Laser-induced breakdown spectroscopy: a new tool for real time melt cognition

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More and more, lightweight materials are being used to improve fuel efficiency and vehicle performance in the aerospace and automotive industries. In order to meet the demands in these critical applications, tight control over the composition and cleanliness of the metal must be achieved before casting. Quick analysis of melt composition and quality, carried out in-situ, is of great value in high-pressure die-casting (HPDC) operations. Such quick measurements in the liquid alleviate analyzing samples in the solid state and thus increase productivity. Laser-induced breakdown spectroscopy (LIBS) has shown great potential for use in the metal processing industry. By using a ceramic probe, LIBS can be performed directly in the molten metal, allowing for quick and representative measurements. Experiments involving chemical analysis and inclusion detection are presented and discussed.

KEYWORDS: METAL QUALITY - PROCESS CONTROL - METAL CLEANLINESS

INTRODUCTION

There has been significant interest in the use of laser induced breakdown spectroscopy (LIBS) as a tool in the metals processing industry. 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 electromagnetic 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. Several studies using probes have been conducted in laboratory and industrial experiments. Most experimental probes operate under the same basic principles as shown in Figure 1. 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 the laser to interrogate.

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Both the laser pulse and the emitted plasma light are transmitted to a fiber optic cable. The use of the fiber optic cables allows for sensitive equipment (laser, spectrometer, etc.) to be situated away from the melt to avoid costly packaging and maintenance. Such probes have been developed by De Saro et. al. [1], Lucas, et. al. [2] and Kim [3].Two examples by the authors highlighting the capabilities of LIBS are presented in this paper.

BULK CHEMISTRY MEASUREMENTS

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 2A, which shows the difference in the magnesium spectral lines taken from molten aluminum samples with different magnesium contents. ERCo's probe for molten aluminum was demonstrated at Commonwealth Aluminum's foundry in Uhrichsville, Ohio, USA [1, 4]. The probe was suspended above the filter bowl of a rolling mill and lowered below the melt surface. A small amount of metal at the probe tip absorbs the laser light to be vaporized into an excited plasma. A photograph of the immersed sensor in use is shown in Figure 2B. LIBS data was collected continuously through the system's spectrometer over several shifts and compared to data from button samples analyzed by Optical Emission Spectroscopy. Table 1 shows a comparison of average data for Al, Cu, Fe, Mg, Mn, and Si, collected over one shift. Data agreed well with the OES data to within 7.1% in all cases. The LIBS relative standard deviation (RSD), a measure of data variance, ranged from 4.5 to 11.6%. Because the probe can be moved, depth, sedimentation, and solute mixing analyses can also be performed. The results from the industrial installation show that LIBS was as accurate as conventional OES in an industrial setting.

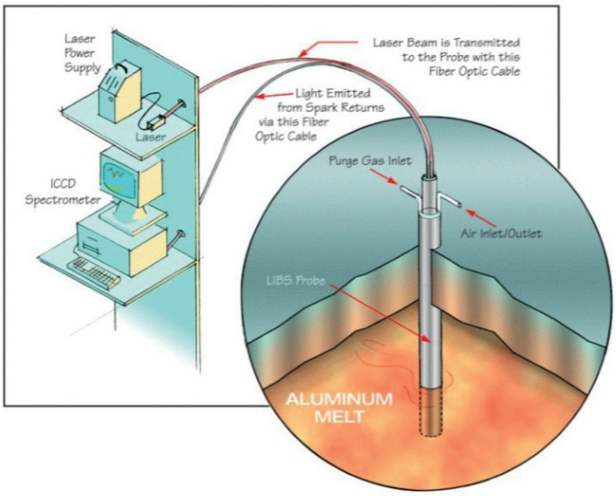

Fig. 1 - Schematic of an immersed LIBS probe [4].

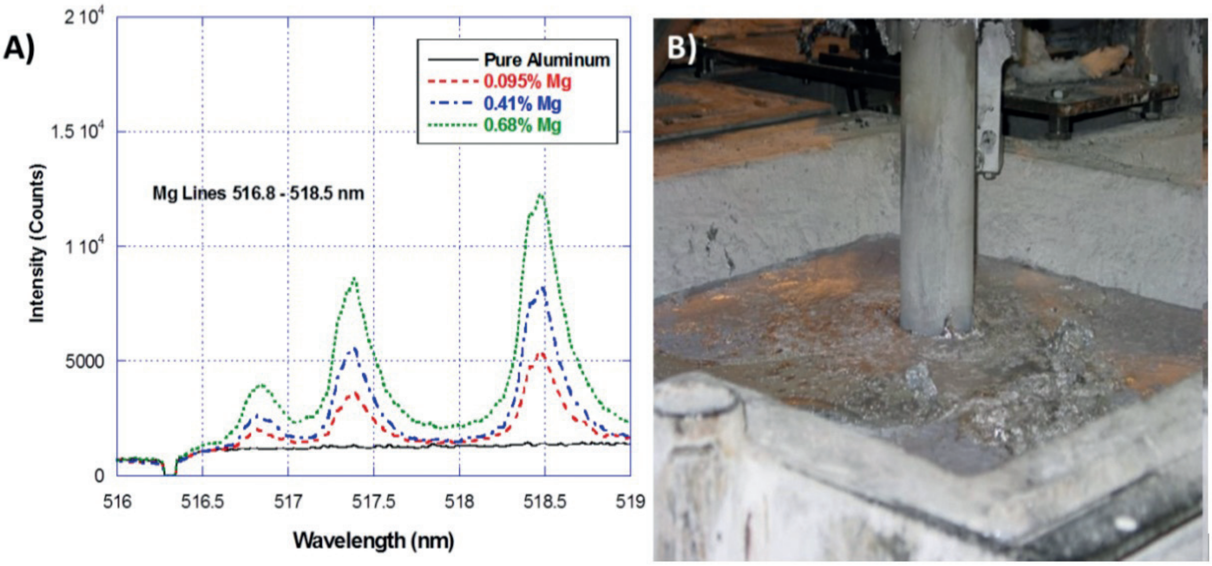

Fig. 2 - (A) Change in LIBS spectrum with addition of magnesium to molten aluminum [5];
(B) Detail of immersed probe over filter bowl [3].

Tab. 1 - Composition data from LIBS tests at Commonwealth Aluminum [3]

	Al	Cu	Fe	Mg	Mn	Si
LIBS	97.87%	0.17%	0.65%	0.47%	0.52%	0.28%
OES	97.56%	0.18%	0.65%	0.49%	0.56%	0.30%
% Difference	0.32%	5.60%	0.00%	4.10%	7.10%	6.70%
LIBS RSD	0.09%	5.06%	4.87%	11.61%	4.54%	6.29%
OES RSD	0.03%	3.51%	3.65%	1.53%	3.37%	2.25%

MELT CLEANLINESS

In addition to determining melt chemistry, LIBS could also be used to assess melt cleanliness. Because of the small size of oxide 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 chemistry. 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. 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. A strict signal analysis procedure is necessary 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. Exploratory work by the authors was performed with Al2O3, in pure liquid aluminum [6].

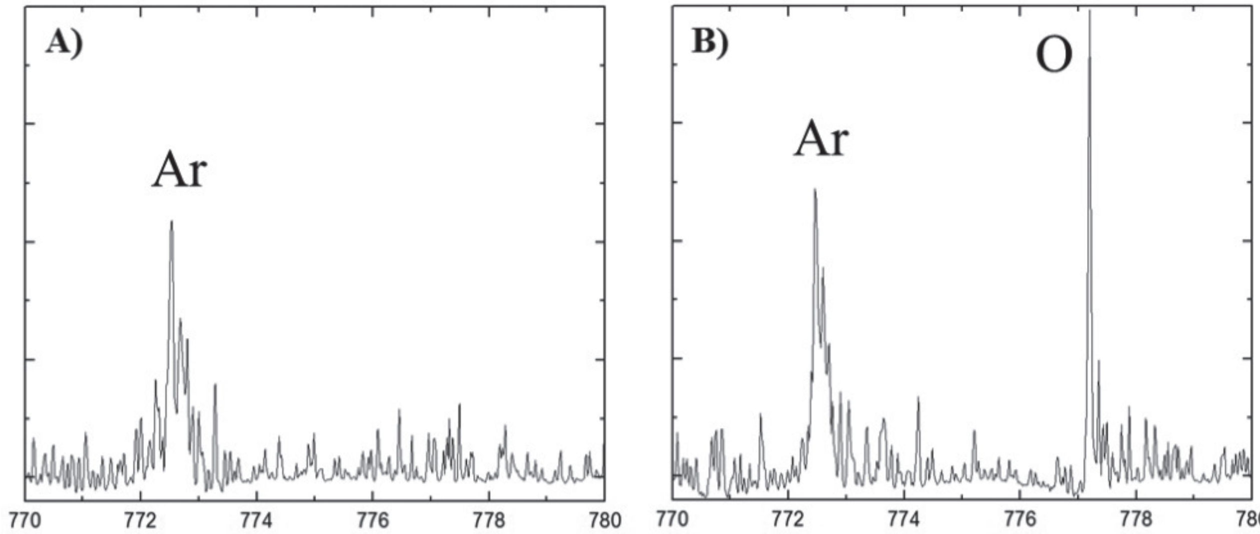

Fig. 3 - Example of LIBS spectra of molten aluminum with (A) no oxide hit and (B) with an oxide hit. The argon peak near 772 nm is from the bubbling gas [7].

In these preliminary experiments, a 2.5 kg charge of pure aluminum (99.99%) was melted in an electrical resistance furnace to 800oC. Oxide inclusions were introduced by bubbling dry air directly in the molten metal through a graphite lance. Before and after the introduction of inclusions, the probe was lowered into the melt to a depth of approximately 5 cm below the melt surface. 500 laser shots at a 1 Hz frequency were performed using the LIBS probe in the clean and dirty melt state. As shown in Figure 3, the frequency of oxygen signal (normalized by aluminum signal) increased as the metal became more and inclusion rich. This was compared to and verified by direct observation of inclusions through X-ray radiography [6]. Experiments showed that LIBS could differentiate between dirty and clean aluminum by monitoring oxygen signal.

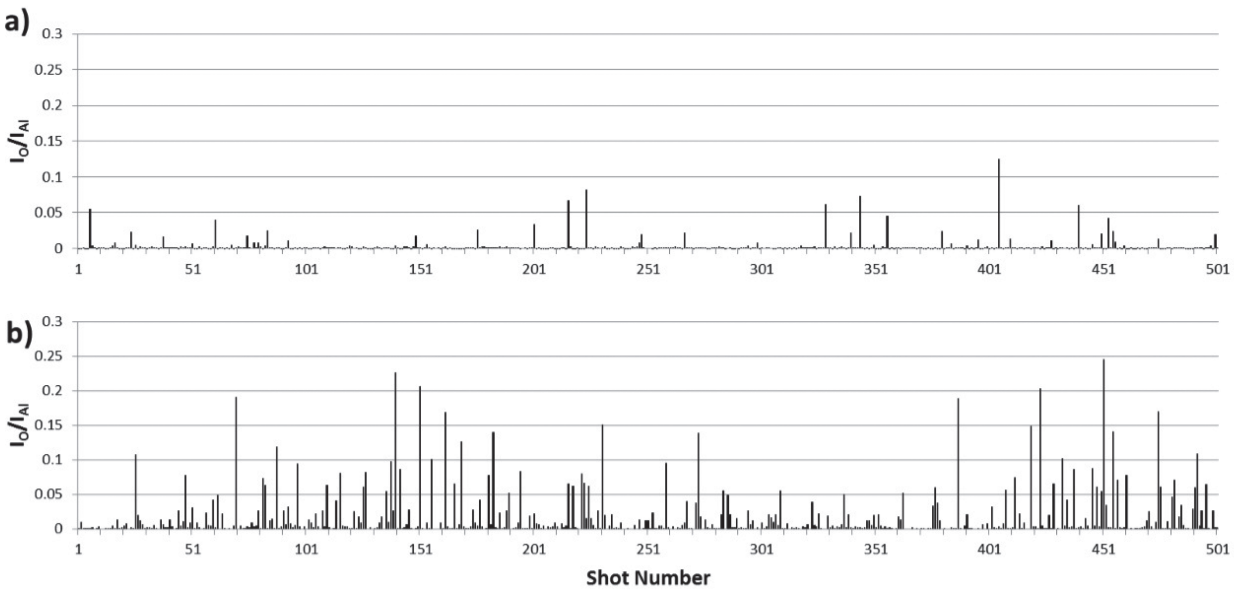

Fig. 4 - Normalized Oxygen Peak Intensity vs. Laser Shot Number for (A) Base Al; (B) Dirty Al [6].

Similar experiments with boride and carbide particles in pure aluminum have also been performed by the authors with similar results [8-10].

CONCLUSIONS

Laboratory and pilot-scale testing have shown that LIBS works well within the harsh environment of aluminum melts and provides good accuracy over a wide range of elements and concentrations. It addition, it can provide continuous readings to a furnace operator, allowing for real time adjustment of feedstock. By statistically analyzing individual spectra, inclusions can possibly be detected using LIBS.

The ability for LIBS to monitor melt cleanliness as well as chemistry 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 liquid metal feeding capability
- Lower scatter in tensile and fatigue properties
- Faster response time if the melt is out of specifications
- Less frequent 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. This work has opened several venues of investigation and provide opportunities for additional research and development.

Ongoing experiments include trials at partner foundries involving verification with industrially accepted techniques (PodFA, LiMCA. etc.). Further development of calibration curves and other metrics of interest, probe design, and testing with different spectrometers and lasers are also ongoing. The ability to detect dissolved hydrogen (another important quality detractor) in molten aluminum is also being explored.

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