LASER-INDUCED BREAKDOWN SPECTROSCOPY: A NEW TOOL FOR PROCESS CONTROL

M. Sabsabi[1], L. St-Onge[1], V. Detalle[2] J.M. Lucas[3]
[1]Industrial Materials Institute, National Research Council of Canada, Boucherville Canada
[2]Laboratoire de Recherche des Monuments Historiques,Champs sur Marne, France (formerly with the NRC-Canada), [3]Formerly with Noranda Technology Centre, Canada

Abstract: Many industrial activities require adequate and timely evaluation of material composition. Laser-induced breakdown spectroscopy (LIBS) has, in recent years, shown a great potential for rapid qualitative and quantitative chemical analysis of various materials. In this paper, we will illustrate the usefulness of the LIBS technique for elemental analysis at different scales: from depth profilometry of thin coatings and the micron-scale mapping of inclusions in metals, to the continuous in-situ analysis of aqueous liquid effluents and industrial-scale molten metal baths.

Introduction: During the lifetime of any material, from its initial mineral state, through numerous processing and manufacturing transformations, to its degradation during use, knowledge of composition is crucial. This is especially true for composite or layered structures. Laser-induced breakdown spectroscopy (LIBS), also known as laser-induced plasma spectroscopy, offers unique capabilities for on-line composition determination. An important advantage of this technique over classical methods stems from the possibility of in-situ analysis of virtually all types of material (solids, liquids, molten materials, and gases) without need for sample preparation.

In LIBS, a small volume of the target is intensely heated by the focused beam of a pulsed laser, and thus brought to a transient plasma state where the sample's components are essentially reduced to individual atoms. In this high-temperature plasma, atoms are ionized, or brought to excited states. Such states decay by emission of radiation, which is observed in the ultraviolet (UV), visible and near-infrared (NIR) regions of the spectrum. An atomic spectrum is obtained by means of a spectrograph, thereby allowing elemental components of the target to be identified and, using a calibration curve, quantified. LIBS measurements are generally carried out in ambient air at atmospheric pressure. For this reason, and also due to its rapidity, non-contact optical nature, and absence of sample preparation, LIBS is particularly suited for at-line or on-line measurements in industrial settings, as well as in the laboratory [1-4]. The capabilities of LIBS for quantitative elemental analysis have been demonstrated in metallurgy, mining, environmental analysis and numerous other fields, including application to specialized materials (e.g. aeronautics and pharmaceuticals).

LIBS cannot be considered a non-destructive technique in the strictest sense, since part of the target to be analysed is vaporized and lost. However, the volumes sampled in this manner are very small: 10^{-8}-10^{-5} cm^3, depending on the material, and the laser wavelength and fluence. Such volumes correspond to masses in the ng to μg range. In the case of a solid sample, the lateral size of the laser-affected zone is typically under 1 mm, and can be made as small as 1 μm. In the vertical dimension, the thickness of material ablated by a laser pulse may, in the case of metals, be only tens of nanometers. When LIBS is applied to the analysis of fluids (e.g. water or molten metal), the issue of destructiveness is irrelevant, since the vaporized mass is negligible and the analysed volume is continuously renewed.

The possibility of concentrating laser radiation on a very small area enables the sampling and analysis of solid heterogeneous materials at high spatial resolution. This constitutes a significant advantage of LIBS compared to other techniques of elemental analysis, which often require sample digestion. Admittedly, X-ray fluorescence (XRF) can be considered a strictly non-destructive technique for elemental analysis, but it cannot match the best spatial resolution achievable by LIBS. XRF is also less sensitive than LIBS, often requires sample preparation and, unlike LIBS, cannot be used for light elements (e.g. boron). Other techniques, such as Auger or X-ray photoelectron spectrometry, secondary ion mass spectrometry, or glow discharge methods, all involve sample preparation, are time consuming, sometimes call for ultra-high vacuum conditions, and require sophisticated and expensive instrumentation. For these reasons, they do not meet the industrial requirements for at-site high-throughput compositional mapping of heterogeneous materials.

In this paper, the use of LIBS for rapid three-dimensional compositional mapping of solids will be discussed, as well as its on-line application to the real-time analysis of aqueous industrial effluents and molten metals.

Depth profilometry and micro-analysis by LIBS: Materials at different stages of transformation from the raw state to finished product often present a heterogeneous elemental composition. In particular, an object's surface may be protected by one, or more, layers of varying composition. There is a growing need in industry, namely in the context of process development and control, for at-site high-throughput methods that can reveal elemental distributions along one or more spatial dimensions. In the following we provide a few examples that demonstrate how LIBS can meet these demands.

The separate analysis of successive laser ablation events at the same position of a solid material enables depth-resolved analysis. In the past, this approach has been applied in our group, and elsewhere, to several types of layered materials (see [5] and references therein). For example, we have used LIBS for the characterization of galvannealed coatings on steel [5,6]. In this case, the zinc coating contains Fe and Al in concentrations of approximately 8-13% and 0.2-0.35%, respectively. Because of widely separated melting and vaporization temperatures, the laser ablation efficiency was different for the coating and the steel substrate: 58 nm/pulse and 17 nm/pulse, respectively. The raw data consisted of Al, Fe and Zn spectral line intensities as a function of pulse number. Calibration strategies were developed to obtain elemental concentrations as a function of depth. The presence of a thin aluminum oxide layer at the surface of the coating was correctly identified, and the global Al content in the coating itself was found to be in good agreement with average concentrations measured using wet chemistry. The Fe profile across the coating was also found to agree with a profile obtained by transmission electron microscopy / energy dispersive X-ray spectrometry, including the region close to the interface with steel where higher Fe concentrations (~25%) were found.

The latter work was carried out with a Gaussian laser beam of non-uniform energy distribution. This tended to limit the depth resolution because the central higher-energy portion of the beam entered the substrate, while the beam's lower-energy periphery was still sampling coating material at a shallower depth [6]. One might instead use a laterally homogenized laser beam to provide a uniform ablation efficiency across the beam [7,8]. This has been shown to significantly improve depth resolution [7]. We have recently developed another approach based on using the same laser to alternately generate beams of different diameter [9,10]. As illustrated in Fig. 1, at first the laser passes through a large diaphragm to produce a large crater on the surface. After a given number of laser pulses, a smaller diaphragm is substituted to produce a narrower beam to thereby generate the analytical plasma inside the crater produced by the larger beam. This eliminates all contributions from the crater walls. Repetition of this sequence serves to generate a depth profile. In Figure 1 we compare the profiles of zinc spectral line intensity for a galvannealed coating on steel using this new approach, with "classical LIBS instrumentation" where the laser beam is only filtered by a large diaphragm. In both cases each data point is based on 100 ablation shots with the large diaphragm, followed by10 measurement shots. It is seen that use of the smaller diaphragm for the measurement shots provided a more accurate profile of the coating thickness. The coating/steel interface is described with more precision: the beginning of the coating/air interface appears in the same place for both profiles, but ends 2 μm sooner using the new approach. The Zn emission quickly falls to zero, which is not the case with conventional instrumentation where the Zn emission persists.
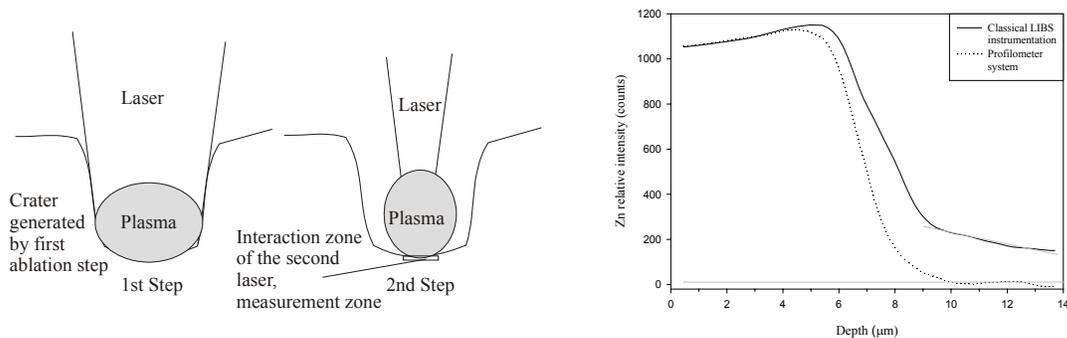
Figure 1. Illustration of depth profilometry approach with alternating laser beam diameters, and depth profiles of zinc emission from galvannealed coating obtained with this approach (dotted line) compared to a conventional measurement (solid line)

As stated above, the laser beam can be reduced to very small sizes using adequate focusing optics. This has opened the way to chemical mapping of surfaces at the micron scale. Examples of this class of LIBS applications can be found in recent LIBS literature, namely for the mapping of inclusions in steel [11,12]. In our group, micro-LIBS analysis was successfully used to locate oxide inclusions in magnesium samples. Figure 2 shows a 1 mm x 1 mm map of oxygen obtained by LIBS, using a laser spot and step size of 10 µm. Comparison with an optical micrograph reveals that the darker features seen in such micrographs correspond to oxide inclusions. Figure 2 also shows that the spatial resolution achieved by micro-LIBS is similar to that with optical microscopy. Although only one element (oxygen) was mapped here, maps for several elements may, in fact, be produced simultaneously, since present day array detectors for LIBS allow multi-element detection.
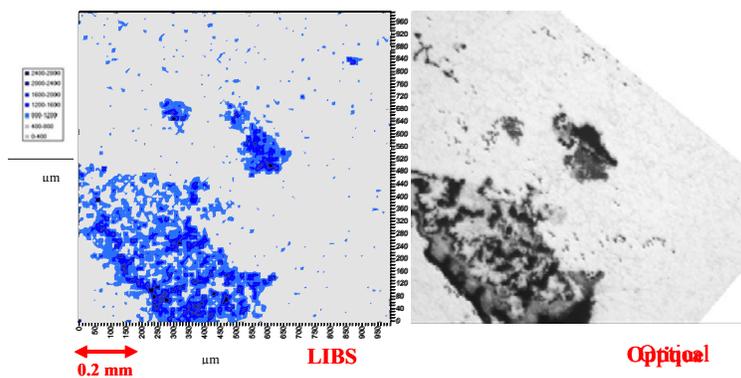

Figure 2. Micro-LIBS map of oxygen in magnesium sample, and optical micrograph showing the same region of the sample

Analysis of liquids: Quantitative and qualitative analysis by LIBS has generally been applied to solids, with much less attention being paid to liquids [13,14]. This is largely due to the fact that analysis of liquid by existing analytical techniques is well established, and does not call for the laborious preparatory steps often needed for solids. However, since the reliable on-line analysis of liquids required to meet demands for improved control of industrial processes is often difficult to achieve by conventional techniques, there is growing interest and

publication in LIBS for liquids. Thus LIBS has been proposed for monitoring various elements in liquids, including molten metal, during industrial processing, as an alternative to sampling for subsequent laboratory analysis. Direct monitoring provides many advantages over discrete sampling, including the ability to adjust the process in real time according to analysis results.

Production of a viable system for the on-line LIBS analysis of liquids required us to address some general problems encountered with plasmas generated from liquids, as well as a number of technical issues. We needed to minimize the frequent cleaning of exposed optical components (focusing lens or window) to remove accumulated matter ejected and splashed from the monitored sample by incident laser pulses. Moreover, under some conditions, the miniature shock waves associated with vaporization of liquid samples create aerosols above the liquid surface. These disrupt both the incident laser beam and light returning to the spectrometer. Shock waves also tend to induce waves on the liquid surface, which increase shot-to-shot signal variation, and hence decrease measurement precision. Furthermore, it appears that laser pulses may induce bubbles inside liquids that are transparent at the laser wavelength. These bubbles may reach the surface being analyzed, and change the characteristics of the laser-induced plasma, thereby affecting measurement reproducibility.

To overcome the problems associated with plasmas generated from liquid samples, a variety of LIBS configurations have been applied in experiments on liquids, including plasma formation on the surface [15,16], in the bulk liquid [17], and on liquid jets [18]. In our laboratory, we used a new configuration to overcome the problems mentioned above (see Fig. 3), and described its use for the quantitative analysis of both low (ppm) and high concentration (%) levels of analyte elements in liquids.

In fact, when the bubbles created inside the liquid by the laser pulse burst at the surface, or the waves induced on the surface by the laser pulse are not dissipated, they change the angle of incidence between the laser beam and the liquid surface. This, in turn, can change the fluence of the laser, and hence line intensity. Also, aerosols created by the laser-liquid interaction absorb the laser beam, and partially prevent the laser from reaching the sample surface. This absorption can change the reproducibility of the measurement by affecting the energy delivered to the sample.

In our instrument, the droplets and aerosols generated by the laser pulse are deflected from the optical path by a nearby air jet or air exhaust fan, as shown in Fig. 3. Furthermore the liquid flow sweeps away laser induced bubbles below its surface, and thus prevents them from reaching the point of laser impact. Also, the shape of the cell promotes a stable liquid surface by breaking the wave generated by the laser pulse. We thus improve measurement reproducibility and accuracy by enabling the laser to sample a stable and flat liquid surface. Provision is made for easy removal of the protective window for cleaning deposits from any residual spray during on-line measurement. Figure 3 also shows an example of results obtained with an industrial on-line application of this configuration, compared with those obtained by conventional laboratory analysis during one complete day of operation. It should be noted that the precision of the measurement obtained with this configuration was around 1%.
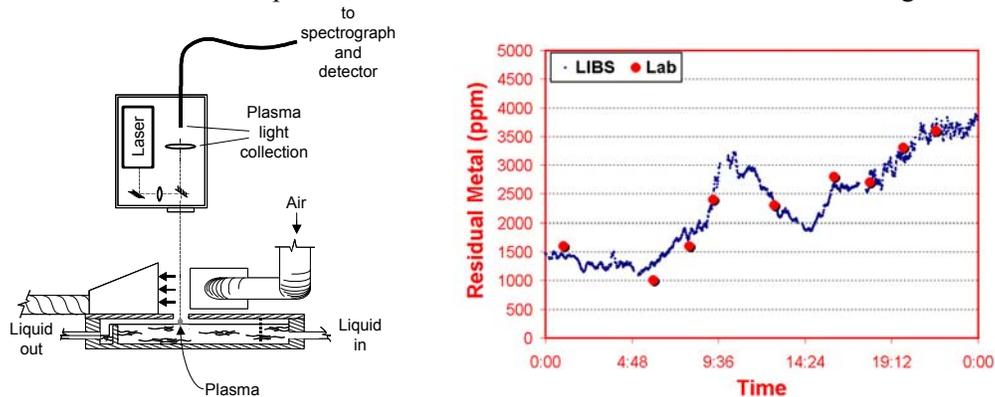

Figure 3. Setup for the analysis of liquid samples by LIBS, and comparison of on-line results obtained by LIBS and off-line measurements by atomic absorption

Analysis of molten metal: The metal-producing industry faces the major challenge of increasing productivity to reduce cost and maximize the benefits from existing equipment. During refining, it is critical that operating parameters be adjusted and controlled so that the chemistry of the melt is within predetermined limits. The current analytical approaches to the determination of the chemical composition of the melt by spark optical emission spectroscopy, atomic absorption (AAS), X-ray fluorescence (XRF), inductively coupled plasma (ICP) spectroscopy, and ICP mass spectrometry (MS) are hampered in practice by their off-line character. Furthermore, these methods are either based on analysis of the cold output materials, or on laborious manual sampling from the melt at elevated temperatures between 500°C and 1600°C. This results in insufficient turn-around time, and increased process and personnel costs. Motivated by potential savings in time, energy, and materials, as well as improved quality assurance, several LIBS groups are investigating the real time analysis of molten metals. However, LIBS analysis of high temperature molten metals in processing vessels often presents several difficulties and analytical challenge. For a reliable and accurate LIBS sensor, the following requirements should be met:

- The vaporized volume should be truly representative of the liquid bulk. This forbids interrogating the same surface for an extended period of time since a hot liquid metal surface can quickly get enriched with elements having higher affinity for oxygen or nitrogen, or become poorer in elements with a lower vaporization threshold.
- Perturbations from aerosols and ejected particles should be eliminated since their plasma emission is not representative of the melt, and they cause variations in the laser power reaching the liquid surface and available for ablation.
- The sensor should be sufficiently rugged for plant use.

Therefore the determination of the composition of molten phase samples by LIBS in a furnace has been the subject of numerous studies in laboratory and several trials in industry [19-31].
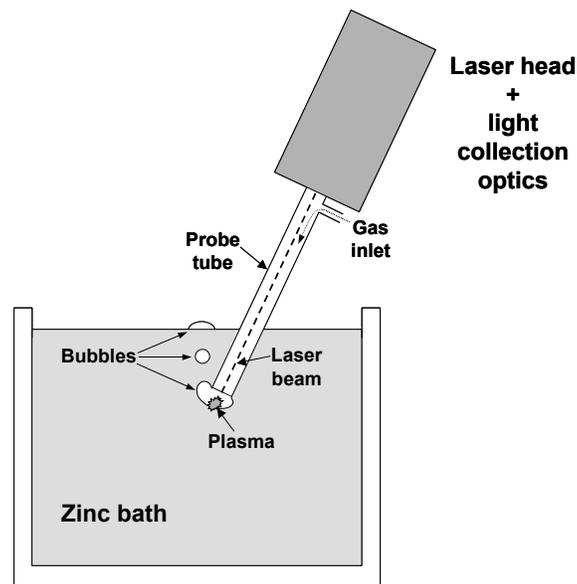

Figure 4. Schematic of the LIBS approach used for on-line analysis of molten metal

In our laboratory, we employed a patented approach [32-34] based on the use of a lance without optical components in which gas under pressure is introduced, thereby producing bubbles inside the molten metal (see Fig. 4). In this approach, a new surface truly representative of the melt is continuously obtained. The problem of analyzing a non stationary surface and insuring high quality data representative of the bulk was solved by selectively processing all acquired data in the presence of bubble motion and classifying spectra from molten or solid phases. The probe has been successfully tested in many industrial facilities for the production and processing of molten materials (zinc, zinc alloys, copper, magnesium, copper matte, electrolyte bath, etc.). For example, for

zinc bath analysis the above software permitted rapid identification and treatment of data from multiple species and/or phases [34]. The probe has also been submitted to the harsh conditions of the copper smelting industry at 1200 °C where it was introduced through a tuyere into a thousand-ton molten matte vessel to monitor Fe, Bi, and Ag content (see Fig. 5) [33]. Probe robustness was established over many days of intense activity. Using a similar probe, IMI has also successfully demonstrated in-situ analysis of molten electrolyte used for magnesium production at 700 °C. Measurements were performed in both a pilot plant and also on-line under hostile conditions in an operating plant. In all these conditions, the patented probe overcame problems related to non-representative melt surfaces due to oxidation, contamination, and surface migration or depletion. Consequently, excellent measurement reproducibility and accuracy of were obtained compared to conventional LIBS measurements on stable and stationary liquid surfaces. To the best of our knowledge, this probe has for the first time demonstrated LIBS measurement reproducibility for molten metal in order of 1% [34].

Conclusion: We have presented here recent applications of LIBS to depth profilometry of layered materials, micron-scale chemical mapping, and continuous in-process analysis of aqueous effluent and molten metals. These applications illustrate the usefulness and uniqueness of LIBS as a tool for rapid (real-time), non-contact and in-situ compositional analysis in laboratory or on-site, during a process, or for quality control. Other applications not illustrated here that have strong potential include scrap sorting, mineral ore analysis, and environmental monitoring. In conclusion, LIBS can help increase productivity by minimizing the rejection of products that do not conform to specifications, and by reducing downtime. It is expected that LIBS will gain a wide acceptance in a broad range of industrial applications.

Figure 5. Photograph of the LIBS sensor used on-site for the analysis of molten copper matte

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