Light Metals 2015
Edited by: Margaret Hyland
TMS (The Minerals, Metals & Materials Society), 2015

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.

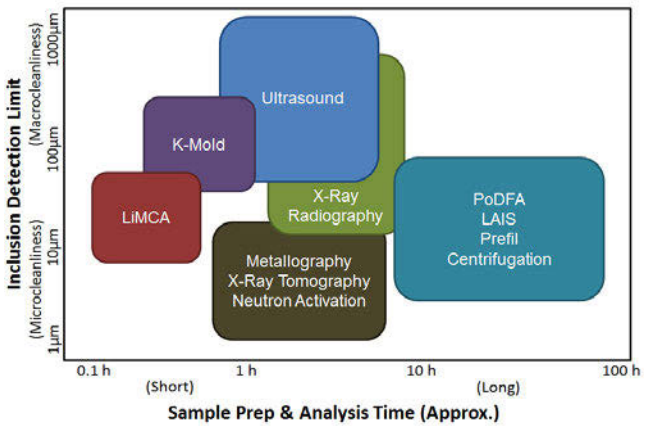

Figure 1: Qualitative comparison of inclusion assessment techniques.

In the 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} cm^3) 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 5-7cm 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 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.

Figure 2: LIBS set-up.

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 in 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.

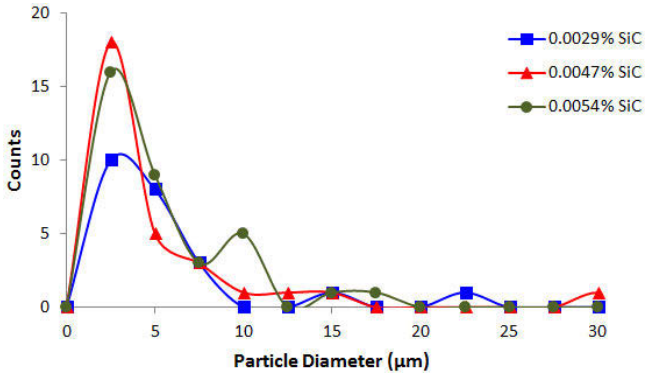

Figure 3: SiC particle size distribution.

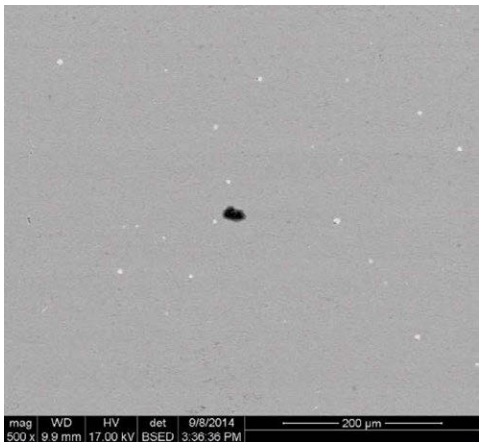

Figure 4: SEM micrograph of SiC particle (black). Fe rich particles appear in white.

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

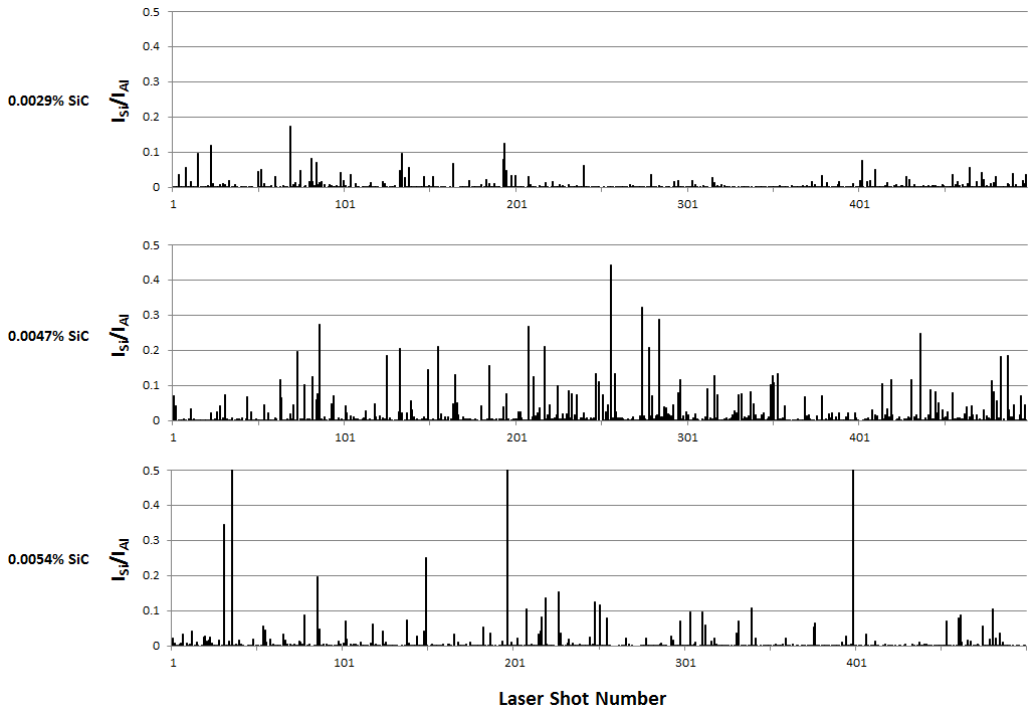

Figure 5: Normalized silicon peak intensity vs. laser measurement number for each SiC concentration tested

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 σ and mean $\bar{x}$ (equation 1).

$$r = \left|\frac{x - \bar{x}}{\sigma}\right| \times \sqrt{\frac{n}{n-1}} \quad (1)$$

If r exceeds a threshold value , then x is an outlier. For data sets with n ≥ 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 (α=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 2: Results from ANOVA for LIBS data sets

F statistic	p value	Critical F statistic
36.429	3.3×10^{-16}	3.002

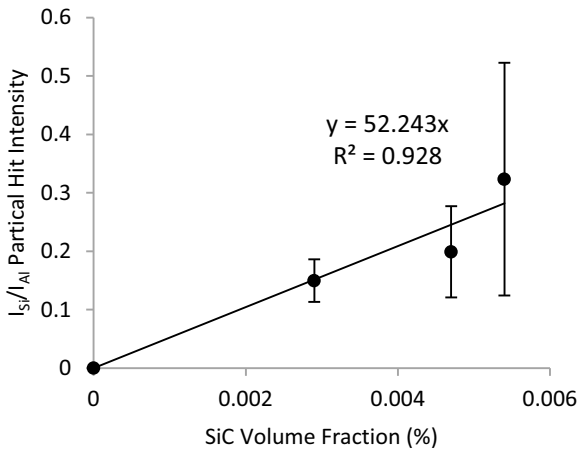

Figure 6: SiC particle hits vs. volume fraction. Error bars represent standard deviation.

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.

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