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CLEAN ALUMINUM PROCESSING: NEW AVENUES FOR MEASUREMENT AND ANALYSIS

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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 (Al_2O_3, SiO_2, 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].

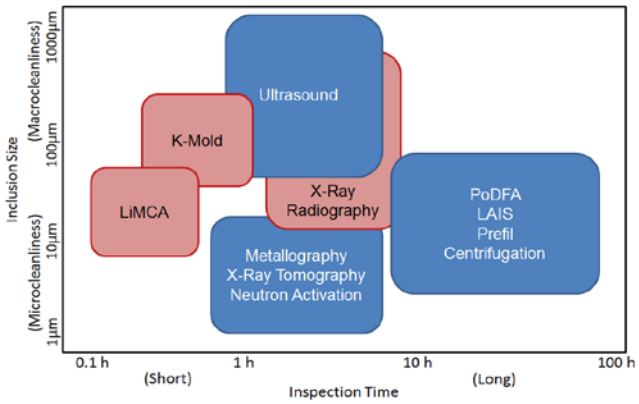

Figure 1: Qualitative comparison of different methods for measuring inclusions in molten aluminum. Dark areas represent methods typically used for process optimization. Light areas represent methods typically used frequently/continuously in production. Inspection time includes sample preparation.

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} cm^3 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 we will see it vary 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 quick 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.

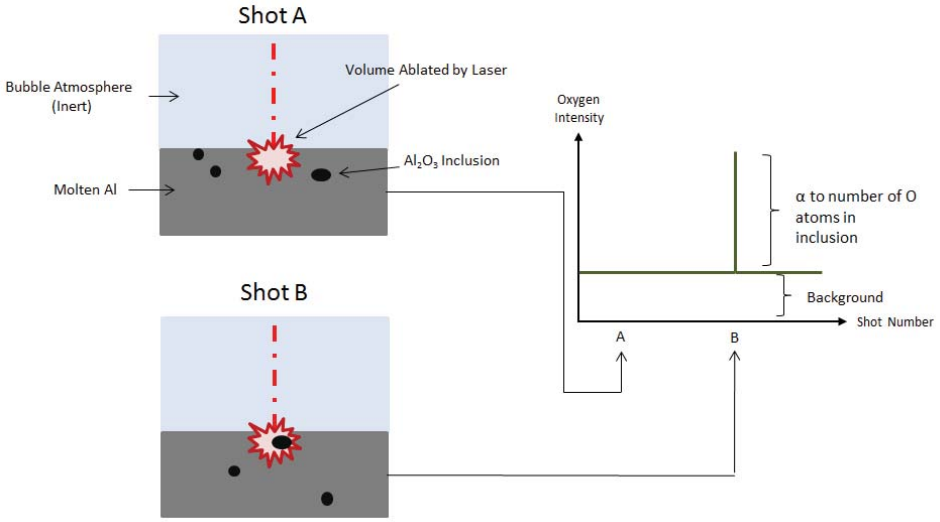

Figure 2: Example of LIBS acquisition for oxide inclusions in molten metal. The number and intensity of oxygen peaks is related to the number and size of inclusions.

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

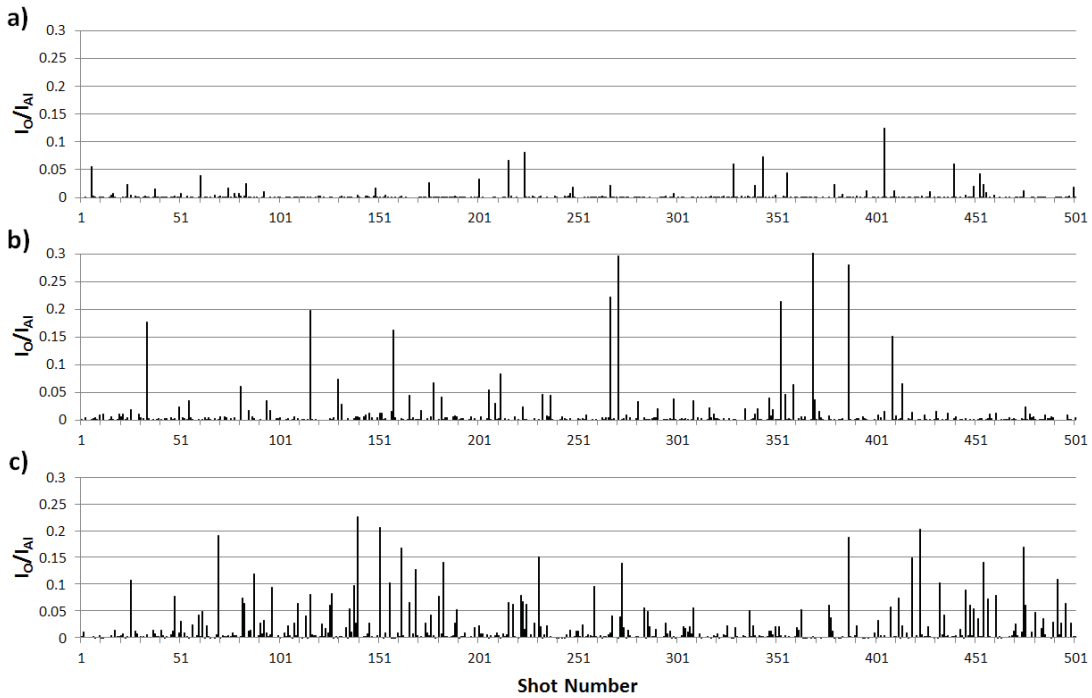

Figure 5: Normalized Oxygen Peak Intensity vs. Laser Shot Number for a) Base Al; b) 50% Diluted Dirty Al; c) Dirty Al

X-Ray Radiography Measurement

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

Sample	Average (Standard Dev.)	Number of Peaks greater than:		
		σ	2σ	3σ
Clean	0.0024 (0.010)	24	15	10
50% Diluted	0.0099 (0.044)	18	11	10
Dirty	0.0168 (0.035)	57	24	14

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

Sample Comparison	t statistic	p value (two tail)	Critical t statistic
Clean vs. 50% Diluted	-3.733	2.08×10^{-4}	1.964
Clean vs. Dirty	-8.806	1.46×10^{-17}	1.964
50% Diluted vs. Dirty	-2.728	6.49×10^{-4}	1.962

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.

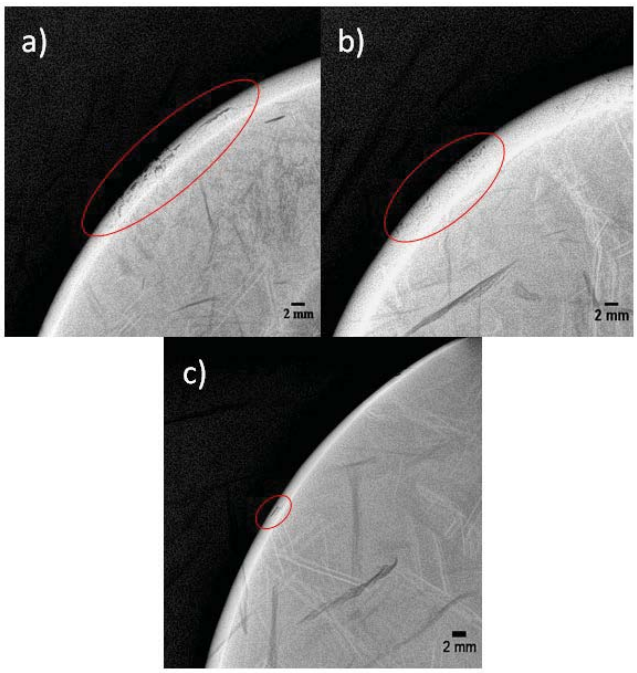

Figure 6: X-ray radiographs of a) Air treated, b) Air treated + 50% diluted, and c) untreated control sample. Inclusions (circled) are seen as black dots/films at the edge of the casting. Scratches are superficial from handling in the x-ray machine.

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 Al_2O_3. 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.

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