}
\hline
Phase & Morphology & Size range (\(\mu\)m) & Impurity elements also commonly present \\
\hline
\hline
Oxides  &  &  &  \\
MgAl\(_2\)O\(_4\) (spinel) & Particles, films & 0.1–5000 & N, Na, K, Ca, Si, Zn and/or Fe  \\
Al\(_2\)O\(_3\) (corundum) & Particles, films & 0.1–5000 & N, Na, Mg, Si, Zn, Fe, Ca, K, Cl and/or F  \\
MgO & Particles, films & 0.1–5000 & –  \\
SiO\(_2\) & Particles, clusters & 0.5–30 & K, Ca, Na and/or Al  \\
CaO & Particles & <5 & –  \\
Calcium silicates (Ca, Si, O) & Particles, clusters & 10–100 & K, Na  \\
Potassium silicates (K, Si, O) & Particles, clusters & 10–1000 & Na, Ca, Al, Mg and/or Ti  \\
\hline
Carbides &  &  &  \\
Al\(_4\)C\(_3\) & Particles, clusters & 0.5–25 & –  \\
Al\(_2\)O\(_4\)C & Particles, clusters & 0.5–25 & –  \\
SiC & Particles & 0.5–5 & –  \\
\hline
Nitrides &  &  &  \\
AlN & Particles, films & 10–50 & –  \\
\hline
Borides &  &  &  \\
TiB\(_2\) & Particles, clusters & 1–30 & V, Zr, and/or Cr  \\
AlB\(_2\) & Particles & 0.1–3 & –  \\
\hline
Others &  &  &  \\
Chlorides and salts (CaCl\(_2\), NaCl, MgCl\(_2\)) & Liquid droplets & 0.5–1 & –  \\
Ultrafine gas bubbles (Ar, N\(_2\)) &  &  &  \\
Intermetallics (TiAl\(_3\), TiAl, NiAl, Ni\(_3\)Al, etc.) & Particles, rods, clusters & 10–100 & –  \\
\hline
\end{tabular}
\end{table}
where $N_A$ is the observed number of particles per unit area in a given field of view and $N_A$ bar is the average number of inclusions per unit area in $n$ fields of view on the sample. If the inclusions are evenly distributed, the standard deviation is small. If there is significant clustering, standard deviation increases. To compare samples with different concentrations or number densities, the coefficient of variation ($\sigma$ normalized by $N_A$ bar) should be used.

Area fraction can also be easily found by image analysis. Similar to number density calculations, the standard deviation and coefficient of variation for area fraction can be determined. If the special distribution of particles is homogeneous, then $\sigma$ and the coefficient of variation are small. Nearest neighbor subdivision of the sample surface into a grid, or creating a Dirichlet tessellation, can analyze spacing and spatial distribution.\(^\text{31}\)

In addition to physical characteristics of inclusions, each particle can be analyzed chemically via energy-dispersive spectroscopy (EDS) in an electron microscope. The combination of particle chemistry, concentration, and size distribution allows for a complete understanding of the inclusions present in a casting process.

Metallography of melt samples can give an excellent view into the nature of inclusions present, but it is limited in several ways. Because samples need to be taken from the melt, and because preparing and analyzing each sample requires some time, this method only yields a small sample size. Although image software and other tools exist to

Figure 2. Micrographs of typical inclusions in aluminum castings.\(^{\text{1}}\)

Figure 3. A K-mold apparatus.\(^{\text{34}}\)
make analysis easier, there is still a delay between taking the sample and obtaining results. In addition to time, metallography only looks at a cross section of the sample. The small amount of metal that can be analyzed cannot be fully representative of a large casting. The size and morphology of inclusions present cannot be fully realized because only a small area is examined, forcing researchers and technicians to quantify the amount by square millimeter of inclusions per kilogram of melt. Nonetheless, certain facets of the size distribution of particles in the bulk melt can be predicted. The methods of predicting the largest inclusion in a large volume of metal is well described and documented in a review paper on clean steels by Atkinson and Shi. Such methods include extrapolation of the size distribution function, statistics of extremes, and generalized Pareto distributions.

K-mold

Metal cleanliness has often been assessed by determining their mechanical properties; hence, fracture tests have also been used for inclusion assessment. The most well-known fracture test for aluminum is the K-mold test, invented by Sanji Kitaoka at the Nippon Light Metal Ltd in 1973. Liquid aluminum (approx. 400 g) is poured into the mold and produces a small casting consisting of a flat plate with four notches that acts as fracture points. A K-mold apparatus is seen in Figure 3.

The K-mold test involves casting one or more of these notched plates. The plate is then broken at each notch. The surfaces are examined either by eye or a microscope. The presence of large inclusions or inclusion clusters will induce failure. Oxides are readily detected on the fracture surface due to their visual difference in contrast compared to the fine aluminum matrix produced by rapid solidification in the K-mold.

The cleanliness level of different pots can be evaluated by comparing the number and size of inclusions on the fracture surface. The visual observation of inclusions on the fracture surface is used to determine a \( K \) value for the batch and compared to a preset standard. This value is calculated as:

![Figure 4. Schematic of the X-ray transmission process. The differences between \( I_1 \) and \( I_2 \) result in contrast between two phases.](image)

![Figure 5. A schematic of the basic principles of ultrasound. An inhomogeneity, such as an inclusion, will reflect the transmitted pulse back to the surface.](image)
$K = \frac{s}{n}$  Eqn. 4

where “$K$” is the K-mold value, “$n$” is the number of examined samples, and “$s$” is the total number of inclusions found in $n$ pieces.\(^3\)

The main advantage of a K-mold is that it allows for easy characterization of the larger inclusions and is good for real-time testing of macroscopic defects (coarse inclusions, gross oxides, and gas bubbles). However, the volume tested is a small part of the bulk and the statistical evaluation of the results is difficult. As a result, this method is not as sensitive for very clean melts and is accurate only for large inclusions.

X-ray Radiography

X-ray radiography is a standard non-destructive technique for determining casting quality. In addition to detecting inclusions and pores, radiography is used to find other flaws such as internal cracks, shrinkage, confluence welds, and hot tears. Radiographs of a sample (or the entire cast part) are analyzed with respect to standardized images (ASTM E155-10). The basic operating principle of radiography involves how certain solid phases absorb X-rays differently. As an X-ray travels through matter, the way it interacts with the material depends on the material’s refractive properties. An example schematic displaying the concept is seen in Figure 4. If two phases are present in the material analyzed, there will be a difference in attenuation leading to image contrast.

Although radiographs allow for detection of inclusions as well as morphology and relative position in castings, it is limited by its inability to generate three-dimensional images and determine particle chemistry. The process is also lengthy and is typically used to analyze parts once they have been cast. Even then, there are limitations with respect to casting thickness. The ability of X-rays to transmit through metal is a function of its thickness. Thick sections of castings cannot be fully interrogated, unless high-energy X-ray sources are used. As a result, only defects larger than 50–100 microns can be detected unless microradiography on small, thin samples is used.\(^3\)

X-ray Tomography

X-ray tomography (XRT) is a more advanced use of X-rays. First used for medical applications, 3D visualization of microstructures by XRT has been successfully performed for many other metallurgical studies, such as Pb-free solder joints, powder metallurgy steels, and metal matrix composites. By analyzing radiographs taken around a single axis of rotation, cross-sectioning images can be compiled to create a 3D image. This eliminates cross-sectioning and allows for superior resolution and image quality with minimal sample preparation. This method requires high-energy, monochromatic X-rays to form the 3D composite image.

Images generated can have a similar resolution to that seen in metallographic samples. Since the sample does not have to be cut and polished, analysis time can be reduced. With proper imaging software, the morphology, size distribution, position, and volume fraction of inclusions can be accurately determined within the sample.\(^3\) Because different phases will have different X-ray absorption coefficients, chemistry of inclusions can be determined in principle. However, in practice, the small difference between X-ray absorbance coefficients of most oxides prevents XRT from being used as a reliable method for inclusion identification. One drawback to tomography is the small sample size (similar to metallography). Even with a decreased sample preparation time, many samples must be taken to get meaningful statistics on cleanliness in the bulk melt. Another drawback is the cost of tomography; at present, it is more of a laboratory-based detection method.

Ultrasound

Ultrasound has been widely used to probe substances via pulsed sound waves. Once such technique used for microanalysis is scanning acoustic microscopy (SAM).\(^4\) Similar to sonar, a sound pulse is generated by a transducer toward the sample surface. The pulse then propagates into the bulk of the sample. When the pulse encounters a feature (like the inclusion in Figure 5), a portion of the pulse is reflected back. The reflected signal, read by the transducer, will contain a transient peak whose magnitude will correspond to the size and shape of the feature. The probe scans over the entire sample area to generate the acoustic image. Depending on the mechanical and acoustic properties of the matrix and internal features, certain amplitudes will be
reflected. This allows SAM to detect features such as phase and grain boundaries, voids, pores, cracks, and inclusions.

For solid materials, sound pulses in the MHz and GHz range are used. In a study on 319 aluminum by Meav et al., microstructural features such as eutectic Si, shrinkage porosity, and dendrite arms were observed. For resolution on the order of 50–100 microns, only a penetration depth of a few millimeters was possible. Although SAM has a resolution comparable to optical microscopy without the need for sample preparation, the fact that penetration is limited depending on the desired resolution is the main drawback for this technique.

The same principles can be applied to molten metal. In situ ultrasound has been explored as early as the 1960s by Pitcher and Young and was further developed by Alcan, Alcoa, and Reynolds Aluminum throughout the 1980s. More recently, using research by Mountford and Sommerville at the University of Toronto, an ultrasonic probe to detect and measure inclusions in liquid metal was developed by Metalvision Manufacturing Canada Ltd. The probe, marketed as the MV20/20, has separate transducers to emit and collect sound waves. The transmitter pulses at a rate of 100 Hz allows for thousands of measurements to be taken in minutes. Because the transmitter and receiver are at an angle to each other, there is an effective sensing zone within the molten metal. This size of this region is not reported in the literature. Metalvision produces portable models and systems that can be integrated for crucibles or a launder system. The MV20/20 outputs three pieces of information: (1) largest particle size, (2) number of particles, and (3) a qualitative cleanliness value. The amplitudes of the reflections from particles in the metal determine inclusion size. However, the machine can only detect particles between 20 and 160 μm due to factors such as signal to noise and the slow degradation of the probe materials. The number count of inclusions is given per 1000 measurements. In a comparative industrial trial reported by Metalvision, the MV20/20 cleanliness values correlate well with PoDFA results.

**Filtration Methods**

Pressure filtration works by forcing a molten aluminum sample under pressure through a fine filter, which traps inclusions. The inclusions are concentrated 5000–10,000 times on the filter surface, which can then be analyzed metallographically. Although samples taken from the melt are relatively small (1–2 kg), concentration of inclusions offers reliable, industrially accepted results. There are several industrial measurement devices that are all based upon this principle, including PoDFA, LAIS, Prefil Footprinter, and Qualiflash; these are reviewed below.

**PodFA**

The porous disk filtration analyzer (PodFA) (Figure 6), manufactured by ABB Inc., is a shop floor technique in which 2 kg of melt is ladled into a preheated crucible. The unit draws the molten sample through a small ceramic filter using a vacuum; this traps the inclusions for later analysis. The test is stopped when approximately 1.5 kg of the metal has been filtered. Since the filter disk must be sliced for study, the concentrations of inclusions are given in mm²/kg.
of melt. A number count of inclusions per kg of metal can also be tabulated. A curve generated during this test shows the filtration rate, which can also be used as cleanliness metric with PodFA. Metallographic analysis results in a classification of inclusions (MgO, spinels, borides, carbides, etc.).

Although this test is inexpensive to set up, it has several disadvantages. Samples are time-consuming to gather and expensive to analyze. Results will not be available for at least 24 h and can take up to 5 days. As a result, PoDFA is often used to optimize a process and/or to distinguish very dirty metal (>1 mm²/kg) and relatively clean metal (<1 mm²/kg).

**LAIS**

The liquid aluminum inclusion sampler (LAIS), developed by Union Carbide, is similar to PodFA but with a more direct sampling method. As seen in Figure 7, the apparatus is submerged within the melt. The molten metal is then pumped through a sampling cup with ceramic frit. Once the steel tube to the vacuum pump is filled, the assembly is placed on a chill block to allow for unidirectional cooling. A typical LAIS sample is a 1.7 in. by 0.7 in. cylinder. Once removed, it is then microscopically analyzed. Like PodFA, the units for inclusion content are mm²/kg. The advantage of this procedure is that it samples directly in the melt and can be manipulated to take measurements at different depths and locations.

**Prefil Footprinter**

The Prefil Footprinter, like PoDFA and LAIS, forces a melt sample through a small filter (Figure 8a). It then measures the flow rate as a metric for metal quality. A fixed volume of metal is poured into the test crucible and filtered at approximately 10–12 psi. A load cell in the collector mold determines the mass flowing through as a function of time (Figure 8b). The shape of the curve is dependent on the mixture of inclusions present. Very clean metal flows quickly giving a steep, straight line in the output graph. The software allows the fluidity curve generated to be compared with previous data and standards developed by the manufacturer. If necessary, the filter can be examined metallographically. Although the Prefil gives a quick readout, it is highly dependent on sampling technique of the user, melt temperature, and gives only a semiquantitative view of melt cleanliness. Concentration and size distribution cannot be directly determined from a flow rate curve.

**Qualiflash**

The Qualiflash technique, like Prefil, uses the mass of metal passing through a filter as a means of assessing cleanliness (Figure 9a). A fixed volume of melt is filtered through a ceramic disk and poured into a 10-stepped ingot mold. The dirtier the melt, the fewer steps filled. The end result is a cleanliness rating based on the number of steps filled known as the Q level (Figure 9b). Like the Prefil, it yields a quick result, but is highly dependent on sampling technique, melt temperature, and gives only a semiquantitative measurements.

**Centrifugation**

Using a hot centrifuge to analyze particles in metals has been used as early as the 1950s. By taking advantage of the differences in density between inclusions and the metal matrix, the particles can be concentrated and analyzed similarly to pressure filtration techniques. As derived by
Siemensen, the smallest possible particle to reach the bottom of the spinning crucible has a defined size:

$$d = \left[ \frac{45\eta \ln\left( \frac{a}{r} \right)}{8g^2 x f^2 (\rho_p - \rho_M) \left( t - \frac{T}{\pi} \right)} \right]^{1/2}$$  \hspace{1cm} \text{Eqn. 5}

where $\eta$—viscosity coefficient of the liquid at time $t \approx 0.2(T(t) - T_M)^{-0.25}$, $r_B$—distance between the axis of rotation and the bottom of the melt, $r_T$—distance between the axis of rotation and the top of the melt, $g$—gravitational acceleration, $a$—relative speed of the particle to that of a sphere with the same volume, $f$—rotational frequency, $\rho_p$—density of a particle, $\rho_M$—density of the melt, $t$—time, $\tau$—time to reach rotational frequency $f$.

Siemensen found, in centrifuge experiments on molten aluminum, inclusions down to 0.5 μm could be forced to the bottom of the crucible. In addition to inclusions, both stable and unstable intermetallics are also forced to the bottom and can be analyzed using standard metallographic techniques.\(^{16}\) Although centrifugation is a relatively simple way to concentrate inclusions, the sample size is quite small. Experiments using this technique have analyzed samples ranging from 100 to 200 g.\(^{16,52}\)

### Electrochemical Dissolution

The use of acid etchants has been used extensively in metallography to dissolve the matrix and retain intermetallic and other secondary phases. The same approach can be used to analyze inclusions by using a strong acid (HCl, HF, or HNO\(_3\)) to completely dissolve the metal matrix. The oxides will, in principle, not dissolve. The particles remaining in solution can be analyzed by a Coulter counter.\(^{17}\) However, complete dissolution is quite lengthy. Siemensen found that it took approximately 7 min to dissolve 20 g of Al–5%Ti–1%B at room temperature using a 20% HCl solution. Assuming the dissolution rate is constant, it would take approximately 6 h to dissolve 1 kg of the same metal. In addition, undissolved and partially dissolved intermetallics as well as surface oxides will skew particle size results in the Coulter counter. Because of the time required and delicate nature of this method, it can only be performed in the laboratory.

### Electrical Resistivity

Another method that is common in the metals processing field is the use of electrical resistivity to sense inclusions, similar to that of a Coulter counter for aqueous solutions. In work done by Doutre and Guthrie in the 1970s and 1980s, technology was developed that allowed molten aluminum to be drawn through a small aperture in the presence of a large DC current. Because inclusions are non-conductive, the resistances through the aperture increases as particles pass through. Because the voltage measurements taken are proportional to the size of the inclusions, and that the amount of liquid drawn through could be quantified, a real-time volumetric distribution of particles could be measured.\(^{54}\) A schematic of this process can be seen in Figure 15. The LiMCA (liquid metal cleanliness analyzer), marketed by ABB Inc. and currently on its third generation, is the most widely used embodiment of this technique.\(^{28}\)

The LiMCA probe consists of a quartz tube with a small orifice approximately 300 μm in size. As shown in Figure 10, electrodes are placed inside and outside the tube. Liquid metal is drawn through the orifice to collect data. A typical sample volume is approximately 7.5 mL (17.5 g). The length of the tube is fixed, and therefore, the sampling...
position is fixed. However, longer quartz tubes, allowing for deeper sampling, have been developed for experimental purposes.55

The resolution of LiMCA is limited by the background electrical noise and the orifice diameter. In general, LiMCA can theoretically capture particles between 20 and 300 μm. In practice, a particle range of 20–100 μm is more common as orifice holes may become easily blocked.18 It has been estimated that as many as 60 % of the total inclusions in a given melt may remain undetected.57

Reduced Pressure Test

The reduced pressure test (RPT) provides qualitative and semiquantitative information of overall melt cleanliness. A molten sample of 100–200 g is solidified under a reduced pressure of 26 mmHg. As a result, formation and growth of hydrogen pores is significantly enhanced because of the decrease in hydrogen solubility with respect to pressure.37 The solidified sample can be analyzed in a number of ways. The most qualitative method is to section the RPT sample in half and examine the cut surface for pores. Another common method is to measure the sample’s density.

If one assumes that a certain fraction of inclusions can be nucleated on or concentrated by the gas pores, then the RPT may also be able to qualitatively provide information on melt cleanliness. Visual comparison charts are used to give an estimate of the overall melt cleanliness. A low number of pores imply a cleaner melt. However, RPT measurements are highly sensitive to many variables, including sampling turbulence, chamber vacuum pressure, vibration, and solidification rate.58 Work has been performed on developing a statistically optimized procedure to increase data reliability. It was found that turbulence during sampling had the largest variation in results.59

Multiple Voltage Probe Sensors

In the early 2000s, Makarov et al., developed a sampling scheme to detect inclusions in liquid aluminum via a voltage probe array (Figure 11). They proposed a sensor that consisted of a flat plate with evenly spaced voltage electrodes. By applying an electric current through the conductive aluminum, the non-conductive inclusion could be mapped by the probe array.60

If an inclusion passes by the array, two peaks would appear on the sensor, one the inverse of the other. It was found that the voltage peak magnitude, “ϕ’max”, is related to particle radius “r” by the relation:

$$\phi'_{\text{max}} = \frac{4}{3\sqrt{3}} \frac{j r^3}{\sigma l^2}$$

Eqn. 6

Here, “l” is the distance between peaks on the voltage sensor, “j” is the applied current density through the molten metal, and “σ” is the electrical conductivity of the metal.60

It was found that the experimental sensor could detect inclusions from 100 to 1000 μm in size.60 Although it may not achieve the same sensitivity as a Coulter counter system, a voltage probe may be less expensive to implement since it does not require an aperture or vacuum pump to draw in liquid for sampling.

Electromagnetic/Optical Sensing

Also proposed by Makarov et al., was a method to concentrate inclusions to a free surface through Lorenz forces. By applying a DC current between two electrodes in a
liquid metal matrix, and a magnetic field perpendicular to the current, a Lorentz force is then applied on the metal. Any non-conductive inclusions would then be forced in the opposite direction to the Lorentz force due to Newton’s third law. The electrodes can be arranged to force inclusions to a free surface, where they can be measured visually. This method was able to detect particles down to $10^{-6}$ m in size and take 200 samples (within a sampling

Table 2. Comparison of Measurement Techniques

<table>
<thead>
<tr>
<th>Method</th>
<th>Test locale</th>
<th>Estimated analysis time</th>
<th>Estimated sample size</th>
<th>Measurement unit</th>
<th>Inclusion size?</th>
<th>Chemistry?</th>
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<tbody>
<tr>
<td>Metallography</td>
<td>Laboratory</td>
<td>4–10 h</td>
<td>5–20 g</td>
<td>mm$^2$/kg</td>
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<td>Yes</td>
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<tr>
<td>K-mold</td>
<td>Floor</td>
<td>2–3 h</td>
<td>1–2 kg</td>
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<td>No</td>
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<td>Qualiflash</td>
<td>Floor/laboratory</td>
<td>2–3 h</td>
<td>1–2 kg</td>
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<td>No</td>
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<td>Prefil</td>
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<td>100–1000 g</td>
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<td>No</td>
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<td>LiMCA</td>
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<td># of particles/kg</td>
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<td>No</td>
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<tr>
<td>Voltage probe</td>
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<td>Ultrasound</td>
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</tbody>
</table>

Figure 12. Qualitative comparison of inclusion detection methods with respect to inspection time and detectable range of inclusions.
volume of 2 cm$^3$) per minute.$^{18,61}$ However, the surface tension of liquid aluminum prevents inclusions from breaking the melt surface. This can be addressed by pulling apart the oxide layer with rotating drums or by mechanical vibration.

**Summary of Liquid Metal Inclusion Measurement Techniques**

A summary of the most common methods of measuring inclusions in terms of sensing volume, type of information obtained, duration of analyses, and advantages and drawbacks is displayed in Table 2 and Figure 12. Most inclusion measurements are given in the measurement units of area per volume or kilogram of metal. Although techniques like LiMCA, ultrasound, and X-ray tomography have the capability of generating volume per volume measurements, they are cost-prohibitive and/or unable to effectively probe large quantities of melt with high enough resolution. It can be seen that no single technique is capable of describing all the information needed to assess inclusions—chemistry, concentration, and size distribution. An appropriate combination of methods is required to reach these goals. The time required of analysis, from sample gathering to measurement, can vary from a few minutes to several days. Further, there are few methods by which a large spectrum of inclusion sizes can be quickly detected.

**Spectroscopy as a Tool**

In situ floor methods that give an analysis of more than one facet of inclusions do not widely exist. In the metals processing field, there has been significant interest in the use of laser-induced breakdown spectroscopy (LIBS) as a tool for bulk chemistry measurement. Similar to conventional spark optical emission spectroscopy (OES), LIBS uses a short laser pulse to form a plasma on the metal surface. The elements present in the plasma emit characteristic EM radiation, which is collected and processed by a spectrograph. Because the sample interrogated is vaporized, LIBS is technically a destructive test. However, the volume sampled is on the order of $10^{-8}$ to $10^{-5}$ cm$^3$, which results in a very small sample size even if thousands of measurements are taken.$^{65}$ Other relevant advantages over other atomic emission techniques include: (1) LIBS can be applied to both conducting and non-conducting materials, (2) sample preparation is not necessary, (3) only an optical line of sight is required for measurement, and (4) measurements are taken in seconds.

Because only a direct line of sight is needed, LIBS is attractive for interrogating materials in extreme environments, including liquid metal. LIBS has been successfully used for monitoring dissolved elements such as C, Cr, Cu, Mn, and Ni in molten steel.$^{66,67}$ More recently, it has been applied to aluminum alloys to monitor Si, Mg, Fe, Mn, and other alloying elements.$^{68,69}$ As shown in Figure 13, developed probes for LIBS in molten metal typically use a ceramic lance with an inert gas stream to form a bubble at the end. The bubble allows for a constant, fresh surface of metal for the laser to interrogate. Fiber optic cables transmit the incoming laser pulse and outgoing light from the spark. Several probes have been developed by Rai, Lucas, and De Saro that apply this principle.$^{70–72}$ An example of one system is shown in Figure 14.

In addition to determining melt chemistry, LIBS could also be used as a means of detecting inclusions. Because of the small size of inclusions and the presence of convection in
resistance and induction furnaces, particles are constantly moving throughout the melt. If an inclusion is present where the metal sample is vaporized, the spectrum will reveal its presence and chemistry. As illustrated in Figure 15, the oxygen peak in the spectrum will vary depending on whether an inclusion is present within the plasma. If an oxide is present, then the concentrated amount of oxygen atoms within the particle will create a spike in oxygen signal observed by the laser. In addition, if an MgO particle is ablated by the laser pulse, both a spike in Mg and O signal will be observed, allowing for differentiation between inclusions of different chemistries. In principle, the size of the elemental intensity spike from a particle “hit,” is proportional to the size of the particle. A large oxide inclusion would emit a higher oxygen signal than a small inclusion.

Similar work has been done on determining the presence and chemistry of inclusions in solid steel samples via statistical evaluation with OES. In work done by Pande et al., OES with pulse discrimination analysis was used to assess the concentration of Al$_2$O$_3$ inclusions in ultralow carbon steels. They found that an aluminum-containing particle with yield significantly higher Al signal than the bulk metal. Signal from dissolved Al will follow a Gaussian distribution, while signals contributing to particles fall out of the distribution. Sabsabi et al. have found similar results on magnesium alloys and were able to achieve elemental mapping on solid samples. No work to date has been performed on aluminum.

In molten metal, particles are attracted to free surfaces due to their high surface-to-volume ratio and poor wettability. Because the LIBS probe forms a free surface through a bubble of inert gas, inclusions may naturally gravitate toward it. Hudson et al. examined the possibility of using LIBS to sense inclusions in liquid aluminum. By bubbling air into liquid Al and subsequently adding clean metal, it was found that oxygen intensity varied with metal cleanliness (Figure 16). Thus, it was concluded that, to a first order, LIBS could differentiate between relatively clean and dirty metal. In similar experiments with SiC particles in molten pure aluminum, a linear relationship was observed between average Si signal and SiC volume fractions of less than 0.006 % (Figure 17). This is similar to typical concentrations of oxide inclusions.

Because of the discrete nature of inclusions in the melt, parameters such as average particle concentration, size distribution, laser repetition rate, and sampling volume must be taken into account. Sampling statistics must be considered to answer such questions as: (1) How many particles must be sampled to determine a representative measurement and (2) can accurate inclusion concentration values be determined with relatively clean aluminum (<1 ppm)?

Hahn and colleagues have carried out extensive work on the nature of LIBS sampling for discrete nanoparticles in aerosols. By knowing the sampling volume as well as the concentration of the element in the particle, Hahn derived that the overall particle size can be expressed as:
Here, ‘\(C_i\)’ is the equivalent mass concentration of the particle and ‘\(f\)’ is the mass fraction of the elemental signal with respect to the overall inclusion mass, ‘\(V_s\)’ is the effective sampling volume, and ‘\(\rho\)’ is the particle density. For a homogeneous particle (an Fe particle, for example), ‘\(f\)’ is equal to one. In experiments done with metal particles in gas streams, it was determined that at least 20 particle hits were required to obtain a representative measure of the particle concentration and size distribution. Successful LIBS measurements of CaO particles in aerosol streams were achieved for concentrations of <1 ppm. Therefore, in principle, the particle size of inclusions can be determined by calculating the concentration of oxygen signal in each laser measurement.

**Conclusion**

The drive to achieve cleanliness in aluminum and its alloys had resulted in a plethora of techniques focused on assessing and quantifying the number of inclusions present. The state of the art with respect to inclusion detection in aluminum and its alloys has been reviewed. These methods include:

- Optical microscopy
- Ultrasound (solid and liquid state)
- X-ray radiography and tomography
- Electromagnetic sensing
- Fracture tests
- Reduced pressure tests
- Filtration and centrifugation
- Chemical dissolution

The key limitation with current methods is that they are unable to quickly determine chemistry, concentration, and size distribution of inclusions within the molten metal. The concept of using in situ laser-induced breakdown spectroscopy (LIBS) as a means of detecting and quantifying
inclusions has been presented. Ongoing experiments have shown that this new technique shows promise, but more research is required to analyze multi-element inclusions, determine optimal sampling schemes, and develop proper procedures for calculating particle size from concentration.

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Appendix B

Applications of LIBS in Molten Metal Processing

Applications of Laser-Induced Breakdown Spectroscopy (LIBS) in Molten Metal Processing

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Abstract
In order for metals to meet the demand for critical applications in the automotive, aerospace, and defense industries, tight control over the composition and cleanliness of the metal must be achieved. The use of laser-induced breakdown spectroscopy (LIBS) for applications in metals processing has generated significant interest for its ability to perform quick analyses in-situ. The fundamentals of LIBS, current techniques for deployment on molten metal, demonstrated capabilities, and possible avenues for development are reviewed and discussed.
Introduction

The ability to analyze liquid metals has direct applications for real-time process control. In the case of liquid metal processing, it is critical that operating parameters be adjusted accordingly so that the chemistry and quality of the melt be within predetermined limits. Current analytical approaches for determining chemical composition of the melt include spark optical emission spectroscopy, atomic absorption spectroscopy (AAS), X-ray florescence (XRF), and inductively coupled plasma spectroscopy (ICP). These methods are limited because they are off-line in nature, based on analysis of solid metal at ambient temperature, and require laborious manual sampling. Because of the potential in saving time, energy, and materials, as well as improved quality assurance, the use of laser-induced breakdown spectroscopy (LIBS) in liquid metal for real time analysis has generated significant interest in metals processing. In-situ and rapid chemistry analysis, as well as inclusion assessment (or melt cleanliness) is a significant enabling tool that can transform the manner in which cast components are manufactured. This paper reviews the work done using LIBS for such applications and also highlights future opportunities for this technology.

Fundamentals of LIBS

Physics

In laser induced breakdown spectroscopy (LIBS), a pulsed laser is repeatedly fired and focused onto a target metal to create a plasma which has the same chemical makeup as the target. Measuring the plasma's chemistry then provides a complete description of the target metal's chemistry.

A typical flash lamp pumped solid-state laser used in LIBS will have a pulse energy of about 100 mJ with a pulse duration of about 10 nanoseconds, and a firing frequency of one to several Hz. While the laser pulse energy is modest, its power is significant; 10 MW since its pulse duration is so brief (power is energy divided by time). Additionally, the laser light can be focused to a tight spot (about one millimeter) at the focal point, so the laser light irradiance can be significant at $10^9$ W/cm$^2$. Since plasmas are created for irradiances as low as $10^6$ W/cm$^2$ small, compact lasers are sufficient for LIBS measurements [1].

The practical application of LIBS requires measurement of the spectral peaks of the electron transitions of each element of interest, which can then be used to determine which elements are present and their individual concentrations. However, it is not possible to achieve this by simply measuring all the plasma light emitted since there will be a significant continuum background, line broadening, and self-absorption which will greatly skew the intended results [2]. Typically, the measured spectrum wavelengths of interest range from 200 to 800 nm
whereas the background continuum spans up to 600 nm and is present during the first 100 nanoseconds of the plasma. On the other hand, discrete spectra of electron transitions go out to microseconds [3].

To avoid these problems, time-resolved LIBS is used in which, first the spectral measurement is delayed by one or two microseconds from the time the plasma is created, to avoid the background emissions, and second the measurement is made during a gated window of a few microseconds to catch the maximum intensity and minimum broadening and self-absorption of the spectra as possible.

LIBS can be used to measure the elemental concentrations since the higher the concentration, the more excited electrons are available to emit radiation leading to a larger spectral peak. This is illustrated in Figure 1, which shows the difference in the carbon spectral lines taken from two solid steel samples with different carbon contents.

The benefits of LIBS over other spectroscopic techniques include: 1) LIBS can be used on conductive and non-conductive materials; 2) sample preparation is unnecessary; 3) only an optical line of sight is required for measurement; 4) measurements are performed in seconds [4], and 5) it can be carried out in-situ.

![Figure 1 - LIBS Measurements of Two Steel Samples showing the Carbon Content of Each.](image-url)
**Calibration Curves**

As with many analytical methods, LIBS relies on calibration curves when performing quantitative analysis. These curves, preferably linear, are used to relate the LIBS signal (usually the height or area of an atomic emission peak) to the property being measured (usually elemental concentration). Generating accurate calibration curves is not trivial since changes in the signal are affected not only by changes in elemental concentration, but also by laser parameters (wavelength, pulse energy and duration, spot size, etc.), surface conditions of the target (height, roughness, angle, reflectivity, etc.), atmospheric conditions (pressure, vacuum, cover gas, etc.), and sample matrix (solid, liquid, gas, powder, etc.) among others [5].

The relationship of LIBS peak intensity at a particular wavelength to elemental concentration can be described by the following Boltzmann equation:

\[
I_{ij} = FC_s A_{ij} \frac{g_i e^{-E_i/k_B T}}{U_s(T)}
\]

where “\(I_{ij}\)” is the peak intensity, “\(F\)” is an experimental factor accounting for the optical efficiency and the plasma size and density, “\(C_s\)” is the concentration of the species in the sample, “\(A_{ij}\)” and “\(g_i\)” are physical constants, “\(U_s(T)\)” is the temperature-dependent partition function, “\(E_i\)” is the upper-level transition energy, “\(k_B\)” is the Boltzmann constant, and “\(T\)” is the plasma temperature. Typically, calibration curves are generated using a set of standards for which the elemental composition is known. It is important that the standards be as similar as possible (matrix, homogeneity, surface condition) to the target and that compositions of all elements of interest span the range of values expected in the material to be analyzed. The standards are analyzed using the exact same optical system (laser, optics, detector) that will be used on the target samples. In this case, we assume that \(F\) and \(T\) in Equation 1 are constant for all measurements and that the concentration of the emitting species is directly proportional to the total concentration of the element in the sample. A calibration curve can then be drawn relating the line intensities from the standards to the known elemental compositions. This curve is then characterized using linear regression or another curve-fitting technique and is used to predict the elemental compositions in unknown samples [6].

Care must be taken when choosing atomic emission lines for analysis to be sure that they are sensitive to concentration changes. Ideally, the lines should be well-defined and isolated away from other peaks to avoid overlapping signals. Resonance lines typically produce the strongest LIBS signals and are used to measure elements present at low concentrations. At higher concentrations, resonance lines can become saturated exhibiting self-absorption or self-reversal. In this case, lines with higher electronic transitions may be used [6-7].
Individual LIBS spectra can be highly variable due to random fluctuations in laser energy, laser-surface interaction, etc. The effect of these fluctuations can be reduced by using an average of multiple spectra to form a single measurement. Bulk changes in the overall spectrum (elevated background levels, for example) can be mitigated by normalizing all spectral peaks by an internal standard, typically a well-defined atomic emission line from an element that has a constant concentration over all samples to be analyzed. The spectra can also be normalized by other parameters such as the laser pulse energy (if known), a local background region, or the summed intensity over the entire spectrum.

The limit of detection (LOD) is defined as the lowest concentration of an element for which an atomic emission peak is discernible above the local background. One measure of LOD is the concentration for which:

$$\left( S_{\text{max}} - \mu_{bg} \right) = 3\sigma_{bg}$$  (2)

where “$S_{\text{max}}$” is the maximum peak height, “$\mu_{bg}$” is the average local background in an area near the peak that is free of atomic emission lines, and “$\sigma_{bg}$” is the standard deviation of the background noise. The LOD for elements detected by LIBS can range from single ppb to tenths of a percent (by weight), depending on the element and application. A compilation of LOD’s reported in the literature can be found in books by Cremers & Radziemski as well as Noll [7-8].

**Sensing Volume**

While the laser used is of relatively low energy (10-100s of mJ), the short time duration of the pulse (fs to ns) allows for the high energy density required to form the plasma spark and ablate the material. Although LIBS is effectively a non-destructive test (only nanograms to micrograms of material are ablated with each laser pulse), it is often of interest to know the volume or mass sampled per spark. On solid samples, it can be easily measured from microscopy [9]. With liquid and gases, the sampling volume is more difficult, sometimes impossible, to measure directly. However, it can be modeled, computed and thus estimated. There are a plethora of models in the literature for laser ablation that take into account laser wavelength, irradiance, pulse length, target material, and gas environment. A large number of these models are based on thermal processes and describe laser-target interaction on a macro scale [10].

As seen in Figure 2, the formation of the breakdown plasma is a complicated process. However, some assumptions can be made. In metals, light is absorbed by interaction with electrons. Optical energy is absorbed by an electron, which is raised to a higher energy state in the conduction band. The excited electrons collide with other atoms and phonons and transfer the absorbed energy. Because the energy relaxation time is on the order of $10^{-13}$ seconds for metals, the optical energy will instantaneously transform to heat for ns-pulsed laser ablation.
The particulars are well described in a comprehensive paper on laser ablation modeling by Bogaerts, et. al [10c].

![Figure 2 – Schematic of laser plasma development during LIBS. Adapted from Cremers [11].](image)

A fraction of the laser energy will not contribute to vaporization. This is in part due to surface reflectivity, R. For solid metals, reflectivity is generally close to 1, but it can drop to values as low as 0.1 during laser ablation, provided that laser irradiance is approximately above $10^8$ W/cm$^2$ [12].

The amount of material, M, that can be ablated by a laser pulse with energy, E, can be roughly estimated through an energy balance. The relationship between the laser energy contributing to ablation and the energy require to heat the liquid metal up to the plasma temperature can be described as:

$$E(1 - R)P = M \left[ \int_{T_o}^{T_b} C_p^l \, dT + \Delta H_V + \int_{T_b}^{T_p} C_p^g \, dT \right]$$  \hspace{1cm} (3)

In Equation 1, “R” is surface reflectivity, “$T_o$” is the ambient temperature, “$T_b$” is the boiling point, “$T_p$” is the plasma temperature, “$C_p^l$” is the heat capacity of the liquid phase, “$C_p^g$” is the
gas phase heat capacity, “ΔH_v” is the enthalpy of vaporization, “M” is the ablated mass, and “P” is a factor that accounts for other missing energy terms (ionization, plasma reheating, etc.).

Although the shape of the plasma is conical, an effective, 1st order, spherical diameter can be calculated, provided the density of the target is known.

\[ d = \sqrt[3]{\frac{6V_p}{\pi}} \]

(4)

A simplified, but similar energy balance was used by Vadillo, et al. to investigate the effect of plasma shielding on the ablation rate of pure metal sheet including Cu, Zn, Fe, W, and Ti. It was found that the observed and theoretical ablation rates matched within 20% [13]. In the context of liquid aluminum, work done in the early 1970s by McMordie and Roberts with a 100 J, CO₂ laser (10.6 μm wavelength, 175-3100 ns pulses) determined reflectivity to be approximately 0.2 for molten aluminum irrespective of temperature [14]. Multari, et. al. investigated optimal sample to lens distances for LIBS on solid targets [15]. A Q-switched Nd:YAG laser was used (1064 nm wavelength, 186 mJ pulse, 10 ns pulse width). After taking thousands of sparks and weighing samples before and after, they found an optimum at approximately 120 ng per pulse for 1100 aluminum. By substituting values for 1100 aluminum into Equation 3, it can be determined that approximately one tenth of the laser energy contributes to ablation. A first-order estimation of the effective sampling volume in liquid aluminum as a function of laser energy is shown in Figure 3. Because of the lack of work done on the optical properties of liquid aluminum at common casting temperatures, and that no optical band gaps exist between 1070 nm and 10.6 μm for liquid aluminum, a reflectivity of 0.2 was considered. From Figure 3, it can be seen that the effective sampling volume increases with laser pulse energy. Assuming a spherical geometry, the sampling volume can range from 20 to over 100 microns in size depending on the laser power.

![Figure 3](image.png)

Figure 3 – First order estimation of sampling volume diameter as a function of laser energy for pure, liquid aluminum at 800°C. Sampling size is the equivalent spherical diameter of the ablated mass.
Schemes for Deployment on Molten Metal

Because LIBS only requires a direct line of sight for analysis, it is adaptable to a variety of different deployment methods as well as attractive for use in extreme environments. The ability to analyze liquids and solids in liquids directly has a number of applications including real-time process control and environmental monitoring. However, using LIBS in molten metal requires solving two major issues: (1) how to present the liquid to the laser spark without contaminating the optics and (2) ensuring the liquid is indeed representative of the bulk. Three methods have been developed to address these issues.

The simplest approach involves focusing the laser pulse at the melt surface [16]. In this configuration, splashing must be minimized to prevent contamination of the optics. This can be easily mitigated by reducing the laser repetition rate and/or placing a transparent, refractory window for the laser to pass through. Another possibility is to replace the window with a constant gas flow to remove aerosols produced by the laser-liquid interactions or from the melt itself. Another method is to pass the melt through a nozzle to form a laminar jet. The metal can be delivered to the nozzle via electromagnetic pumps or gas pressure. While similar work using liquid jets have been performed on aqueous mixtures, no such experiments using liquid metal have been reported [17]. Although these techniques are relatively straightforward, they have several drawbacks. Sampling with LIBS at the melt surface may not give an accurate measure of the bulk. Melt surfaces will often have oxide slags, molten salts, or other compounds that are not present in the bulk metal. Aerosols and ejected particles present above the melt surface cause variations in the amount of laser power that reaches the liquid surface and hinder the quality of data extracted. In addition, surface measurements will not provide information about melt uniformity. Therefore, it is desirable to analyze liquid metal in-situ by using immersed probes.

Several studies using probes have been conducted in laboratory and industrial trials. All probes operate using the same basic principles as illustrated in Figure 4 [18]. The probe, typically a refractory ceramic tube, is lowered into the melt and is flushed with an inert gas. A constant, fresh metal surface is at the tip for the laser to interrogate. The light emitted from the plasma spark is collected through a fiber-optic cable to the spectrometer. Because the laser spark is below the melt surface, measurements do not require specialized eye protection. In addition, the probe’s position can be moved allowing for furnace depth profiles, sedimentation analysis, and solute mixing analysis.
One of the earliest probes was developed by Cremers, et. al in the mid-1980s for molten steel [19]. As seen in Figure 5, the upper section of the probe, made of stainless steel, contains the focusing optics for the laser and is shielded using a ceramic disc. The optics are protected from the melt with a quartz plate. The bottom of the probe is a refractory ceramic. Argon gas is pumped in as a cooling gas and to flush away dust and vapor from the quartz window.
More recently, similar probes have been developed that use inert gas to form a semi stable bubble at the probe tip. An example of such a probe, developed by Rai, et. al. for liquid aluminum, is shown in Figure 6 [20]. Here, inert gas contributes to purging and lens protection as well as form the sampling surface. Similar probes have been developed by De Saro, et. al [18, 21], Lucas, et. al. [22], and Kim [23].
Use of LIBS in molten metal processing

Ferrous Systems

The first reported experiment of LIBS on molten metal was done by Runge and colleagues at the Ford Motor Company in 1966 [16a]. Using a ruby laser with a xenon flashtube aimed at the melt surface, spectra from chromium and nickel were observed well enough to plot calibration curves. At the time, spectrographic data was recorded as bands on a photographic plate. Lengthy, specialized processing was required to extract peak intensity data from elements present. A schematic of the experimental apparatus is detailed in Figure 7. In this case, the laser is aimed 30° to the melt surface. The light emitted from the plasma is collected through a focusing lens directly above the crucible. Although these first experiments were successful, it was not until the late 1980s that LIBS gained further interest as a tool for melt measurement, when atomic emission lines could be quickly gathered using digital data acquisition systems.
Building upon Runge's work, Ozaki, et al., performed similar, successful experiments on molten iron with varying concentrations of C, Si, and Mn [24]. In addition, they carefully examined the effect of focusing lens-melt surface distance and cover atmosphere on spectra intensity. In an effort to help control the atmosphere over the sampling area and protect the optics from dust and fumes, the focusing lens was covered with a quartz cone flushed with Ar. A hole at the tip of the cone, just about the melt, allowed for laser interrogation. They determined that the best method to minimize errors was to keep the laser and spectrometer optics co-axial. That way, the emitted plasma light would not be blocked by random perturbations on the melt surface. In addition, Ozaki recommended that elemental intensity should be measured with respect to that of iron to further reduce shot-to-shot variation. This practice of analyzing intensity ratios has become standard in the LIBS community. Although, these experiments were fruitful, they were still surface measurements. It was not until a few years later that Cremers et al. developed a similar apparatus that could be immersed in the melt [19]. Even so, laser repetitions were too slow to allow LIBS to be industrially suitable. Current systems at the time were unable to measure at more than 1 Hz [24].

With the development of higher energy, Q-switched solid state lasers and higher resolution spectrometers, LIBS became much more industrially practical during the 1990s. The first patents for LIBS on molten metal appeared in 1991 by Carlhoff and Kim [23, 25]. Using a Nd:YAG Q-switched laser and a Czerny-Turner spectrometer, Lorenzen and colleagues were able to achieve a detection limit for carbon of 200 ppm [26]. This was later verified by Aragon, et al. [27]. By the early 2000s, single digit ppm detection limits of alloying elements were achieved by Noll, et al. using a probe developed at the Institute of Ferrous Metallurgy at the University of Aachen on a 100 kg steel melt. The probing lance consisted of a water-cooled copper shield and an Ar-flushed alumina tip [28]. Liquid metal flows into the probe tip to provide a surface of fresh metal. The immersion depth of the tip was estimated to be 20 cm. As shown in Figure 8, the entire apparatus was placed on a lifting platform next to the furnace. The
laser source, spectrometer, and signal evaluation hardware is within the protective box. With a 100 Hz sampling rate, measurement runs at a given composition were performed in seconds. Although enough data was gathered to draw a calibration curve, carbon proved to be a difficult element to measure due to oxidation at the melt surface. Similar calibration curves were drawn from P, S, Ni, and Cr. More recent work by Sun, et al also successfully performed LIBS on steel melt with a similar probe design but different optical set up. Their experiments yielded LODs 1-2 orders of magnitude higher than Noll’s values, which demonstrates the importance of choosing the correct optics, laser, and spectrometer [29].

Figure 8 – A) Noll, et al’s LIBS Apparatus for steel melts in use; B) Carbon calibration curve in molten steel; C) Sulfur calibration curve in molten steel [28a].

Although probing the melt in-situ gives the most representative data, it is often impossible to do so in foundries employing vacuum degassing (VD) chambers or vacuum induction melters (VIM) to process metal. Nonetheless, LIBS measurements can be performed through chamber viewports on the melt surface. Done by Gruber and colleagues at the Bohler Edelstal steel foundry in Kapfenberg, Austria, it was found that surface measurements gave satisfactory calibration curves for Ni, Mn, and Cr even though surface slags were present. Because of the large distance between the focusing lens and melt surface (~4 m), detection limits for elements of interest were not as low as Noll’s experiments [30].

Detection limits from Noll, Gruber, and Sun’s work is presented in Table 1.
Table 1: Reported limits of detection for various elements in steel melts. Units are in parts per million unless specified otherwise.

<table>
<thead>
<tr>
<th>Element</th>
<th>LOD (ppm)</th>
<th>Matrix</th>
<th>Atmosphere</th>
<th>Location</th>
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<td>Plant</td>
<td>[28b]</td>
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<tr>
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<td>Vacuum</td>
<td>Plant</td>
<td>[30]</td>
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<td>9</td>
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<td>Air</td>
<td>Plant</td>
<td>[28b]</td>
</tr>
<tr>
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<td>649</td>
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<td>Air</td>
<td>Lab</td>
<td>[29a]</td>
</tr>
<tr>
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<td>Plant</td>
<td>[28b]</td>
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<td>Low Alloy Steel</td>
<td>Air</td>
<td>Lab</td>
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</table>

**Non-Ferrous Systems**

More recently, LIBS has been used to make in-situ measurements of elemental chemistry in molten, nonferrous metals. Energy Research Company (ERCo) developed and constructed a LIBS immersion probe for molten aluminum that was demonstrated at Commonwealth Aluminum's foundry in Urichsville, OH [21b]. A ceramic probe was suspended above the filter bowl of Commonwealth's rolling mill and lowered approximately 3-4 inches below the molten metal surface. Photographs of the sensor are shown in Figure 9. Optical fibers were used to carry the laser pulses to and the plasma light from the sensor. All electronic equipment was located in a climate-controlled cabinet located well away from the molten metal surface. An inert gas purge was used to cool the optics and to keep the molten aluminum out of the probe. LIBS data was collected continuously over several 8 hour shifts and compared to data from button samples collected from the melt and analyzed by Optical Emission Spectroscopy in Commonwealth's laboratory. The button samples were time-stamped to coincide with the LIBS measurements. Table 2 shows a comparison of average data for Al, Cu, Fe, Mg, Mn, and Si, collected over one shift. The LIBS data agreed well with the laboratory data to within 7.1% in all cases.
Rai et al. reported laboratory measurements of molten aluminum alloys using an immersion probe [20a]. A stainless steel optics tube was protected by a ceramic sheath and immersed into a crucible of molten aluminum to a depth of approximately 25 cm. A single optical fiber was used to both deliver the laser pulse and collect the resulting plasma light. A purge of argon gas was used to protect the optics from the molten metal. LIBS data were collected from seven different molten aluminum alloys of known compositions. Calibration curves were then presented for Cu, Fe, Mg, and Cr on a relative basis - the normalized LIBS intensity was plotted against a similarly normalized weight percentage (i.e. Cu/Fe, Fe/Al). All curves exhibited a linear trend with the exception of Cu/Fe, which flattened out at Cu concentrations above 3.8 wt% due to self-absorption of the chosen Cu line. The molten LIBS data was compared to data collected from solid samples of the same alloys. Peak ratios from the solid samples differed significantly from those from the molten samples. The authors theorized that this is caused by selective vaporization of elements at the molten metal interface. They concluded that calibration curves from solid samples cannot be applied to molten metal.

Another LIBS immersion probe concept is described by Lucas et al. for analysis of molten copper and zinc [22, 31]. In one configuration, the LIBS sensor is introduced into the melt through a tuyere in the holding vessel, typically used to mix gases into the molten metal. A gas is blown through the LIBS tube at sufficient pressure and flow to keep molten metal and debris away from the optics. Laser pulses are focused onto the interface between the molten metal and the bubble formed by the
purge gas through a system of mirrors and lenses. In this case, the laser head is mounted directly to the LIBS probe - no optical fiber is used. A second optical train is used to collect the plasma light and focus it into an optical fiber which runs to a spectrometer. Laboratory and on-line LIBS data was collected to measure iron in a molten copper matte. Fe concentrations ranged from 1.3-4.4 wt %. The LIBS Fe line was normalized by a nearby Cu line and plotted as a function of known concentration determined by XRF. The resulting calibration curve was linear over the entire range. A similar calibration curve was presented for aluminum (100-1150 ppm) in molten Zn. The Al line was normalized by a nearby Zn line. Again, the curve was linear over the measurement range. The authors concluded that LIBS is a suitable measurement technique for \textit{in-situ} monitoring and process control of molten zinc, copper, and other materials.

\textbf{Potential of LIBS in metal processing}

\textit{Other Metals}

Although significant work has been done with LIBS on molten aluminum and steel, very little work has been reported on other metals. This includes limited work on liquid magnesium, copper, zinc, and tin by Sabsabi, and Lucas [22, 31]. However, no other information regarding detection limits or calibration curves for these systems are readily available. In addition, there are no reports in the current literature on LIBS for refractory metals. Given the successes that were previously stated in this paper, LIBS would have significant promise for the industries that process metals such as titanium, tungsten, copper, nickel, and silicon.

\textit{Melt Chemistry}

Although calibration curves of common alloying elements in iron and aluminum have been documented, not all have been fully explored. No calibration curves regarding aluminum alloying elements such as cobalt, bismuth, strontium or tin have been reported in the literature. Only recently has a curve for titanium in aluminum been reported (Figure 10) [32].
In addition, the total sensing range for elements in the melt has not been fully explored. Ideally, there will be a linear relationship between element response and concentration. A linear fit of the data would pass through the origin (0,0). However, actual calibration curves can yield nonlinear behavior and lower and high concentrations, regions indicated by shading in Figure 11. The range over which the curve is linear is termed the linear dynamic range (LDR). The loss of sensitivity at low concentrations can be due to spectral interference with elemental emission line of interest from the background or an interfering species. The loss of signal at high concentrations is most often due to plasma self-absorption or saturation of the detector. LDRs for alloying elements in molten metal have not yet been explored.

Figure 10 – Calibration curve of titanium in molten aluminum [32].

Figure 11 – Generalized calibration curve indicating ranges of differing sensitivities. Shaded regions indicate area of nonlinearity. Adapted from Cremers and Radmenski [33].
**Melt Cleanliness**

In addition to determining melt chemistry, LIBS shows promise as a means of assessing melt cleanliness in addition to chemistry. In general, melt cleanliness refers to the concentration of inclusions (typically oxide particles and skins) as well as dissolved gases and residual elements. These often inhibit mechanical properties of castings. Many laboratory and shop floor techniques exist to assess inclusion content. They range from traditional metallography to filtration and ultrasound but few techniques exist that can detect the presence of inclusions in-situ [34]. No one technique can quickly determine particle chemistry, concentration, and size distribution.

If an inclusion is present where the metal was vaporized, the spectra will reveal its presence and chemistry [34a]. Because a particle is a concentrated mass of elements, elemental signal would be significantly higher than that of the matrix. As illustrated in Figure 12, if we focus on an oxygen peak in the spectra, it will vary depending on whether an inclusion is present within the sampling volume. In addition, if an MgO particle is ablated by the laser pulse, both a spike in Mg and O signal will be observed, allowing for differentiation between inclusions of different chemistries. In principle, the size of the elemental intensity spike from a particle “hit,” is proportional to the size of the particle. A large oxide inclusion would emit a higher oxygen signal than a small inclusion.

![Figure 12 – Example of LIBS acquisition for oxide particles in molten metal.](image)
The use of spectroscopy to sense particles has been conducted before in solid and gaseous matrices. Such work includes characterizing MnS and Al₂O₃ inclusions in solid steel through spark optical emission spectroscopy (OES) [35]. LIBS has been used in a similar manner on elemental mapping on solid light metals where oxide inclusions were observed [22b, 36]. In the case of particle detection in fluids, much work has been performed by Hahn and colleagues on metal particles in aerosol streams [26, 37]. From his work, particle size can be calculated through the following relationship:

\[
D_p = \left( \frac{6 C_s V_p}{\pi \rho_p} \right)^{1/3} \tag{5}
\]

“\(D_p\)” is the equivalent spherical diameter of one particle, “\(C_s\)” is the equivalent mass concentration of the particle, “\(V_p\)” is the sampling volume, and “\(\rho_p\)” is the particle’s density [37d].

By substitution of equation 1 into 5, particle diameter can be calculated.

\[
D_p = \left( \frac{6 V_p}{\pi \rho_i} \times I_{ij} F \times \frac{g_i A_{ij}}{U_i(T)} e^{-E_i / k_B T} \right)^{1/3}
\]

\[
\therefore 3 I_{ij} \propto D_p \tag{6}
\]

Inclusion concentration, \(X\), can be calculated, through the relationship:

\[
X = (Average \ particle \ concentration \ for \ hits) \times (sampling \ frequency \ of \ hits) \tag{7}
\]

Because elemental concentration relates directly with intensity and that, provided the same number of shots are taken every sampling run, frequency can be substituted by the number of particle hits. Therefore, for the case of sensing inclusions in molten metal, an equivalent relationship, relating the product of average particle hit intensity and number of hits, can be established.

\[
X \propto I_{avg} \times N_{Hits} \tag{8}
\]

The overall inclusion concentration measurement is reduced to the product of two statistical samples: the particle size/hit intensity distribution and the particle sampling frequency. The use of particle hit average, instead of the average over all measurements, has been shown to increase the signal-to-noise ratio and sensitivity. In Monte Carlo simulations and actual experiments performed by Hahn et al, calculated and actual concentrations were in good agreement [37b]. Provided particle concentration can be measured through other means, a calibration curve can be drawn.
In a time series where measurements are taken at a given rate, a particle hit would appear as an outlier above the background noise. Unlike most experiments, the goal of LIBS particle analysis is to investigate outliers in signal. Conditional analyses and/or statistical tests would need to be used to discern particle hits from random fluctuations in background noise (Figure 13) [38].

![Figure 13](image)

**Figure 13** – Example of LIBS data acquisition for oxide inclusions in molten metal. Shot 2 exhibits an oxygen peak at 777 nm while shot 1 and 3 do not. Therefore, shot 2 is a “hit.”

In order to determine the feasibility and for LIBS to sense oxides and other particles in liquid metal, experiments were performed in recent work by Hudson, et. al. with Al₂O₃, AlB₂, SiC, and TiB₂ particles in pure liquid aluminum. A proof-of-concept of LIBS as a cleanliness assessment tool was demonstrated by taking hundreds of laser pulses and extracting only those shots with elemental spectra from particles. From this data, linear calibration curves relating volume fraction of particles and average hit intensity were drawn [39]. An in-situ technique with the ability to quickly determine both melt chemistry and inclusion content would be of great benefit for metals processing, offering a faster and more complete analysis of the melt before casting.

**Conclusions**

In this article, the general steps and approach of LIBS in gathering analytical signal from molten metal was highlighted. LIBS has a number of positive attributes that make it appealing for molten metal processing including the lack of a need for sample preparation, only a direct line of sight is required, it can be applied *in situ*, and measurements are performed in seconds.

Throughout this review, we have attempted to collect and summarize the current state of the literature, pointing out advancements in instrumentation and methodologies of particular interest for melt analysis. It has been shown that LIBS can be successfully used in a plant
setting, whether it is ferrous or nonferrous production. By performing spectroscopy directly within the molten metal, the problems arising from chemical analysis on solid samples (segregation gradients, artifacts from machining or grinding, etc.) can be completely avoided. Because hundreds, even thousands, of measurements can be taken in a short amount of time, discrete inclusions could even be detected and analyzed.

References
Appendix C

*Clean Aluminum Processing: New Avenues for Measurement and Analysis*

CLEAN ALUMINUM PROCESSING: NEW AVENUES FOR MEASUREMENT AND ANALYSIS

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Keywords: Metal Cleanliness, LIBS, Inclusion Detection, Liquid Aluminum

Abstract

Aluminum alloy castings are becoming commonplace in important and critical applications in the automotive and aerospace industries where materials failure is not an option. In order to meet such property demands, tight control over the cleanliness of the melt, namely, mitigation of inclusions and dissolved hydrogen must be achieved. Having a cleaner melt will yield sound castings with more reliable performance. In order to control cleanliness, it must first be well defined and measured. Very few techniques exist in industry that can quantitatively measure inclusion levels in-situ. In addition, there are no practical methods in which all quality detractors can be measured simultaneously. The use of laser-induced breakdown spectroscopy (LIBS) has shown promise as a technique to quantify all facets of quality in aluminum melts. Current progress of this work is presented and discussed.

Introduction

In general the cleanliness of aluminum alloys refers to the concentration of inclusions, dissolved hydrogen, and residual elements. Inclusions are defined as unwanted solid particles and can act as nucleation sites for hydrogen pores and cracks [1]. Such particles can be exogenous or form in situ and can be characterized by their composition, size distribution, morphology, and phase. The most commonly found inclusions are oxides (Al2O3, SiO2, CaO, etc.) [2]. Their quantity depends on a number of factors including initial melt composition, solidification rate, and pouring atmosphere. It has been shown that cleaner metal results in: greater metal fluidity, higher casting properties, improved machinability, better surface finish, and overall reduction in reject castings [3-5].

Many laboratory and shop floor techniques exist to assess inclusion content in aluminum and its alloys. As illustrated in Figure 1, they range from traditional optical metallography to filtration (PoDFA, Prefil) and coulter counters (LiMCA) and X-ray techniques with each method having its pros and cons [6-11]. However, very few techniques exist that can detect the presence of inclusions in-situ.

Much work has been done using laser-induced breakdown spectroscopy (LIBS) as a tool for metal chemistry assessment. Similar to spark OES, LIBS uses a laser pulse to induce a microplasma from a sample of material which is then analyzed with a spectrograph. Although this is a destructive test, the volume ablated ranges from 10⁻⁸ to 10⁻⁵ cm³ which allows for many samples to be taken without compromising the bulk [12]. In addition to solids, LIBS has also been performed upon liquids including molten aluminum to determine melt composition [13]. Other relevant advantages to LIBS over other atomic emission spectroscopy techniques include: (1) It can be applied to both conducting and non-conducting materials, (2) sample preparation is not necessary, (3) only an optical line of sight is required for measurement, allowing for the possibility of use in hostile environments, and (4) measurements are performed in seconds, allowing for use on-line [14, 15]. The basic features and theory of LIBS are described in several review papers [16, 17].

In addition to determining melt chemistry, LIBS could also be used as a means of detecting inclusions. If an inclusion is present where the metal was vaporized, the spectra will reveal its presence and chemistry [11]. As illustrated in Figure 2, if we focus on an oxygen peak in the spectra, it will be seen varying depending on whether an inclusion is present within the plasma. Work has been done on determining the presence and chemistry of inclusions in solid steel samples via statistical evaluation with OES [18, 19]. An in-situ technique with the ability to quickly determine both melt chemistry and inclusion content would be of great benefit for metals processing, offering a faster and more complete analysis of the melt before casting.

In the present work, oxide inclusions were introduced in an aluminum melt and diluted to create samples with varying oxide content. The samples were then analyzed by LIBS and X-ray radiography. Preliminary results show higher oxygen signal with increased inclusion content, demonstrating that LIBS could be used as an in-situ tool in inclusion detection and analysis.

Experimental

Sample Preparation

13.6 kg of Belmont 1009A 99.99% pure aluminum was melted in an Inductotherm 35 kW VIP push-out induction furnace to a temperature of 700±20°C. A graphite rotating impeller degasser
was lowered 20 cm into the melt and fed with extra dry compressed air at 10.3 kPa with a flow rate of 1 L/min. A photograph of the degasser head is shown in Figure 3. The degasser was operated at 200 rpm. The melt was treated for 10 minutes, after which the resultant dross layer was thoroughly mixed into the melt. Ingots (2.3-2.7 kg) were then poured into a cast-iron ingot mold. Several ingots were then remelted and diluted to 50% by weight. Untreated ingots were also poured as control samples. Elemental composition was verified by Spark OES (SpectroMaxX).

LIBS Measurement

Preliminary tests were conducted using an immersed probe developed by Energy Research Company (ERCo, Plainfield, NJ) [20]. Ingots were placed in a fused-silica crucible and melted in a Lindberg electric crucible furnace. The furnace was quickly ramped to 500°C and heated to 800°C at 2°C/min. The probe was lowered over the melt until the internal temperature reached 93°C. It was then submerged to a depth of approximately 5 cm below the melt surface. Purified nitrogen gas from a liquid nitrogen tank was used as probe coolant and to provide a constant, fresh metal surface at the probe tip. A photograph of the apparatus is shown in Figure 4.

ERCo’s LIBS apparatus was made up of a Q-switched, 20Hz Nd:YAG laser, operated at 1064 nm with a 50 mJ maximum pulse energy (Big Sky Laser, Bozeman, MT). Emitted plasma light was collected via a fiber-optic cable and fed into an ESA 3000 Echelle-type spectrometer (LLA Instruments).

10-20 test measurements were then taken before sampling to account for any initial transient readings. 500 successive laser shots were then fired one at a time into the melt. After measurements, the aluminum was allowed to cool in the crucible. Spectra data, gathered with ESAWIN software, was then analyzed via Microsoft Excel.

Figure 2: Example of LIBS acquisition for oxide inclusions in molten metal. The number and intensity of oxygen peaks is related to the number and size of inclusions.

Figure 3: Degasser head after use (Four 1.5 mm outlets, 10.2 cm disk diameter, 3.8 cm shaft diameter).

Figure 4: LIBS Probe immersed in the furnace
After LIBS measurement, a 1 in. slice was cut from the middle of each solidified sample and ground down with 180 grit sandpaper. Samples were then analyzed at V.J. Technologies (Bohemia, N.Y.) using a 225 kV Microfocus X-Ray system. This was performed to verify the presence of inclusions within the casting.

**Preliminary Results and Discussion**

**LIBS Measurements**

Oxygen’s highest intensity peaks in emission spectroscopy occur as a triplet in the 777-778 nm range. The most intense peak, found at 777.147 nm, was analyzed for these experiments. To account for the variability in signal between individual measurements, oxygen peak intensity was normalized by the 308.852 nm aluminum peak intensity [21]. As seen in Figure 5, peak frequency noticeably increases with inclusion content. Peaks are seen in the control sample, likely due to entrainment of the surface film upon handling and probe immersion. Statistics on each sample are compiled in Table 1.

To ensure statistical validity, a two-tailed student’s t-test assuming unequal variances was performed between each data set. If the absolute value of the t-statistic is greater than the calculated critical t-statistic, then the two data sets are statistically significantly different from one another. The results, as seen in table 2, show that this is so.

**X-Ray Measurements**

Radiographs, as shown in Figure 6, reveal that more inclusions (seen as black specks) are present with increased air treatment. Such particles were seldom seen in the clean control samples. The presence of inclusions correlates with the presence of oxygen peaks from LIBS measurements.

**Table I: Statistics of normalized oxygen peak heights for aluminum samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average (Standard Dev.)</th>
<th>Number of Peaks greater than:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean</td>
<td>0.0024 (0.010)</td>
<td>σ 2σ 3σ</td>
</tr>
<tr>
<td>50% Diluted</td>
<td>0.0099 (0.044)</td>
<td>18 11 10</td>
</tr>
<tr>
<td>Dirty</td>
<td>0.0168 (0.035)</td>
<td>57 24 14</td>
</tr>
</tbody>
</table>

**Table II: Comparison of data series via a student’s t-test.**

<table>
<thead>
<tr>
<th>Sample Comparison</th>
<th>t statistic</th>
<th>p value (two tail)</th>
<th>Critical t statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clean vs. 50% Diluted</td>
<td>-3.733</td>
<td>2.08×10^{-4}</td>
<td>1.964</td>
</tr>
<tr>
<td>Clean vs. Dirty</td>
<td>-8.806</td>
<td>1.46×10^{-17}</td>
<td>1.964</td>
</tr>
<tr>
<td>50% Diluted vs. Dirty</td>
<td>-2.728</td>
<td>6.49×10^{-4}</td>
<td>1.962</td>
</tr>
</tbody>
</table>

**Conclusions and Future Work**

Pure aluminum with varying amounts of oxide inclusions, controlled by air bubbling and subsequent dilutions, were sampled using LIBS in-situ. It was found that over the course of many laser measurements, LIBS was able to detect the presence of oxide inclusions and differentiate between molten samples.
Due to the small melt size, there was substantial turbulence within the melt, possibly altering inclusion content over time. In addition, cooling from the probe caused noticeable increases in melt viscosity over extended periods. Laboratory tests involving larger melt sizes will be conducted to overcome these issues.

In previous literature, it was assumed that each spark represents one inclusion. In aluminum and its alloys, it is well known that such particles can aggregate together in the melt. In the 50% diluted dirty sample, oxygen peaks were more intense (but less frequent) than the dirty, undiluted sample. Whether or not this is due to oxide film clumping will require further analysis. Characterization of inclusions will be performed to determine size distribution and morphology.

Not all inclusions found in aluminum are Al₂O₃. CaO, MgO, and others frequently occur in aluminum alloys. In cases where alloying elements can also oxidize, LIBS must be able to differentiate elements dissolved in the matrix versus elements within an inclusion. Experiments involving common industrial alloys will be conducted to determine whether LIBS can detect other types of inclusions.

Acknowledgements

We thank Joe Craparo and Robert De Saro at ERCo for the use of their LIBS equipment and facilities. We also thank Vijay Alreja and Vrindesh Shetty at V.J. Technologies for the use of their X-ray equipment as well as the member consortium of WPI’s Advanced Casting Research Center for funding this ongoing project.

References


Appendix D

*Boride Particle Detection in Al Melts via Laser-Induced Breakdown Spectroscopy*

BORIDE PARTICLE DETECTION IN Al MELTS VIA LASER-INDUCED BREAKDOWN SPECTROSCOPY

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Keywords: Grain Refinement, LIBS, Particle Detection, Liquid Al

Abstract

Aluminum alloy castings are becoming commonplace for critical applications in the automotive and aerospace industries where materials failure is not an option. In order to meet such property demands, tight control over the cleanliness of the melt (mitigation of solid particle inclusions) and microstructure must be achieved. In order to control cleanliness, it must first be well defined and measured. Very few techniques exist in industry that can quantitatively measure inclusion levels in-situ. Laser-induced breakdown spectroscopy (LIBS) is presented as a promising technique to quantify solid particles, desired or undesired, in aluminum melts. By performing LIBS with subsequent statistical analysis on liquid Al with varying amounts of AlB₂ particles, a calibration curve was generated. Ongoing progress of this work is presented and discussed.

Introduction

In general, the cleanliness of aluminum alloys refers to the concentration of inclusions, dissolved hydrogen, and residual elements. Inclusions are defined as unwanted solid particles and can act as nucleation sites for hydrogen pores and cracks [1]. Such particles can be exogenous or form in-situ and can be characterized by their composition, size distribution, morphology, and phase. The most commonly found inclusions are oxides (Al₂O₃, SiO₂, CaO, etc.), but they can also be of other chemistries such as borides, carbides, and aluminides [2]. Inclusion quantity depends on a number of factors including initial melt composition, solidification rate, and pouring atmosphere. It has been shown that cleaner metal results in: greater metal fluidity, better mechanical properties, improved machinability, better surface finish, and overall reduction in reject castings [3-5].

Many laboratory and shop floor techniques exist to assess inclusion content in aluminum and its alloys. They range from traditional optical metallography to filtration such as the Porous Disc Filtration Analyzer (PodFA), and Prefil. Coulter counters such as the Liquid Metal Cleanliness Analyzer (LiMCA) as well as X-ray techniques also exist on the market [6-11]. With exception of LiMCA, and ultrasound to a lesser extent, there are no other industrial techniques that can measure inclusion quantity in-situ [12]. Even then, inclusion chemistry cannot be determined.

Much work has been done using laser-induced breakdown spectroscopy (LIBS) as a tool for determining melt composition. Similar to spark optical emission spectroscopy (OES), LIBS uses a laser pulse to induce a microplasma from a sample of material which is then analyzed with a spectrograph. Although this is a destructive test, the volume ablated ranges from 10⁻⁸ to 10⁻⁵ cm³
which allows for many samples to be taken without compromising the bulk [13]. In addition to solids, LIBS has also been performed on liquids, including molten aluminum, to determine bulk composition [14]. Other relevant advantages to LIBS over other atomic emission spectroscopy techniques include: (1) It can be applied to both conductive and non-conductive materials, (2) sample preparation is not necessary, (3) only an optical line of sight is required for measurement, allowing for the possibility of use in hostile environments, and (4) measurements are performed in seconds, allowing for use on-line [15, 16]. The basic principles and theory of LIBS are described in several review papers [17, 18].

In addition to determining melt chemistry, LIBS could also be used as a means of detecting solid particles within the liquid. If a particle is present where the metal was vaporized, the spectra will reveal its presence and chemistry (see Figure 1) [11]. In principle, signal for a given element will vary depending on whether a particle of that chemistry is present within the plasma. Work has been done on determining the presence and chemistry of inclusions in solid steel samples via statistical evaluation with OES [19, 20]. LIBS has also shown promise as a technique to detect oxide inclusions in molten aluminum [21]. An in-situ technique with the ability to quickly determine both melt chemistry and particle content would be of great benefit for metals processing, offering a fast and more complete analysis of the melt before casting.

In the present work, an Al-5B master alloy was introduced in an aluminum melt to create samples with varying concentrations of AlB₂ particles. The samples were then analyzed by LIBS and electron microscopy. Results show boron signal increases with increased particle content within the compositions measured. Volume fraction measurements correlate well with LIBS data. It was concluded that LIBS shows good promise as an in-situ tool for particle detection and analysis in liquid metal.

Figure 1: Example of LIBS acquisition for boride particles in molten metal. The number and intensity of boron peaks is related to the particle number and size, respectively.
Sample Preparation

Belmont 1009A 99.99% pure aluminum was melted in a Lindberg-Blue resistance furnace to a temperature of 800±1°C. An Al-5B master alloy was used to introduce AlB₂ particles into the melt. Elemental composition was verified by Spark OES. Base metal and master alloy additions were measured beforehand to ensure each charge had a total weight of 2.5 kg. After master alloy addition, the melt was gently agitated.

LIBS Measurements

Preliminary tests were conducted using an immersed probe developed by De Saro, et al [22]. Ingots were placed in a fused-silica crucible and melted in a Lindberg electric crucible furnace. The furnace was heated to 800°C at 2°C/min. The probe was lowered over the melt until the internal temperature reached 93°C. It was then submerged to a depth of approximately 5 cm below the melt surface. Purified nitrogen gas from a liquid nitrogen tank was used as probe coolant and to provide a constant, fresh metal surface at the probe tip. A photograph of the apparatus is shown in Figure 2.

ERCo’s LIBS apparatus was made up of a Q-switched, 20 Hz Nd:YAG laser, operated at 1064 nm with a 50 mJ maximum pulse energy. Emitted plasma light was collected via a fiber-optic cable and fed into an ESA 3000 Echelle-type spectrometer. 10-20 test measurements were then taken before sampling to account for any initial transient readings. 500 successive laser shots were then fired one at a time into the melt. After measurements, the aluminum was allowed to cool in the crucible. Spectra data, gathered with ESAWIN software, was then analyzed via Microsoft Excel.

Figure 2: LIBS Probe immersed in the furnace.
Microanalysis

Immediately after LIBS measurements, a small amount of metal was removed from the crucible and cast in a cast-iron, cylindrical mold. Castings had a 7.5 cm approximate height and 4 cm approximate diameter. The bottom 1.5 cm of each cylinder was then sectioned off for metallographic analysis. Samples were mounted in diallyl phthalate studs, ground, and polished with diamond suspension using a semi-automatic polisher. SEM/EDS analysis was employed to analyze particle composition. ASPEX particle analysis software was used to determine average diameter, area, and aspect ratio of the particles. Particles were identified based on contrast or high EDS counts. EDS spectra were analyzed and particles were classified based on software rules. Particles with both a dark contrast (video level > 55) and Al signal (> 750 counts with no other elements present) were classified as AlB_2. This was due to the difficulty of measuring low atomic number elements with EDS. Volume fraction and aspect ratio were also calculated.

Results and Discussion

LIBS Measurements

Boron’s highest intensity peaks in emission spectroscopy occur within the 206-208 nm range. The most intense observed peak, found at 207.703 nm, was analyzed for these experiments. To account for the variability in signal between individual measurements, boron intensity was normalized by the intensity of the aluminum peak at 308.852 nm [23]. Figure 3 displays normalized intensity for each laser measurement. As seen in Figure 4, average peak intensity noticeably increases with boron content.

Figure 3: Normalized boron peak intensity vs. laser measurement number for each boron concentration tested.
To ensure statistical validity, one-way analysis of variance (ANOVA) was performed upon the LIBS data sets (Table 1). Calculations were performed with a 95% confidence interval (α = 0.05). It can be concluded that the mean LIBS signal for each concentration is statistically, significantly different (calculated F > critical F value). A Student’s t-test was applied post hoc to determine how data sets compared with one another (Table 2). Signal comparisons showed significant difference (calculated t > critical t value) except between 0.05 and 0.1 wt.%.

<table>
<thead>
<tr>
<th>Table 1: Results from ANOVA for LIBS data sets</th>
</tr>
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<tbody>
<tr>
<td><strong>F statistic</strong></td>
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<td>4.119</td>
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</table>

<table>
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<th>Table 2: Comparison of data sets via a Student’s t-test</th>
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</thead>
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<tr>
<td><strong>Sample Comparison (wt.%)</strong></td>
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<td>0.01 vs 0.05</td>
</tr>
<tr>
<td>0.01 vs 0.1</td>
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<tr>
<td>0.05 vs 0.1</td>
</tr>
</tbody>
</table>

As seen in Figure 4, LIBS experiments delivered a linear calibration curve. It is of note that 0.05 wt.% B is approximately at the liquidus line at 750-800°C in the Al-B phase diagram [24]. The presence of peaks at 0.05 wt.% (very close to equilibrium liquidus) and 0.1% B (well inside the L+ AlB₂ region) gives some evidence that the limits of detecting AlB₂ particles in liquid Al is a function of the equilibrium diagram, not of the LIBS apparatus.

Figure 4: A) Calibration curves relating LIBS signal to wt.% B and B) AlB₂ volume fraction (right).
Microanalysis

Irrespective of boron weight percentages, 90% of AlB$_2$ particles were less than 20 µm and small, round morphologies (Figure 5 and 6). Sizes of small particles (< 10 µm) were narrowly distributed except with 0.01 wt.% addition where bimodal behavior was observed. Only AlB$_2$ volume fraction varied with boron content. As seen in Figure 4, there is good agreement between volume fraction of AlB$_2$ and average boron intensity from LIBS.

Figure 5: A) Representative SEM micrograph of Al+0.01 wt.% B. Black particles are AlB$_2$. B) AlB$_2$ size distribution.

Figure 6: AlB$_2$ particle area plotted against aspect ratio. Particles are heavily clustered at the origin, indicating small and round morphologies.
Conclusions and Future Work

Pure aluminum with varying amounts of AlB$_2$ particles, controlled by master alloy additions, was measured using LIBS in-situ. It was found that over the course of laser measurements, LIBS was able to detect the presence of boride particles and differentiate between molten samples. A linear trend was observed between AlB$_2$ volume fraction and boron LIBS signal.

More tests are planned with greater AlB$_2$ additions to determine the full limits of detection. In LIBS, nonlinear behavior is often observed at extremely high and low concentrations. Poisson analysis and statistics of extremes will also be performed on gathered data to investigate the relationship between particle size distribution and LIBS intensities.

Because emission behavior may change in the presence of other elements, similar experiments in the Al-Ti-B system are planned. Experiments involving common alloy systems should also be conducted. Due to the small melt size, cooling from the probe caused noticeable increases in melt viscosity over extended periods. Tests involving large melt sizes should be conducted to overcome changes in viscosity as well as to investigate the degree of agitation required to gather representative LIBS data.

Acknowledgements

The authors kindly thank Joe Craparo and Robert De Saro (ERCo) for the use of their LIBS equipment and facilities, Dave Smith and Wenwu Shi (Foseco) for metallography and image analysis, and the membership of WPI’s Advanced Casting Research Center for funding this ongoing project.

References

Appendix E

*SiC Particle Detection in Liquid Aluminum via Laser-Induced Breakdown Spectroscopy*

SiC PARTICLE DETECTION IN LIQUID ALUMINUM VIA LASER INDUCED BREAKDOWN SPECTROSCOPY

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Keywords: Metal Cleanliness, LIBS, Inclusions, Liquid Aluminum

Abstract

Aluminum alloy castings are becoming commonplace for critical applications in the automotive and aerospace industries where materials failure is not an option. Tight control over the cleanliness of the melt (mitigation of solid particle inclusions and dissolved gases) and microstructure must be achieved. Very few techniques exist that can quantitatively measure inclusion levels in situ. The use of laser-induced breakdown spectroscopy (LIBS) has shown promise as a technique to quantify solid particles, wanted and unwanted, in aluminum melts. SiC particles were added to pure aluminum and analyzed with LIBS, and traditional metallography. An algorithm, based on the Nalimov test, was used to differentiate between LIBS signal from the matrix and particles. Initial tests show a linear relationship between SiC concentration and LIBS signal.

Introduction

There is a plethora of laboratory and foundry floor techniques to assess inclusion content in aluminum and its alloys. As compiled in Figure 1, they range from traditional optical metallography to filtration and ultrasound with each method having its own pros and cons [1-6]. Other than LiMCA (Liquid Metal Cleanliness Analyzer), a coulter counter technique, there are no other methods of measuring inclusion concentration in situ.

In this metals processing field, laser-induced breakdown spectroscopy (LIBS) has been primarily explored as tool for bulk chemistry measurement. Like conventional OES, LIBS uses a short laser pulse to form a micro-plasma from a sample of metal. The plasma light is processed with a spectrograph to determine the concentration of elements present. The volume ablated due to this process is quite small (10-8 to 10-5 cm3) and allows for many measurements to be taken without compromising the bulk material [7]. LIBS systems have been adapted for high temperature applications and have been used to measure composition of molten metals [8]. The fundamentals of LIBS can found in several books and review papers [9-11].

In this work, the premise has been that LIBS can be used as a means of detecting inclusions and second phase particles in molten metals. If a particle is present in the sampling volume, the spectra will reveal its presence and chemistry. Such work has been performed on solid steel [12, 13] and aluminum [14, 15]. A proof of concept for this application has been recently demonstrated [15].

Experimental

Sample Preparation

Twenty five kg of 1070 aluminum (99.7% purity) was transferred from a quiescent reservoir furnace to a holding furnace and kept at 725°C ± 5°C. Simulated inclusions were introduced by stirring in two small tablets, one at a time, of Duralcan MMC (Al+ SiC). 13.4 g of MMC were added in total. In between additions, 2.5 kg ingots were cast for LIBS tests. Actual volume fractions were measured via metallography.

LIBS Measurements

LIBS trials were performed using a probe developed by Energy Research Company (Plainfield, NJ) [16]. Ingots were placed in a fused silica crucible and melted in a Lindberg electric furnace to 800°C ± 5°C. The probe was submerged 5-7 cm below the melt surface. Purified nitrogen gas from a liquid source was used for coolant and bubbling flow. The immersed probe is shown in Figure 2.

The laser apparatus consisted of a Q-switched, 20 Hz Nd:YAG laser, operated at 1064 nm with a 50 mJ pulse energy (Big Sky Laser, Bozeman, MT). Emitted plasma light was collected via a fiber-optic cable and fed into an ESA 2802 Echelle-type spectrometer (LLA Instruments). Only silicon signal was analyzed during these trials due to the difficulty of measuring carbon in minute quantities with the given LIBS settings.

10-20 test measurements were taken to account for any transient signals. 500 successive laser shots were then fired one at a time into the melt. Spectra data was gathered with ESAWIN software.
and analyzed via Microsoft Excel. Measurement frequency was approximately 1 Hz.

Immediately after LIBS measurements, a small sample of the oxide skin was also collected to investigate the nature of the probe-metal interface. A small amount of metal was also drawn from the crucible and cast in an iron, cylindrical mold. Castings had a 7.5 cm height and 4 cm diameter. The bottom 1.5 cm of each cylinder was then sectioned off for metallographic analysis. OES measurements (Spectromax X) were performed before and after LIBS to investigate any compositional changes in the melt.

Microanalysis

Samples were mounted in diallyl phthalate studs, ground, and polished with diamond suspension on a semi-automatic polisher. Back-scatter SEM/EDS analysis was employed to determine particle composition. ASPEX analysis software was used to determine diameter, volume fraction, of the inclusions. Particles were identified based on contrast and EDS count. EDS spectra were analyzed and particles were classified based on software rules. Particles with both dark contrast (low video level) and high Si content (> 20% after subtracting background Al signal) were classified as SiC.

Results and Discussion

Microanalysis

No particles were observed in the control Al sample. Irrespective of volume fraction, most SiC particles were less than 20 µm and were narrowly distributed (Figure 3). As seen in Figure 4, SiC particles showed no signs of agglomeration and were sparse within the Al matrix, yielding low volume fractions of (0.0029, 0.0047, and 0.0054% SiC). These values are similar to typical inclusion concentrations found in industry [17]. As seen in figure 6, all SiC particles were solitary. No particle agglomeration was observed.

LIBS Measurements

Silicon’s peak at 288.158 nm was analyzed for these experiments. To account for variability in signal between individual laser pulses, silicon intensity was normalized by aluminum’s peak at 308.852 nm [18]. As seen in Figure 5, peak frequency above baseline signal noticeably increases with SiC content with the exception of the 0.0054% SiC sample. No Si peaks were observed in the control Al sample. Peaks were observed when normalized signal was approximately greater than 0.05.

OES measurements were performed before and after LIBS to investigate any bulk compositional changes in the melt. As seen in Table 1, there was a noticeable change in bulk Si content likely due to leaching from the crucible. Even so, these amounts of dissolved Si are below the lower limits of detection for LIBS [19]. It is therefore safe to say that Si signal was due to SiC particles being ablated by the laser, not due to homogeneous Si in the melt.

| Table 1: Melt composition (wt%) before and after LIBS |
|----------------|-------|-------|-------|-------|-------|-------|
|                | Si    | Fe    | Mg    | Na    | Ti    | Al    |
| Before LIBS    | 0.015 | 0.044 | 0.013 | 0.009 | 0.0025| 99.9  |
| After LIBS     | 0.050 | 0.044 | 0.012 | 0.0009| 0.0025| 99.9  |
The Nalimov test was used to separate out baseline signal from that of a particle hit [20]. A spike in Si signal, compared to baseline, will be seen as an outlier. This test determines whether the value \( x \) is or is not an outlier within the data set of \( n \) values, taking into account the standard deviation \( \sigma \) and mean \( \bar{x} \) (equation 1).

\[
r = \frac{|x - \bar{x}|}{\sigma} \times \sqrt{\frac{n}{n-1}}
\] (1)

If \( r \) exceeds a threshold value, then \( x \) is an outlier. For data sets with \( n \geq 500 \), the threshold is 1.960. The test determined that intensity spikes greater than approximately 0.1 were true outliers (particle hits). As seen in Figure 6, plotting the average intensity of particle hits appears to correlate with SiC concentration.

Because of the wide standard deviation of the data point corresponding 0.0054% SiC, a one-way analysis of variance (ANOVA) test was performed to ensure statistical validity. Calculations were performed with a 95% confidence interval (\( \alpha=0.05 \)). As shown in Table 2, it can be concluded that, with 95% confidence, the mean LIBS signal for each concentration is statistically, significantly different (calculated \( F > \) critical \( F \) value).

<table>
<thead>
<tr>
<th>F statistic</th>
<th>p value</th>
<th>Critical F statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.429</td>
<td>( 3.3 \times 10^{-16} )</td>
<td>3.002</td>
</tr>
</tbody>
</table>

It is also of note that the particle size in the 0.0054% SiC sample was not as narrowly distributed as the other two samples, as alluded to in Figure 3. In principle, the signal produced from a particle hit will be a function of particle size. With a greater standard deviation of particle sizes, the corresponding LIBS signal would also exhibit similar behavior. More work investigating the effect of particle size distribution is planned.
Conclusions and Future Work

Pure aluminum with varying amounts of simulated SiC inclusions was analyzed using LIBS in-situ. It was found that over the course of many laser measurements, LIBS was able to detect the presence of inclusions by monitoring Si signal. Microscopy data points towards a relationship between inclusion concentration and LIBS signal.

More tests are planned with greater SiC additions to determine the full limits of detection in terms of particle concentration. Poisson analysis and statistics of extremes show promise of enabling a direct calculation of particle size given elemental peak intensity.

Due to the small size of the melt, there was enough turbulence to enable random sampling with the laser. However, this is not the always case in larger melt sizes. In addition, the cooling presence of the probe in the melt caused noticeable increases in liquid viscosity. Further tests upon with larger crucibles will be conducted.

Acknowledgements

We kindly thank Dave Smith and Wenwu Shi (Foseco) for metallography and image analysis as well as the member consortium of WPI’s Advanced Casting Research Center for funding this ongoing project.

References

Appendix F

$\textit{TiB}_2$ Particle Detection in Liquid Aluminum via Laser-Induced Breakdown Spectroscopy

TiB₂ PARTICLE DETECTION IN LIQUID ALUMINUM VIA LASER INDUCED BREAKDOWN SPECTROSCOPY

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Keywords: Metal Cleanliness, LIBS, Inclusions, Liquid Aluminum

Abstract

Because aluminum alloy castings are becoming commonplace for critical applications in the automotive and aerospace industries, tight control over the cleanliness of the melt (mitigation of solid particle inclusions) and microstructure must be achieved. In order to control cleanliness, it must first be well defined and measured. Very few techniques exist in industry that can quantitatively measure inclusion levels in-situ. Laser-induced breakdown spectroscopy (LIBS) is presented as a promising technique to quantify solid particles, desired or undesired, in aluminum melts. By performing LIBS with subsequent statistical analysis on liquid Al with varying amounts of TiB₂ particles, calibration curves for B and Ti were generated.

Introduction

There is a plethora of laboratory and foundry floor techniques to assess inclusion content in aluminum and its alloys. They include methods ranging from traditional optical metallography to filtration and ultrasound with each method having its own pros and cons [1-6]. Other than LiMCA (Liquid Metal Cleanliness Analyzer), a coulter counter technique, and Metalvision, an ultrasonic technique, there are no other methods of measuring inclusion concentration in-situ [7]. One of the main drawbacks to these techniques is their inability to discern particles with different chemistries.

Laser-induced breakdown spectroscopy (LIBS) has been of great interest to the metals processing field as tool for bulk chemistry measurement. Similar to conventional OES, LIBS uses a short laser pulse to form a micro-plasma from a sample of metal. The plasma light is processed with a spectograph to determine the concentration of elements present. The volume ablated in this process is quite small (10⁻⁶ to 10⁻³ cm³ depending on laser parameters and substrate material) and allows for many measurements to be taken without compromising the bulk material [8]. LIBS requires a direct line of sight to the substrate for analysis, making it attractive for use in extreme environments.

LIBS systems have been adapted for high temperature applications and have been used to measure composition of molten metals [9]. The fundamentals of LIBS can found in several books and review papers [10-12].

In this work, the premise has been that LIBS can be used as a means of detecting inclusions and second phase particles in molten metals. If a particle is present in the sampling volume, the spectra will reveal its presence and chemistry. Such work has been performed on solid steel [13, 14] and aluminum [15, 16]. Studies with Al₂O₃, AlB₂, and SiC particles in liquid Al have been recently performed by the authors [16-18].

Experimental

Sample Preparation

99.99% pure aluminum (Belmont Metals) was melted in an electric resistance furnace to a temperature of 800±1°C. Al-Ti-B master alloy rods (Milward Alloys) were used to introduce boride particles into the melt. Base metal and rod additions were weighed beforehand to ensure each charge had a total weight of 2.5 kg. The melt was gently agitated immediately after master alloy addition. Composition of the base aluminum is compiled in Table I. Weights and compositions of each trial are compiled in Table II.

Elemental composition of the metal was measured by Spark OES (SpectroMaxX). The maximum level of boron detectable via OES was 0.026 wt%. To estimate the actual amount of boron in the metal, the measured amount of Ti was multiplied by the B/Ti ratio of the master alloy.

<table>
<thead>
<tr>
<th>Element</th>
<th>wt.%</th>
<th>Fe</th>
<th>Ga</th>
<th>Others</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.00079</td>
<td>0.00092</td>
<td>0.0007</td>
<td>Trace</td>
<td>99.995</td>
</tr>
</tbody>
</table>

Table I: Composition of base aluminum used in experiments

<table>
<thead>
<tr>
<th>Base Al (kg)</th>
<th>Master Alloy (kg)</th>
<th>Ti/B Ratio</th>
<th>Composition (wt.%, From OES)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>2.40</td>
<td>Al-3Ti-1B (0.10)</td>
<td>3</td>
<td>0.092</td>
</tr>
<tr>
<td>2.30</td>
<td>Al-3Ti-1B (0.20)</td>
<td>3</td>
<td>0.151</td>
</tr>
<tr>
<td>2.22</td>
<td>Al-3Ti-1B (0.30)</td>
<td>3</td>
<td>0.319</td>
</tr>
<tr>
<td>2.37</td>
<td>Al-2.6Ti-2.2B (0.10)</td>
<td>1.18</td>
<td>0.064</td>
</tr>
<tr>
<td>2.38</td>
<td>Al-5Ti-1B (0.10)</td>
<td>5</td>
<td>0.205</td>
</tr>
</tbody>
</table>

Table II: Weights, compositions, and elemental ratio of each experiment.

LIBS Measurements

LIBS trials were performed using a ceramic probe developed by Energy Research Company (Plainfield, NJ) [19]. The probe was submerged 5-7cm below the melt surface. Purified nitrogen gas from a liquid source was used for coolant and bubbling flow. The immersed probe is shown in Figure 1.

The laser apparatus consisted of a Q-switched, 20 Hz Nd:YAG laser, operated at 1064 nm with a 50 mJ pulse energy (Quantel Laser). Emitted plasma light was collected via a fiber-optic cable and fed into an Echelle-type spectrometer (LLA Instruments).

10-20 test measurements were taken to account for any transient signals. 500 successive laser shots were then fired one at a time.
into the melt. Spectra data was gathered with ESAWIN software and analyzed via Microsoft Excel. Measurement frequency was approximately 1 Hz.

A small amount of metal was also drawn from the crucible and cast in an iron, cylindrical mold. Cast cylinders had a 7.5 cm height and 4 cm diameter. The bottom 1.5 cm of each cylinder was then sectioned off for metallographic analysis.

Microanalysis

Samples were mounted in diallyl phthalate studs, ground, and polished with diamond suspension on a semi-automatic polisher. Back-scatter SEM/EDS analysis was employed to determine particle composition. ASPEX analysis software was used to determine diameter, volume fraction, of the inclusions. Particles were identified based on contrast and EDS count. Particles with both bright contrast (high video level) and high Ti content (> 3% after subtracting background Al signal) were classified as TiB₂.

Results and Discussion

LIBS Measurements

Boron’s highest intensity peaks in emission spectroscopy occur within the 200-300 nm range. Boron’s emission line at 249.772 nm was analyzed for these experiments. Titanium produces a large number of lines within the 300-400 nm range. Its peak at 399.8636 nm was used to analyze the effect of Ti concentration on the melt. To analyze individual particles, a weaker but more sensitive peak at 323.4513 nm was used. To account for the variability in signal between individual measurements, boron and titanium peak intensities were normalized by the intensity of the aluminum peak at 308.852 nm [20].

As seen in Figure 2 and 3, elemental signal noticeably increases with solute content. Data points represent the averaged signal over 500 laser pulses. There is a good linear agreement for the ranges of Ti and B desired in grain refinement. Depending on the alloy, typical target chemistries range from 0.2-0.5 wt.% Ti and 0.01-0.03 wt.% B [21]. The solubility of boron in liquid aluminum is extremely low (less than 0.05% at 750-800°C) [22]. This is lower than the typical limits of detection of LIBS for solute elements in aluminum [23]. Therefore, the assumption can be made that any time a boron line is detected, a boron containing particle was present in the sampling volume.

![Figure 1: LIBS Probe Immersed in the furnace [16].](image1)

Figure 1: LIBS Probe Immersed in the furnace [16].

![Figure 2: Calibration curve of average Ti signal vs. concentration.](image2)

Figure 2: Calibration curve of average Ti signal vs. concentration.

![Figure 3: Calibration curve of average C signal vs. concentration.](image3)

Figure 3: Calibration curve of average C signal vs. concentration.

Two-tailed analysis of variance (ANOVA) was applied to the LIBS datasets. Statistics on each element, compiled in Table III, show that with 95% confidence there is no statistically significant overlap between the data.

<table>
<thead>
<tr>
<th>Element</th>
<th>Calculated F</th>
<th>p-Value</th>
<th>Critical F</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>33.268</td>
<td>4.52×10⁻⁷</td>
<td>2.375</td>
</tr>
<tr>
<td>Ti</td>
<td>286.417</td>
<td>7.40×10⁻²⁰³</td>
<td>2.375</td>
</tr>
</tbody>
</table>

Table III: ANOVA on Ti and B measurements
The Nalimov test was used to separate baseline signal from that of a particle hit. For boron, the solubility is extremely low in liquid aluminum and below the sensing capabilities of the spectrometer. Therefore, any substantial signal above the background can be attributed to a boride particle. For titanium, there is an appreciable amount dissolved within the matrix. In this case, the baseline is the signal coming from dissolved titanium. By using the Nalimov test on the Ti and B datasets, it was found that for approximately 10% of the time, a spike in B intensity did not coincide with a spike in Ti intensity. This indicates that the test requires some optimization, or perhaps a more conditional analysis approach is required to separate out background elemental signal from signal corresponding to a particle hit. Application of the Nalimov test to Ti and B signals yielded linear relationships between average particle hit intensities and volume fraction determined by microanalysis (Figure 4 and 5). Even though there is a linear relationship between particle hit intensity and volume fraction, using overall Ti and B signal from Figure 2 and 3 can be used to determine when grain refining elements are at their optimal levels.

Microanalysis

Irrespective of volume fraction, most TiB₂ particles were less than 20 µm and were narrowly distributed. Little to no AlB₂ or TiAl₃ particles were observed during microanalysis. TiB₂ was seen as bright particles in the pure Al matrix. Irrespective of volume fraction, over 90% of particles were less than 10 µm and were narrowly distributed (Figure 6). It should be noted that LiMCA, with a detection limit of 20 µm, would in principle be unable to detect such particles. The fact that they were able to be detected by LIBS is significant.

Both the number and volume fraction of TiB₂ particles are linearly proportional to the concentration of Ti and B. However, deviations occurred when the ratio of Ti/B was too skewed. It is known that, for most alloys, the optimal ratio is approximately 2.22 wt.% Ti to 1 wt.% B for optimal grain refinement [21]. If the ratio is too high, the resultant volume fraction of particles will decrease due to the lack of boron in the matrix. This can be seen in Figure 7, where the data point for Al-0.205Ti-0.041B (Ti/B ratio of 5) significantly deviates from the linear relationship.

Figure 4: Ti particle hits from LIBS as a function of TiB₂ volume fraction. Diamonds correspond to average values.

Figure 5: B particle hits from LIBS as a function of TiB₂ volume fraction. Diamonds correspond to average values.

Figure 6: TiB₂ particle size distribution.

Figure 7: TiB₂ particle count and volume fraction as a function of Ti concentration.
Conclusions and Future Work

Pure aluminum with varying amounts of Al-Ti-B master alloys were analyzed using in-situ LIBS. It was found that over the course of many laser measurements, TiB$_2$ particles could be detected by monitoring Ti and B signal. Calibration curves were developed for Ti and B in pure Al within the compositional ranges for grain refinement, allowing LIBS to be used as a possible tool for monitoring grain refining elements. Nearly all particles that were observed in microanalysis were less than 6 μm in size, well below the 20 μm sensing limit of LiMCA. The Nalimov test was used to determine elemental signal that was not from the bulk chemistry, but from particles. In the case of separating out Ti signal from a particle hit from that in the bulk metal, the Nalimov test performs a reasonable job. However, its identification of false negative requires a more conditional analysis.

Due to the small size of the melt, there was enough turbulence to enable random sampling with the laser. However, this is not always the case in larger melts. Further tests with larger melt sizes need to be conducted.

Acknowledgements

We kindly thank Dave Smith and Wenwu Shi (Foseco) for metallography and image analysis as well as the member consortium of WPI’s Advanced Casting Research Center for funding this ongoing project.

References

Appendix G

Inclusion Detection in Cast and Wrought Aluminum Alloys via Laser-Induced Breakdown Spectroscopy

Inclusion Detection in Aluminum and Aluminum Alloys via Laser-Induced Breakdown Spectroscopy

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Abstract
Laser induced breakdown spectroscopy (LIBS) has shown promise as a technique to quickly determine molten metal chemistry in real time. Because of its characteristics, LIBS could also be used as a technique to sense for unwanted inclusions and impurities. Simulated inclusions (Al₂O₃, TiB₂, and SiC) were added to molten aluminum. LIBS was performed in situ to determine whether particles could be detected. Outlier analysis was performed on LIBS data and compared to particle volume fraction measured through metallography. It was determined that LIBS could differentiate between melts with different amounts of inclusions by monitoring the fluctuations in signal for elements of interest. LIBS shows promise as an enabling tool for monitoring metal cleanliness.
Introduction

The cleanliness of aluminum alloys refers to the concentration of inclusions, dissolved hydrogen, and residual elements. Inclusions are defined as unwanted solid particles and can act as nucleation sites for hydrogen pores and cracks [1]. The most commonly found inclusions are oxides (Al₂O₃, SiO₂, CaO, etc.) [2]. Their quantity depends on a number of factors including initial melt composition, solidification rate, and pouring atmosphere. It has been shown that cleaner metal results in greater metal fluidity, higher casting properties, improved machinability, better surface finish, and overall reduction in reject castings [3-5]. Melt cleanliness can be controlled by the removal of these elements and particles. To properly control melt cleanliness it must be measurable. Many laboratory and shop floor techniques exist to assess inclusion content in aluminum and its alloys. They range from traditional optical metallography to filtration (PoDFA, Prefil), coulter counters (LiMCA) and X-ray techniques with each method having its pros and cons [6-11]. However, very few techniques exist that can detect the presence of inclusions in situ [12].

Recently, laser-induced breakdown spectroscopy (LIBS) has garnered interest as a tool for probing liquid metal. Similar to conventional spark optical emission spectroscopy (OES), LIBS uses a short laser pulse to form a plasma on the metal surface. The elements present in the plasma emit characteristic EM radiation, which is collected and processed by a spectrograph. Because the sample interrogated is vaporized, LIBS is technically a destructive test. However, the volume sampled is on the order of 10⁻⁸ to 10⁻⁵ cm³, which results in a very small sample size even if thousands of measurements are taken [13]. Other relevant advantages over other atomic emission techniques include: 1) LIBS can be applied to both conducting and non-conducting materials, 2) sample preparation is not necessary, 3) only an optical line of sight is required for measurement, and 4) measurements are performed in seconds [14, 15]. As illustrated in Figure 1, Energy Research Company (ERCo, Plainfield, NJ) developed and constructed a LIBS immersion probe for molten aluminum [16-18]. An inert gas streams through a lance to form a bubble at the end. The bubble allows for a constant, fresh view of the metal for the laser. Fiber optic cables transmit the incoming laser pulse and outgoing light from the spark.
Particles constantly move throughout the melt due to their small size and the presence of convection in the furnace. If an inclusion is present where the metal was vaporized, the spectra will reveal its presence and chemistry. If an oxide particle is vaporized by the laser, a spike in oxygen will be detected in the spectrum. In principle, the intensity of the spike will relate directly to the size of the inclusion. In addition, a multi-element inclusion, such as MgO, would register a spike in both O and Mg which allows for detection of inclusions with different chemistries.

Although no work has been reported on sensing inclusions with LIBS in molten metal, similar work has been done in solid and gaseous matrices. This includes MnS and Al₂O₃ in solid steel samples through pulse discrimination analysis with spark OES by Kuss et al and Falk [19-21]. Much work has also been performed by Hahn and colleagues on metal and oxide particles in aerosol and aqueous streams. The following relationship was derived where $X$ is the concentration of particles within a given matrix [22-25]:

$$X = (\text{Average particle concentration for hits}) \times (\text{sampling frequency of hits})$$

In LIBS, concentration is proportional to the emission line intensity of the element of interest [26]. Provided that each measurement run performs the same amount of laser sparks, equation 1 can also be written as:
$X \propto I_{Avg} \times N_{Hits}$ \hfill (2)

where $I_{Avg}$ is the average elemental intensity of inclusion hits, and $N_{Hits}$ is the number of hits. By performing the necessary analysis to identify spikes in elemental intensity and collecting the hit spectra, the resultant LIBS data can be compared to metallography or another method to create a calibration curve. An example of this process is shown in Figure 2.

LIBS has the promise to be able to probe the melt and to provide knowledge on: (i) chemistry of the inclusions present; (ii) the amount, the volume fraction of inclusions; and (iii) potentially the size distribution of inclusions. This is further discussed in a review paper on LIBS by the authors [27].

In the present work, synthetic inclusions were introduced in molten aluminum. In situ LIBS was performed in the molten metal in an effort to detect inclusions. Metallographic samples were collected to compare to LIBS data. Depth and repeatability trials were also performed on molten A356 aluminum.

Figure 2 - Example of LIBS data acquisition for oxide inclusions in molten metal. Shot 2 exhibits an oxygen peak at 777 nm while shot 1 and 3 do not. Therefore, shot 2 is a “hit.”

Experimental Procedures

Microanalysis

For all experiments, metallographic samples were drawn from the melt to determine inclusion volume fraction. Samples were cast into a cylindrical cast iron mold (4 cm diameter, 10 cm height). To avoid any shrinkage porosity that might form and to ensure the bulk metal was analyzed (not dross), the bottom 1.5 cm of the casting was analyzed. The procedure for metallography involved initial cutting
with an abrasive cutting wheel and subsequent mounting in diallyl phthalate studs. The studs were ground with SiC paper and polished with diamond slurry. Polished samples were analyzed through backscatter and secondary electron SEM. Particles of interest were identified and tabulated through EDS and image contrast using ASPEX particle analysis software.

**Signal Analysis**

In the case of sensing particles, especially those with elements that are also dissolved in the matrix, it’s essential to filter out signals corresponding to a particle hit from those corresponding to the matrix. Because a particle is a concentrated mass of elements, elemental signal would be significantly higher than that of the matrix. Table 1 contains optical emission peak wavelengths for the elements of interest. Data comes from the NIST Atomic Spectra Database [28].

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>777.198</td>
</tr>
<tr>
<td>Boron</td>
<td>249.772</td>
</tr>
<tr>
<td>Titanium</td>
<td>323.451</td>
</tr>
<tr>
<td>Silicon</td>
<td>288.158</td>
</tr>
<tr>
<td>Aluminum</td>
<td>308.852</td>
</tr>
</tbody>
</table>

A strict baseline must be drawn to avoid mistaking an errant spike in background noise as an elemental peak. In a time series where measurements are taken at a given rate, a particle hit would appear as an outlier in the resultant data set. Unlike most experiments in the LIBS community, the goal of particle analysis is to investigate outliers in signal. Statistical criteria for estimating outliers have existed for decades, but some tests are not optimal for large sets of data [29]. The Nalimov test, developed by V.V. Nalimov, is one such way of determining whether or not a measurement is an outlier. In the realm of spectroscopy, this test was used by Kuss, Mittelstaedt and Mueller to determine the content of non-metallic inclusions in ferrous materials via scanning laser OES [20]. To the authors’ knowledge, the use of the Nalimov test in this application has not been previously used in LIBS.

The test is as follows. Given \( n \) values, standard deviation \( \sigma \) and mean \( \bar{x} \), the test calculates an \( r \) value, expressed as:

\[
r = \left| \frac{\bar{x} - \bar{x}'}{\sigma} \right| \times \sqrt{\frac{n}{n - 1}}
\]  

(2)
If $r$ exceeds a threshold value, then the data point $x$ is an outlier. For example, for data sets with $n \geq 500$, the critical $r$ is 1.960. Threshold values for a given sample size are tabulated in several statistics papers and textbooks [29].

In our experimental program, the Nalimov test was used to create a threshold criterion to classify an elemental spike from errant background. The average pixel intensity in a one nanometer range close to the emission line of interest was gathered over all laser shots during a measurement run. Pixel average and standard deviation was used to determine the critical value, $r$. If the spike at the wavelength of interest was larger than $r$, then it was indeed an elemental emission line. A flow chart of spectrum processing operations and a summary of their main features is shown in Figure 3.

![Flow chart of spectrum processing operations to extract LIBS data on inclusions.](image-url)
Sample Preparation

Pure Al Experiments

The possibility of using LIBS to sense inclusions was examined with proof-of-concept experiments on 2.5 kg melts with both SiC and TiB₂ additions.

For SiC particle experiments, 25 kg of 1070 aluminum (99.7% purity) was transferred from a quiescent reservoir furnace to a holding furnace and kept at 725°C. Simulated inclusions were introduced by stirring in two small tablets, one at a time, of Duralcan MMC (Al+ SiC). 13.4 g of MMC were added in total. In between additions, 2.5 kg ingots were cast for LIBS tests. Actual volume fractions were measured via metallography. The ingots were then remelted in an electric resistance furnace to temperature of 800±1°C.

For TiB₂ particle experiments, 99.99% pure aluminum was melted in an electric resistance furnace to 800±1°C. Al-Ti-B master alloy rods were used to introduce boride particles into the melt. Base metal and rod additions were weighed beforehand to ensure each charge had a total weight of 2.5 kg. The melt was gently agitated immediately after master alloy addition. Weights and compositions from spark OES of each trial are compiled in Table 2.

<table>
<thead>
<tr>
<th>Master Alloy</th>
<th>Ti/B Ratio</th>
<th>Composition (wt%, From OES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-3Ti-1B (0.10)</td>
<td>3</td>
<td>0.092 0.030</td>
</tr>
<tr>
<td>Al-3Ti-1B (0.20)</td>
<td>3</td>
<td>0.151 0.050</td>
</tr>
<tr>
<td>Al-3Ti-1B (0.30)</td>
<td>3</td>
<td>0.319 0.162</td>
</tr>
<tr>
<td>Al-2.6Ti-2.2B (0.10)</td>
<td>1.18</td>
<td>0.064 0.054</td>
</tr>
<tr>
<td>Al-5Ti-1B (0.10)</td>
<td>5</td>
<td>0.205 0.041</td>
</tr>
</tbody>
</table>

Alloy Experiments

Aluminum alloy experiments consisted of three cast (A356, A206, A380) and three wrought alloys (3104, 5182, 7050). All casting alloys and 7050 were melted as ingots. 3104 and 5182 were melted as cut sheets. 13.6 kg (30 lbs) of metal was melted in an Inductotherm 35 kW VIP push-out induction furnace to a temperature of 780±20°C. Melt compositions from spark OES, are disclosed in Table 3. Each melt was skimmed before and after a measurement was run. A metal matrix composite, AA6061 + 20% Al₂O₃ Duralcan (RioTinto Alcan) was added to the melt in 5±0.5 g increments.
Table 3: Compositions of Alloys Used in LIBS Tests

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Si (wt.%)</th>
<th>Cu (wt.%)</th>
<th>Mg (wt.%)</th>
<th>Mn (wt.%)</th>
<th>Fe (wt.%)</th>
<th>Ti (wt.%)</th>
<th>Zr (wt.%)</th>
<th>Zn (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A380</td>
<td>9.31</td>
<td>3.50</td>
<td>0.048</td>
<td>0.100</td>
<td>0.70</td>
<td>0.025</td>
<td>0.0024</td>
<td>1.55</td>
</tr>
<tr>
<td>A356</td>
<td>7.27</td>
<td>0.104</td>
<td>0.451</td>
<td>0.259</td>
<td>0.324</td>
<td>0.088</td>
<td>0.0018</td>
<td>0.103</td>
</tr>
<tr>
<td>A206</td>
<td>0.069</td>
<td>4.44</td>
<td>0.218</td>
<td>0.348</td>
<td>0.053</td>
<td>0.240</td>
<td>&lt;0.0003</td>
<td>0.013</td>
</tr>
<tr>
<td>7050</td>
<td>0.041</td>
<td>2.44</td>
<td>2.11</td>
<td>0.0042</td>
<td>0.091</td>
<td>0.033</td>
<td>0.123</td>
<td>6.24</td>
</tr>
<tr>
<td>3104</td>
<td>0.220</td>
<td>0.191</td>
<td>1.20</td>
<td>0.88</td>
<td>0.60</td>
<td>0.021</td>
<td>0.0003</td>
<td>0.024</td>
</tr>
<tr>
<td>5182</td>
<td>0.146</td>
<td>0.069</td>
<td>5.02</td>
<td>0.373</td>
<td>0.387</td>
<td>0.011</td>
<td>&lt;0.0003</td>
<td>0.011</td>
</tr>
</tbody>
</table>

**LIBS Measurements**

**Pure Al Experiments**

Preliminary tests were conducted using an immersed probe developed by Energy Research Company [17]. Ingots were placed in a fused-silica crucible and melted in an electric crucible furnace. The furnace was quickly ramped to 500°C and heated to 800°C at 2°C/min. The probe was submerged below the melt surface. Purified nitrogen gas from a liquid nitrogen tank was used as probe coolant and to provide a constant, fresh metal surface at the probe tip. A schematic of the apparatus is shown in Figure 4.

The apparatus consisted of a Q-switched, 20Hz Nd:YAG laser, operated at 1064 nm with a 40 mJ maximum pulse energy. Emitted plasma light was collected via a fiber-optic cable and fed into an echelle-type spectrometer. 10-20 test shots were performed before sampling to account for any initial transient readings. 500 successive laser shots were then fired one at a time into the melt. After measurements, the aluminum was allowed to cool in the crucible. Spectra data, gathered with the spectrometer software, was analyzed through OriginPro software.

**Alloy Experiments**

Tests on aluminum alloys were conducted using a modified LIBS probe and system developed by Energy Research Company. A, Q-Switched, Nd-YAG laser (1064 nm wavelength, 330 mJ pulse energy) was used to provide the sparks necessary to perform spectroscopy. The laser was suspended over the melt with a manual forklift. A ceramic probe was used to penetrate the melt. An echelle spectrometer (200-800 nm sensing zone) was used to collect emitted light induced by the laser pulse. Every sampling run comprised of 600 measurements at a frequency of 1.5 Hz. A schematic of the apparatus is shown in Figure 5. Elemental lines of interest were analyzed with OriginPro.
Repeatability tests, consisting of three measurement runs in sequence, were performed on A356 with 15g of MMC. Depth trials were also performed on the same melt and consisted of measurement runs at three different depths below the melt surface.

Figure 4 – Schematic representation of the LIBS apparatus for tests on pure aluminum.

Figure 5 – Schematic representation of the LIBS apparatus for tests on aluminum alloys.
Results and Discussion

**Sampling Volume**

For use in liquid metal, the volume of mass sampled per laser spark must be known. On solid samples, the effective sampling volume can be measured through microscopy [30]. With liquids, it is difficult or impossible to measure by direct observation. However, it can be approximated through an energy balance relating the energy contributing to ablation to the enthalpy in heating the material to the plasma temperature [31, 32]:

\[
E(1 - R)P = M \left[ \int_{T_o}^{T_b} C_p^l \, dT + \Delta H_v + \int_{T_b}^{T_p} C_p^g \, dT \right]
\]

(3)

Where:

\[
C_p^l = \sum_{i} f_i C_{p,i}^l
\]

(4)

\[
C_p^g = \sum_{i} f_i C_{p,i}^g
\]

(5)

In Equation 3, “R” is surface reflectivity, “T_o” is the ambient temperature, “T_b” is the boiling point, “T_p” is the plasma temperature, “C_p^l” is the heat capacity of the liquid phase, “C_p^g” is the gas phase heat capacity, “\Delta H_v” is the enthalpy of vaporization, “M” is the ablated mass, and “P” is a factor that accounts for other processes (ionization, plasma reheating, etc.). For Equation 4 and 5, “f_i” is the fraction of element i in the alloy, “C_{p,i}^l”, and “C_{p,i}^g” are the respective liquid and gas phase heat capacities of element i. Thermodynamic data was gathered through the NIST Chemistry Database [33, 34]. Provided the density of the material is known, a first order effective sampling volume can be calculated.

In the context of liquid aluminum, work done in the early 1970s by McMordie and Roberts with a 100 mJ, CO₂ laser (10.6 μm wavelength, 175-3100 ns pulses) determined reflectivity to be approximately 0.2 for molten aluminum irrespective of temperature [35]. Because of the lack of work done on the optical properties of liquid aluminum at common casting temperatures, and that no optical band gaps exist between 1070 nm and 10.6 μm for liquid aluminum, a reflectivity of 0.2 was assumed. Multari, et. al. investigated optimal sample to lens distances for LIBS on solid targets using a Q-switched Nd:YAG laser was used (1064 nm wavelength, 186 mJ pulse, 10 ns pulse width).[36] After taking thousands of sparks and weighing samples before and after, they found an optimum at approximately 120 ng per pulse for 1100 aluminum. By substituting this value into Equation 1, it can be determined that
approximately one tenth of the laser energy contributes to ablation. As listed in Table 4, the estimated sampling volume is 141.5 ± 0.98 microns and does not significantly change with compositions tested.

**Table 4: Estimated sampling volume and equivalent spherical diameter for pure aluminum and alloys tested.**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Sampling Volume (10^6 μm³)</th>
<th>Equivalent Spherical Diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Al</td>
<td>1.46</td>
<td>140.7</td>
</tr>
<tr>
<td>A356</td>
<td>1.47</td>
<td>140.9</td>
</tr>
<tr>
<td>A380</td>
<td>1.51</td>
<td>142.3</td>
</tr>
<tr>
<td>A206</td>
<td>1.50</td>
<td>141.9</td>
</tr>
<tr>
<td>3104</td>
<td>1.47</td>
<td>141.0</td>
</tr>
<tr>
<td>5182</td>
<td>1.46</td>
<td>140.6</td>
</tr>
<tr>
<td>7050</td>
<td>1.54</td>
<td>143.2</td>
</tr>
</tbody>
</table>

**Pure Al + SiC**

No particles were observed in the control Al sample. Irrespective of volume fraction, most SiC particles were less than 20 μm and were narrowly distributed (Figure 6). As seen in Figure 7, SiC particles showed no signs of agglomeration and were sparse within the Al matrix, yielding low volume fractions of 0, 29, 47, and 54 ppm. These values are similar to typical inclusion concentrations found in industry [37]. No particle agglomeration was observed from metallography (Figure 7).

Silicon’s peak at 288.158 nm (Figure 8) was analyzed and normalized by the aluminum signal to account for variability between individual laser pulses. OES measurements were performed before and after LIBS to investigate any bulk compositional changes in the melt. As seen in Table 5, bulk Si content increased by 0.035% and is attributable to Si leaching from the crucible. Even so, such amounts of dissolved Si are below the lower limits of detection for LIBS [38]. Because of the low amount of dissolved Si and the infrequent presence of Si emission lines during testing, it is safe to say that Si signal was due to SiC particles being ablated by the laser, not due to homogeneous Si in the melt. Conditional analysis yielded a linear correlation between LIBS data and volume fraction (Figure 10).
Figure 6 – Size distribution of SiC particles encountered during experiments as measured by microanalysis of samples drawn from the melt.

Figure 7 – Backscatter electron micrograph of a SiC particle.
Figure 8 – LIBS spectra during a confirmed SiC hit showing a Si emission line at 288.158 nm as well as the averaged spectra over all shots during the measurement run.

Table 5: Melt composition (wt%) before and after LIBS

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Fe</th>
<th>Mg</th>
<th>Na</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>0.015</td>
<td>0.044</td>
<td>0.013</td>
<td>0.009</td>
<td>0.0025</td>
<td>99.9</td>
</tr>
<tr>
<td>After</td>
<td>0.050</td>
<td>0.044</td>
<td>0.012</td>
<td>0.0009</td>
<td>0.0025</td>
<td>99.9</td>
</tr>
</tbody>
</table>
Irrespective of volume fraction, over 90% of particles were less than 10 µm and were narrowly distributed (Figure 11). Both the number and volume fraction of TiB₂ particles were proportional to the concentration of Ti and B. However, deviations can occur when the ratio of Ti/B is too skewed. The optimal ratio for most alloys is approximately 2.22 wt.% Ti to 1 wt.% B for optimal grain refinement [39]. If the ratio is too high, the resultant volume fraction of particles will decrease due to the lack of boron in the matrix. This can be seen in Figure 12, where the data point for Al-0.205Ti-0.041B (Ti/B ratio of 5) significantly deviates from the linear relationship.

Boron’s emission line at 249.772 nm and Titanium’s line at 323.4513 nm were analyzed. To account for the variability in signal between individual measurements, boron and titanium peak intensities were normalized by the intensity of the aluminum peak at 308.852 nm [28].

As seen in Figure 13, boron signal noticeably increases with solute content. Data points represent averaged particle hit intensity over 500 laser pulses. Depending on the alloy, typical target chemistries range from 0.2-0.5 wt.% Ti and 0.01-0.03 wt.% B [39]. The solubility of boron in liquid aluminum is extremely low (less than 0.05% at 750-800°C) [40]. Therefore, if a boron line and a statistically significant increase in the titanium line are observed in the same spectra, then a TiB₂ particle was present in the sampling volume.

The Nalimov test was used to separate true boron emission lines from errant background fluctuations. It was also used to identify spikes in titanium signal. In this case, the “background” is the element...
signal coming from titanium dissolved within the liquid metal. Linear calibration curves were drawn from shots with coincident spikes in B and Ti signal. As seen in Figures 14, and 15, there is a good correlation between TiB₂ volume fraction and LIBS data for B and Ti in the compositional ranges desired in grain refinement.

![Graph showing size distribution of TiB₂ particles encountered during experiments](image1.png)

**Figure 10** – Size distribution of TiB₂ particles encountered during experiments

![Graph showing TiB₂ particle count and volume fraction as a function of Ti concentration](image2.png)

**Figure 11** – TiB₂ particle count and volume fraction as a function of Ti concentration. The data point at 0.205 wt.% Ti has a low Ti/B ratio.
Figure 12 – Averaged LIBS spectra of boron hits compared to pure Al. B has emission lines at 249.676 and 249.772 nm.

Figure 13 – Calibration curve relating boron LIBS signal to TiB₂ volume fraction. R² = 0.9681

Figure 13 – Calibration curve relating boron LIBS signal to TiB₂ volume fraction.
Al Alloys + Al₂O₃

Nearly all Al₂O₃ particles added through MMC additions were less than 20 µm in size and were narrowly distributed (Figure 16). Through metallography, it was observed that the simulated inclusions did not cluster (Figure 17). Oxide volume fractions ranged between 1-5 ppm, which are typical values encountered in cast alloys.

The ratio of the oxygen 777.198 nm emission line to an aluminum emission line was used for analysis. A slight increase was observed in averaged oxygen hit intensity with increasing volume fraction as shown in Figure 18. By multiplying by the number of hits, the measurement becomes significantly more sensitive, as exhibited by calibration curves for cast and wrought alloys (Figure 19 and 20, respectively). Curves exhibited good agreement between oxygen signal and oxide volume fraction. The differences in slope between curves are due to the difference in aluminum signal in the different alloys. It should be noted that it is poor practice to use one calibration curve for all alloys (e.g. using a 3XX series curve for a 2XX series measurement).

As seen in Tables 4 and 5, there was no statistically significant difference in oxygen signal during repeatability and depth experiments. Both the oxygen hit average and frequency did not significantly change with depth or with subsequent measurements. This behavior was expected due to the constant mixing in the induction furnace.
Figure 15 – Size distribution of $\text{Al}_2\text{O}_3$ added to the molten metal and encountered during experiments.

Figure 16 – Secondary electron micrograph of an $\text{Al}_2\text{O}_3$ particle (white) with silicon phases (grey) in an A356 matrix.
Figure 17 – Averaged oxygen hit spectra of molten 7050. An argon emission line is at 772.4207 nm. The oxygen line of interest is at 777.198 nm.

Figure 18 - Calibration curve relating oxygen LIBS signal to oxide volume fraction in molten cast alloys (A206, A356, and A380).
Figure 19 - Calibration curve relating oxygen LIBS signal to oxide volume fraction in molten wrought alloys (3104, 5182, 7050).

Table 4 – LIBS data from repeatability trials

<table>
<thead>
<tr>
<th>Measurement</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage of Oxide Hits</td>
<td>8.43%</td>
<td>9.00%</td>
<td>8.57%</td>
</tr>
<tr>
<td>Hit Intensity (avg±st dev)</td>
<td>0.013±0.007</td>
<td>0.013±0.007</td>
<td>0.014±0.008</td>
</tr>
</tbody>
</table>

Table 5 - LIBS data from depth trials

<table>
<thead>
<tr>
<th>Depth</th>
<th>2 in.</th>
<th>3 in.</th>
<th>4 in.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage of Oxide Hits</td>
<td>10.42%</td>
<td>9.00%</td>
<td>10.00%</td>
</tr>
<tr>
<td>Hit Intensity (avg±st dev)</td>
<td>0.012±0.006</td>
<td>0.011±0.007</td>
<td>0.013±0.008</td>
</tr>
</tbody>
</table>
Conclusions and Future Work

In these experiments, the concept of using LIBS as a means for determining melt cleanliness has been established. After adding simulated inclusions into molten aluminum, it was found that over the course of many laser measurements, such particles could be detected by monitoring elements of interest. Nearly all particle systems investigated were less than 20 μm in size and had volume fractions of 54 ppm or lower. LiMCA is currently unable to detect such particles.

The validation of LIBS as an inclusion detector will be of significant interest to the metal processing field as it can: (i) provide melt chemistry data directly from the liquid state; (ii) detect inclusions with different chemistries; (iii) probe molten metal at almost any depth; and (iv) provide the data quickly and be used in continuous operation. Such qualities cannot be matched by current technology.

Further investigation is required to develop the technology into a robust measurement technique. More experiments must be carried out to fully understand the relationship between what LIBS detects and what is actually in the melt. It is necessary to perform experiments at lower and higher inclusion concentrations to assess detection limits and to see if the linear trends deviate. Trials should be performed to determine the technique’s feasibility and ease of use in an actual cast house setting with oxides of different size distributions and chemistries. Because the capabilities of LIBS are equipment dependent, the importance of laser parameters, types of spectrometers, and sampling rates must also be investigated.

Acknowledgements

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References
