Improved Metal Recycling

Industrial processes based on laser induced breakdown spectroscopy (LIBS) can benefit from the use of compact high-repetition-rate solid-state lasers.

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Laser-induced breakdown spectroscopy (LIBS) is an atomic-emission spectroscopy technique that enables rapid chemical analysis of a wide range of materials, including metals, semiconductors, glasses, biological tissues, plastics, soils, thin paint coatings, and electronic materials.

The LIBS technique has gained increased interest in recent years as a result of the development of more compact systems that enable in-field use and the construction of tools for on-line material analysis. This development has been made possible by the increased availability of more compact and industrial-grade system components, including lasers and spectrometers.

A recent study conducted by the Swedish national research labs Acreo Swedish ICT and Swerea KIMAB, in collaboration with laser manufacturer Cobolt AB, exemplifies this trend and shows how a new class of compact, industrial-grade lasers with multikilohertz pulse-repetition rates enables significant reduction of the footprint of a LIBS system and opens new opportunities for the use of LIBS to improve efficiency in industrial processes, such as sorting of metals for recycling. The compact pulsed dioded-pumped solid-state (DPSS) laser used in the study gives nice LIBS signals on dirty scrap parts of Al with penetration depths of > 50 µm at a peak power density of 3.5 GW/cm^2.

Fig. 2 The Cobolt Tor is a compact, high-repetition-rate 1064 nm or 532 nm laser system.

The major strength of the LIBS technique is its ability to perform fast and remote chemical analysis to determine the elemental composition of the tested samples without the need of any sample preparation. The LIBS technique relies on focusing short, high-energy laser pulses onto the surface of a target sample to generate a plasma consisting of small amounts of ablated material (**Fig. 1**).

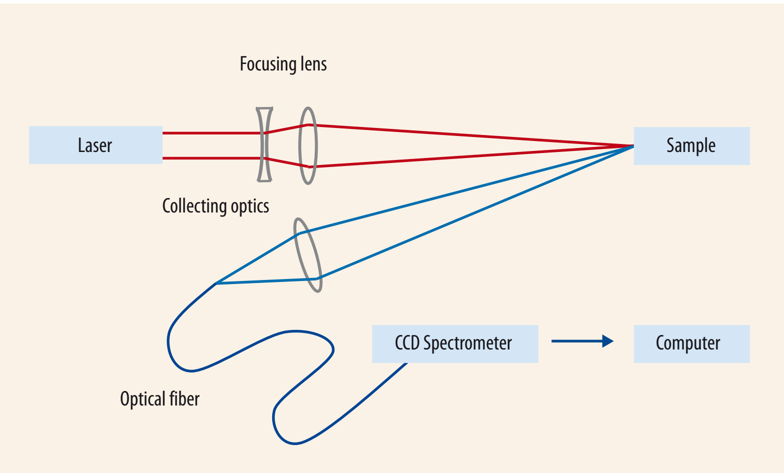

Fig. 1 Schematic illustration of a typical LIBS setup

The extremely high temperatures within the early plasma (more than 100 000 K) cause the ablated material to dissociate into excited atomic and ionic species; as the plasma cools, the characteristic atomic emission lines can be detected by a spectrograph. The method enables fast and sensitive chemical analysis of, in principle, any kind of matter (solid, liquid, or gas).

Detection limits are typically in the low parts per million for heavy-metal elements. Sample preparation is normally not necessary and the method is also considered essentially nondestructive as only a small amount of the material is removed. Other advantages of LIBS are its ability to provide depth profiles and to remove surface contamination.

LIBS is an attractive technique for a wide range of scientific and industrial analytical applications, including metal-content analysis, solar silicon quality control, plant and soil analysis, mining and prospecting, forensic and biomedical studies, and explosives and biological warfare detection. Its potential use in tools for on-line monitoring of industrial processes is particularly interesting, especially for the metal industry. For example, LIBS can be applied to monitor and optimize critical metallurgical processes (slag or molten metal analysis), to control the quality of metal products (rolls, tubes, foils, and so on), or to analyze and sort metal scrap before recycling.

Lasers for LIBS

Most laboratory LIBS set-ups have traditionally been based on flashlamp-pumped Q-switched Nd:YAG lasers that deliver pulses with energies of hundreds of millijoules in short pulse widths (4 to 5 ns) at relatively low pulse-repetition rates, typically 10 to 30 Hz. More recently, industrial fiber lasers have been shown to provide good results in generating plasmas with millijoule pulses of slightly longer pulse widths (10 ns) and with multi-kilohertz pulse rates [1]. However, a major drawback of these laser sources is their large size and high power consumption.

Although high-pulse-energy lasers perform well in many scientific LIBS applications, it has become understood from research over the last decade that the generation and properties of the plasma are affected not only by the pulse energy, but also by the laser pulse width, repetition rate, and wavelength [2 – 4]. It is also clear that another important attribute of the laser is its beam quality, as this parameter affects the power density at the sample. These new understandings encourage the use of other types of LIBS laser sources that have a slightly different set of performance parameters and a much more compact format.

A compact LIBS set-up

With the purpose of developing a LIBS system that could meet the requirements on robustness and compact size for use in industrial applications such as aluminum recycling, researchers at Acreo and KIMAB integrated a Cobolt Tor laser from Cobolt AB in their LIBS set-up as an alternative to the high-pulse-energy, low-repetition-rate Nd:YAG laser previously used. The Cobolt Tor laser represents a new class of compact, high-performance diode-pumped Q-switched lasers that can help advance the trend of extending the use of LIBS systems from laboratory work to industrial applications (**Fig. 2**).

The laser design provides a combination of stable multikilohertz repetition rate greater than 7 kHz with less than 1 μs pulse-to-pulse jitter (**Fig. 3**), pulse energies in the 100 μJ range at 1064 nm, pulse widths of a few nanoseconds, and a high beam quality ($M^2 < 1.3$). A key advantage of the laser is its substantially more compact size compared to traditional high-pulse-energy Nd:YAG lasers. The laser head measures 125 × 70 × 45 mm^3 and is accompanied by an electronics unit measuring 190 × 72 × 28 mm^3. Typical heat load of the laser head is less than 30 W which, when combined with the small size, allows for compact integration into portable industrial LIBS systems. The laser is manufactured into hermetically sealed packages that have proven insensitive to 60 G mechanical shocks and repeated thermal cycling over –30 to 70 °C. The thermo-mechanical stability of the packages ensures robust performance and long lifetime of the laser in varying ambient conditions as they exist in demanding industrial applications.

The LIBS set-up in this work involved a Cobolt Tor pulsed laser (1064 nm, 8 kHz, 4 ns, 150 μJ), with a focal length of 50 cm to focus the laser beam onto the sample to create a plasma, and collecting optics to transport the emitted plasma light to a compact spectrometer (the HR2000+ made by Ocean Optics, Dunedin, FL).

Experimental results

A first round of experiments was conducted on aluminum reference samples to investigate the capability of the set-up to classify different aluminum alloys with good confidence. It was found that the high repetition rate Cobolt Tor laser

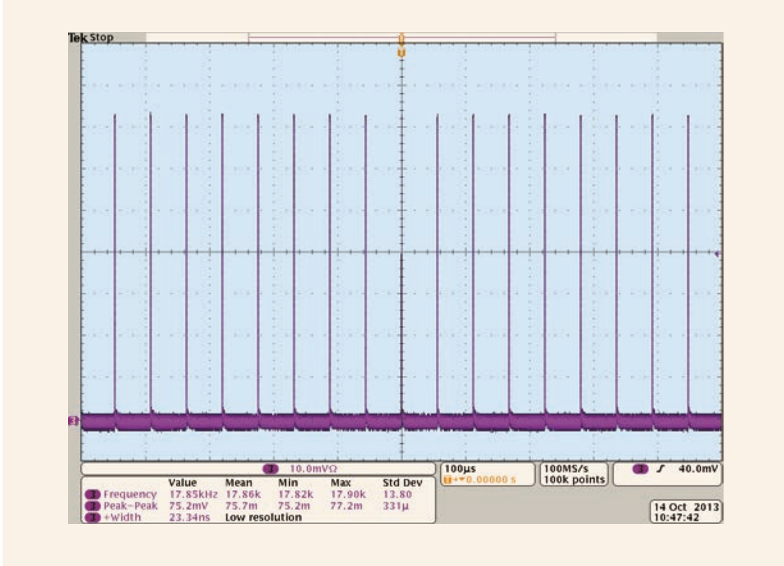

Fig. 3 A measured pulse train for a Cobolt Tor 1064 nm laser operating at a repetition rate of 8 kHz.

generated high-quality LIBS spectra with good signal-to-noise ratios. All the alloying elements that are critical for aluminum scrap classification can be clearly quantified (**Fig. 4**).

Encouraged by the promising results on reference samples, experiments with dirty scrap samples collected at scrapyards were conducted to confirm the practical applicability of a LIBS system based on this compact high-repetition-rate laser. The system was proven to be capable of clearly resolving the elemental composition of various alloys also from dirty scrap samples, as evidenced by the two spectra presented in **Fig. 5**. By optimizing the laser and collecting optics, it was possible to achieve good-quality LIBS signals at free distances of more than 50 cm. In a continued investigation, LIBS plasma were taken on polished samples of Al, in order to study the ablation profiles generated with the Cobolt Tor 8 kHz repetition rate laser. The laser was applied to the sample surface as a single burst of a pre-defined number of pulses. The generated ablation craters were imaged by Scanning Electron Microscopy (SEM) and their depth profiles measured by a confocal microscope set-up (**Fig. 6**). The results show that the ablation depth increases from about 18 µm at 100 pulses (20 ms burst) to about 50 µm at 200 pulses (40 ms burst) which is usually more than enough to penetrate through layers of oxide or paint on the sample surface. The ablation depth is believed to increase even further up to a burst-on time of around 1 s where the plasma starts to fade. However, as the crater diameter appears to remain the same also for longer pulse bursts, the depth profile becomes too narrow and too deep to be measured in the confocal set-up. From the measured crater diameter of about 40 µm, the optical peak power density per pulse can be estimated to 3.5 GW/cm^2.

The strong performance of this compact high-repetition-rate laser in LIBS applications is most likely related to its good beam quality and short pulse length which enable high peak power density. Additionally, its relatively low-energy pulses create short-lived continuum plasma backgrounds which allows the use of non-gated detectors for quantitative analysis, simplifying the detector requirements and system cost. The high repetition rate of the laser also helps to enhance the signal-to-noise ratio at the detector level. Moreover, the high repetition rate and low pulse-to-pulse jitter enable rapid scanning along a sample and allow for synchronized gating of the detection system which could lead to even lower detection limits.

Conclusion

The LIBS technique has great potential as an analytical tool for improving industrial processes such as on-line scrap metal sorting for more efficient recycling. The results presented show that compact high-repetition-rate pulsed lasers with good beam quality can provide high-quality LIBS results while drastically reducing the system size allowing the integration into portable LIBS systems suitable for the use in industrial environments.

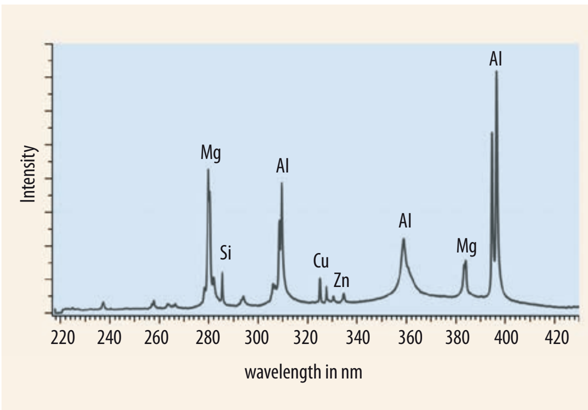

Fig. 4 LIBS data from an aluminum reference sample collected using a Cobolt Tor high repetition rate pulsed DPSS laser.

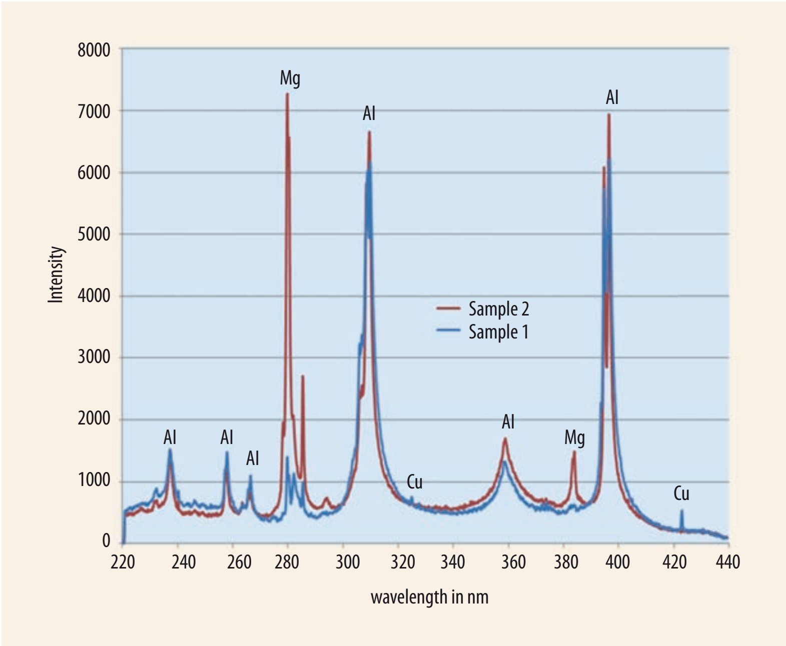

Fig. 5 LIBS data obtained for two different scrap samples representing different aluminum alloys with different material compositions.

Acknowledgments
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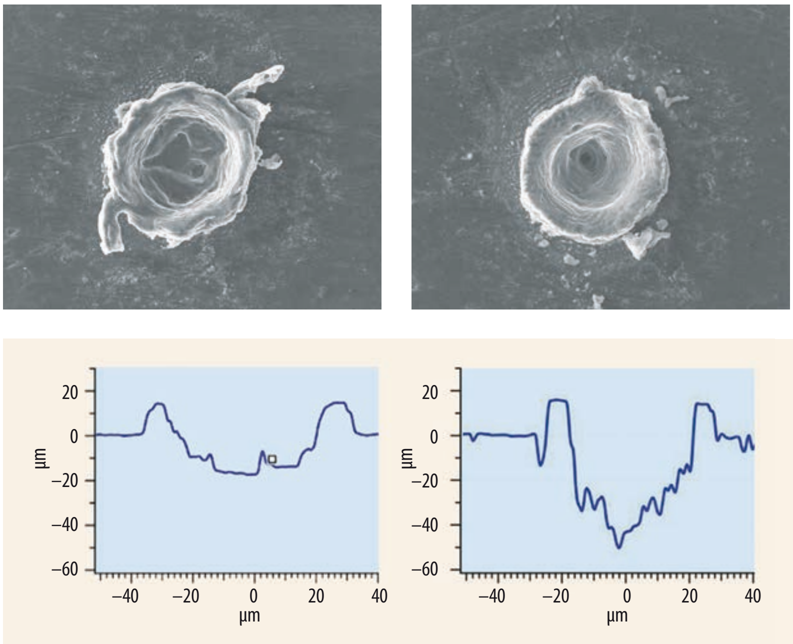

Fig. 6 SEM images and depth profiles of ablation craters generated on Al samples with the Cobolt Tor laser in burst-mode: burst of 100 pulses (a) and burst of 200 pulses (b).