Spectrochimica Acta Part B 74–75 (2012) 46–50

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Laser induced breakdown spectroscopy for fast elemental analysis and sorting of metallic scrap pieces using certified reference materials

J. Gurell [a,]*, A. Bengtson [a], M. Falkenström [a], B.A.M. Hansson [b]

[a] Swerea KIMAB AB, Box 7047, SE-16407 Kista, Sweden
[b] Acreo AB, Electrum 236, SE-16440, Kista, Sweden

ARTICLE INFO

Article history:
Received 12 October 2011
Accepted 16 June 2012
Available online 30 June 2012

Keywords:
Laser-induced breakdown spectroscopy
LIBS
Scrap sorting
Steel industry
Rapid analysis

ABSTRACT

A setup utilizing laser induced breakdown spectroscopy (LIBS) for performing elemental analysis in order to classify metallic samples is currently under construction. The setup uses short laser pulses to locally ablate the sample and create luminous plasmas. The emitted light is analyzed spectroscopically for instantaneous determination of the elemental composition. A table-top system based on a compact CCD spectrometer has been constructed and combined with fast software in order to test the concept of remote, single shot material classification with LIBS. Certified reference materials with known elemental compositions were used in the laboratory tests. We report on successful laboratory tests in which samples were classified using an analysis based on optical emission following a single laser pulse and with an operating distance of approximately 1 m. Details regarding field tests of this versatile and promising technique are discussed.

1. Introduction

According to the World Steel Association the demand and production of steel in the world has doubled in the last 30 years and increased 5–10% per year during the last ten years. This is a consequence of the increased use of steel in the construction of infrastructure such as buildings, roads, bridges, railroads etc. This development seems to continue in the foreseeable future and the recycling of metal, which in principal could be 100%, need to be at a high level in order to minimize the environmental effects of this increased metal and steel demand and production. Recent reports claim that if e.g. austenitic steels were to be produced solely from scrap, energy use would be 67% less than for virgin-based production and CO_2 emissions would be cut by 70% [1]. In parallel, the need for high strength steel is also increasing drastically partly due to efforts of decreasing the weight of e.g. trucks and cars in order to keep their emission of greenhouse gases at minimum levels. High strength steel uses increasing amounts of different alloy elements which often are expensive due to the complications in mining and producing them. Mining of ore is a process with severe direct and indirect environmental consequences and keeping the demand for virgin metal production at a minimum would result in less impact on nature.

Metallic scrap is usually sorted into categories such as magnetic and non-magnetic scrap before it is brought back to the production stage. However, the non-magnetic part of a scrap flow might still be complex and contain e.g. aluminium, copper, low alloy steel and high alloy steel. The remaining scrap is therefore often hand sorted in order to ensure a high industrial value of the final product. The following article presents the development of a fully automated laser based system for fast elemental analysis with the main objective to provide elemental analyses which in the future could allow sorting of metallic scrap pieces. Similar laser systems have been developed previously for sorting e.g. aluminium alloys [2,3] and treated wood waste [4] but also for slag and steel analysis [5–8].

2. Experimental setup

Our experimental setup is based on laser-induced breakdown spectroscopy (LIBS). The LIBS-technique utilizes a short and highly energetic laser pulse to ablate a very small amount of material from the surface of a sample. In the process, a hot plasma is generated where the ablated material emits element-specific optical emission. By analyzing the light with a spectrometer the elemental composition of the sample can be determined.

The experimental setup used by the authors is built around a pulsed Quantel Brilliant Nd:YAG laser which emits laser pulses of a few ns at a wavelength of 1064 nm. Each pulse has an energy of several tens of mJ implying a pulse peak power of the order of MW. The plasma formed on the surface of the sample is imaged by a spherical mirror, with an optical aperture of 75 mm and positioned 700 mm away from the sample, onto the tip of an optical fibre which guides the light into a compact Ocean Optics HR2000 + CCD spectrometer covering the wavelength range 220–440 nm. A photograph of the setup is shown in Fig. 1.

It is crucial that the laser pulse is focused onto the target to ensure a high enough energy density in order to achieve ablation. The system is therefore equipped with an optical distance meter which in combination with electronics makes sure that the laser pulse is triggered

---

* Corresponding author.
E-mail address: jonas.gurell@swerea.se (J. Gurell).

0584-8547/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.sab.2012.06.013

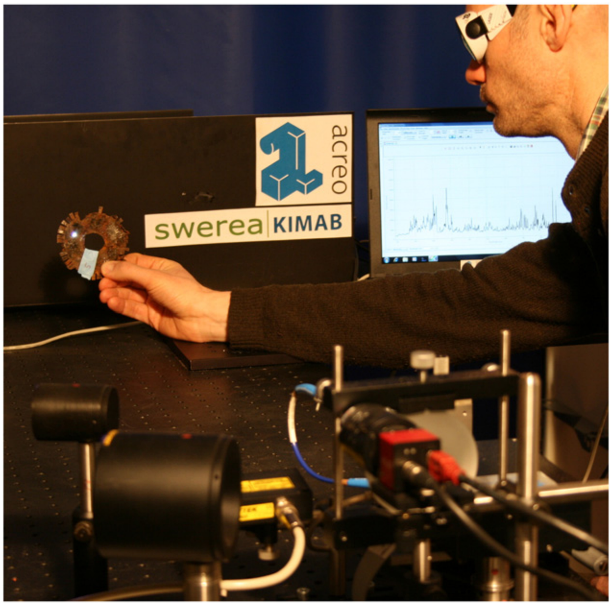

Fig. 1. Photograph of the LIBS-setup under development. An illuminated scrap piece is held in the back of the picture and the blue optical fiber guides the light into the spectrometer in the bottom right corner. The corresponding spectrum is displayed on the screen of the laptop.

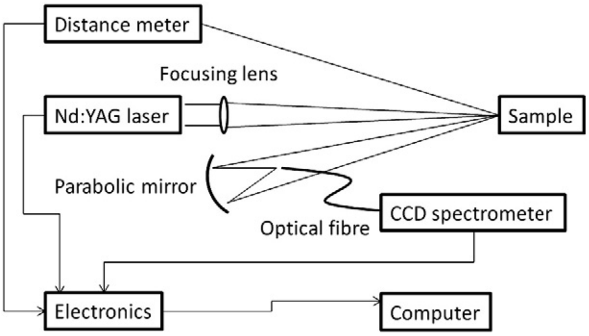

Fig. 2. Schematic view of the LIBS-setup.

only when a sample is passing through the focus of the laser. The distance meter used was a MEL sensor M9-i 750 with a resolution of 50 μm. Due to the fact that the distance meter and the ablation laser is not collinear a separation between the two beams will appear on the sample surface if the distance to the sample, at the time of the trigger pulse, varies. This has proven to be a small effect and the resolution of the distance meter is not causing any significant variations in the amount of light collected from shot to shot. By choosing a suitable arrangement of the setup in front of or above a conveyor belt the system is suitable to be used for on-line fully automated measurements. A schematic view of the setup is shown in Fig. 2.

The laser was operated at 1 Hz and maximum pulse energy and externally attenuated to about 20 mJ pulse energy. This proved to be a high enough energy to ensure high signal to noise spectra from single laser shots as shown in Fig. 3.

As can be seen in Fig. 3, the spectrum shows a great number of partly resolved spectral lines, to a large extent belonging to the spectra from neutral and singly ionized iron, chromium and nickel. A LabVIEW-based software has been developed in order to automatically analyze the spectrum and classify the sample material immediately after read out of the spectrometer. The time for doing so is of the order of a ms. Since many of the lines used for analysis are unresolved, a highly accurate quantitative analysis is difficult to perform. 18 different certified reference materials (CRMs) have been used to gather spectral information from different kinds of steel. Routines for performing complete coincidence searches were constructed and used in order to correlate channel intensity ratios to known relative elemental concentrations in the samples. For each element of interest a number of the best correlated channel ratios were selected and quadratic calibration curves were constructed, see Fig. 4.

This multivariate analysis gives an estimate of the elemental content of the sample but can, more importantly, be used to classify the different material. This makes the LIBS-system suitable for mix up investigations and quality control. The LabVIEW-software allows elemental content to be fed into the program to define a material class, but for improved quality the software can instead be trained to recognize a material based on a series of measurements. Each future sample which is analyzed is then assigned the most similar material class by the software.

3. Results

A number of measurement series were performed in order to study how the signal and result varied between different laser shots. Even with fairly clean samples the first few shots showed strong signals from surface elements e.g. calcium and magnesium which were not present in the bulk of the sample. After approximately 5–10 20 mJ laser pulses, these surface layers were ablated and more stable results with better correlation to the actual bulk composition were achieved, see Fig. 5.

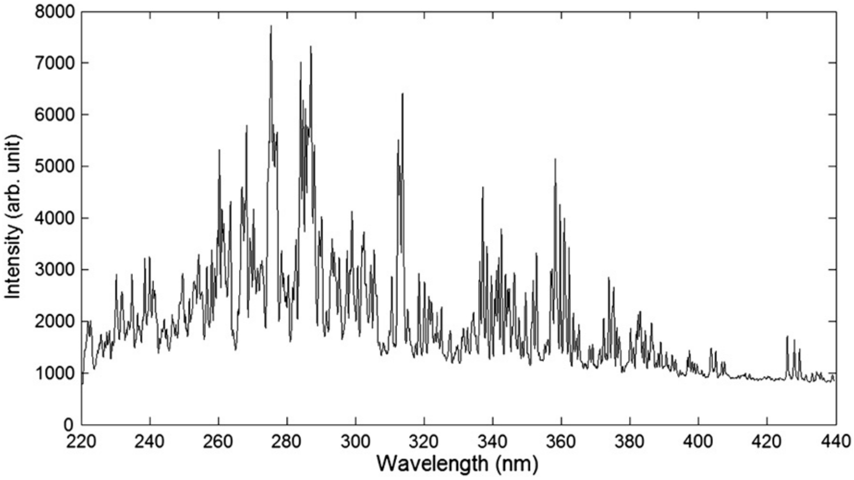

Fig. 3. Typical 20 mJ single shot spectrum from a high alloy steel.

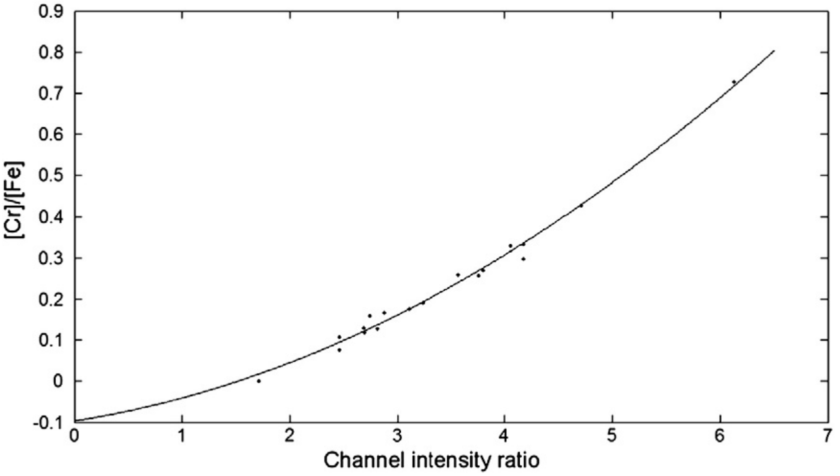

Fig. 4. Cr/Fe calibration curve based on the correlation between several channel intensity ratios and the actual chromium/iron content ratio for 18 different certified reference materials. Each data point corresponds to 40 laser shots and materials with Cr contents between 0 and 27% were used.

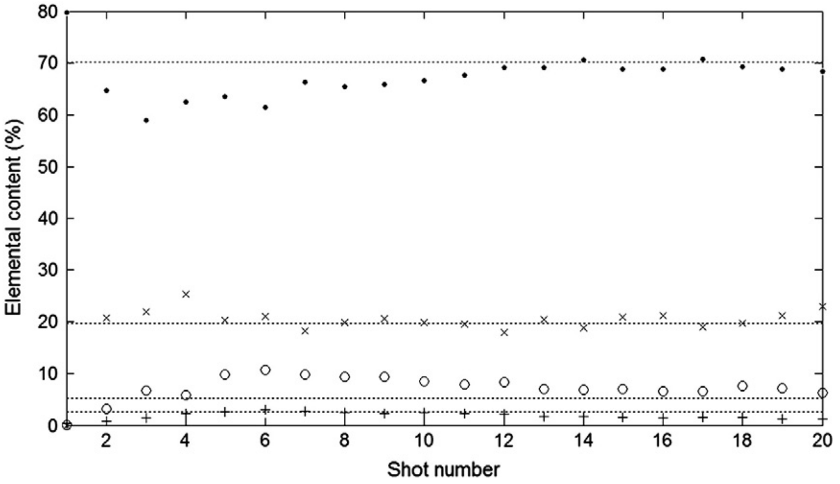

Fig. 5. Elemental content measurements of a high alloy steel certified reference material BCO44H as a function of shot number at the same impact spot. Iron is indicated as solid circles, nickel as crosses, chromium as open circles and manganese as pluses. The average measured values with one standard deviation given as uncertainty are [Fe] = 67.4 ± 4.3%, [Ni] = 19.5 ± 4.9%, [Cr] = 7.2 ± 2.4% and [Mn] = 1.8 ± 0.7% while the corresponding reference values are [Fe] = 70.1%, [Ni] = 19.8%, [Cr] = 5.3% and [Mn] = 2.5% respectively.

Since the signals stabilized after 5–10 shots, the later shots were used when constructing the calibration curves. Correlation of the elemental content to intensity ratios in spectra from the first couple of shots were attempted and proved possible but with significantly lower accuracy. Instead it is proposed to equip the system with an additional Nd:YAG laser to clean the surface of the sample through laser-induced ablation and then use the initial laser to ablate and analyze material from within the border of the cleaned spot. This is a future task which is currently under development, however, the technique of using laser ablation for surface cleaning is well documented [9–11].

The available system without the proposed cleaning laser was used in order to classify different steel samples into one out of eight classes defined in the software prior to the start of the measurement series. Each of the eight samples was analyzed at five different spots and each spot was ablated with 50 laser shots each. The signal from each shot was analyzed which resulted in 2000 measurements. All eight samples were CRMs and are listed in Table 1. The success rate of the classification increased with the shot number at each spot due to the perturbation from surface elements and the result is shown in Fig. 6.

The ability to quantitatively determine the elemental content was also evaluated by calibrating channel intensity ratios to relative abundances for the following elements: Fe, Cr, Ni, Mn, Mo, Cu and Si. The method was tested by measuring the elemental content of 18 different CRMs and comparing the measured abundances to the certified values. A graph showing the result for Fe and Cr can be seen in Figs. 7–8.

4. Conclusions

The LIBS-system developed by Swerea KIMAB in collaboration with Acreo has shown results which make the system a promising candidate to be used for automated material analysis of metallic samples. With the system, it is not only possible to discriminate between different metals e.g. iron, zinc, aluminium and copper but also to

Table 1
Elemental content of the eight certified reference materials used in the classification attempt.

		Certified reference material							
		86B	1768	BCO30H	BCO40H	C1151	D845	JK8C	JK37
Content (%)	Fe	43.5	100.0	85.5	70.4	67.2	83.7	66.8	36.8
	Cr	18.9	0.0	9.2	9.2	22.1	13.3	17.2	26.7
	Ni	34.5	0.0	1.5	15.0	7.0	0.3	11.0	30.8
	Mn	1.8	0.0	1.1	0.3	2.2	0.8	1.6	1.7
	Mo	0.2	0.0	0.2	2.5	0.8	0.9	2.6	3.6
	Cu	0.2	0.0	0.1	0.1	0.3	0.1	0.1	0.9
	Si	1.2	0.0	0.9	0.7	0.4	0.5	0.4	0.1

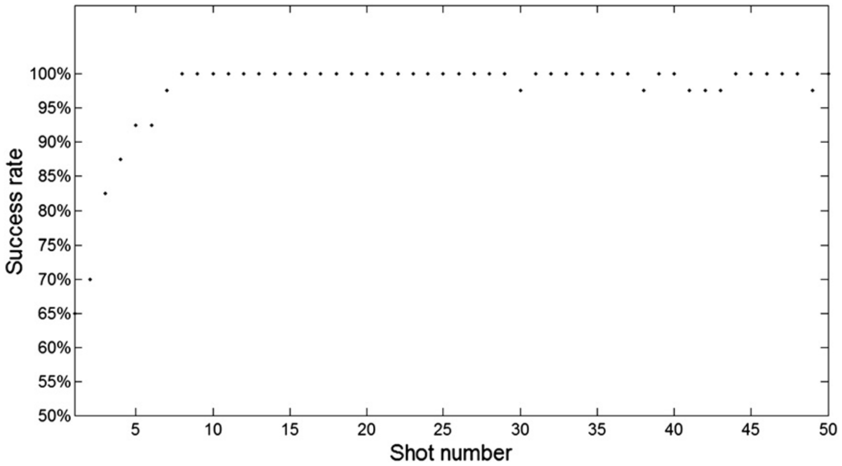

Fig. 6. Success rate when classifying the eight steel samples listed in Table 1. It is clearly shown that the classification is successful after 5–10 shots when the surface layers of the samples have been ablated.

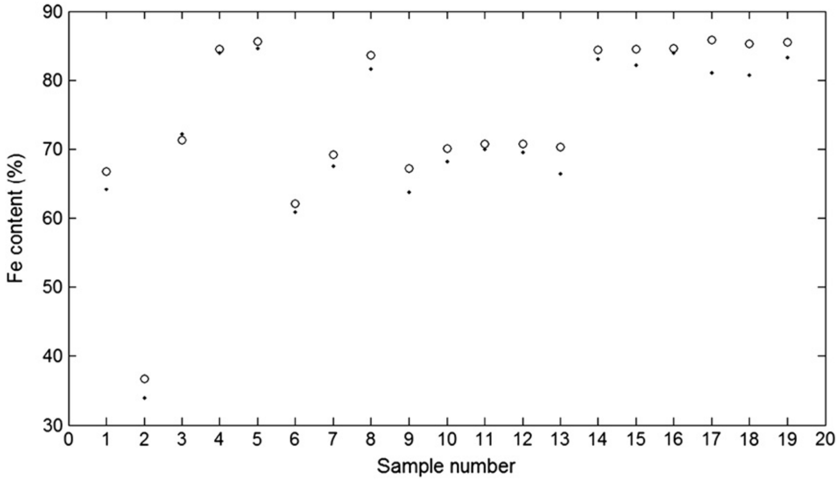

Fig. 7. Fe content measurements (solid circles) for 18 certified reference materials compared to their certified Fe content (open circles). The data points are based on 200 averaged laser shots.

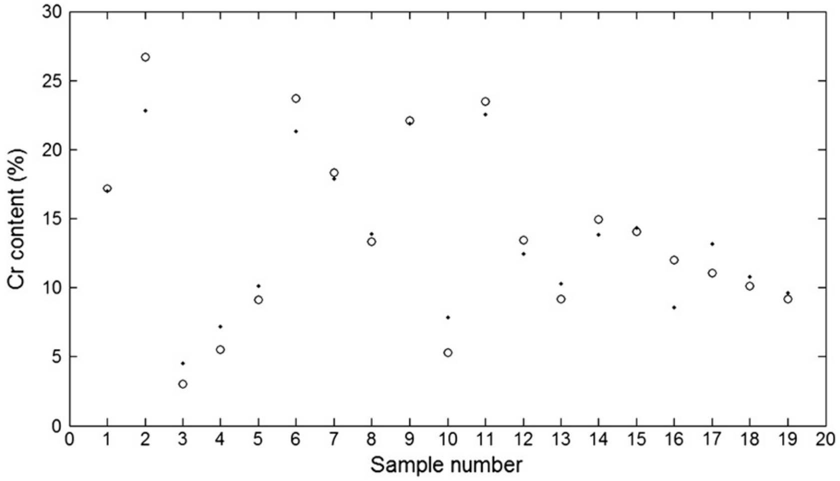

Fig. 8. Cr content measurements (solid circles) for 18 certified reference materials compared to their certified Cr content (open circles). The data points are based on 200 averaged laser shots.

separate different steel alloys from each other based on an algorithm integrated in its LabVIEW-based software. The elemental content of a sample can be determined on the order of a few percent from single 20 mJ laser pulses. The system is very likely to benefit from being equipped with an additional laser which through laser ablation cleans the surface of the sample right before the analysis pulse is triggered to interact with the material. The work of implementing such a feature into the existing system is ongoing.

5. Outlook

The LIBS-setup will be tested in field during 2011/2012 at a non ferrous scrap flow at one of the scrap yards belonging to Stena Recycling in Huddinge, Sweden. In parallel, the laboratory work continues by implementing a cleaning laser into the available setup in order to increase the accuracy of the analysis. The system will also be tested at Outokumpu Stainless AB in Avesta, Sweden in order to increase the quality control of their internally recycled scrap.

Acknowledgments

The authors gratefully acknowledge the financial support from the Foundation of Strategic Environmental Research (MISTRA) through the research programme The Steal Eco-cycle administered by Jernkontoret as well as from Miljöfonden, Sveriges Ingenjörer.

References

[1] J. Johnson, B.K. Reck, T. Wang, T.E. Gradel, The energy benefit of stainless steel recycling, Energy Policy 36 (2008) 181–192.

[2] Ü. Aydin, R. Noll, J. Makowe, Automatic sorting of aluminum alloys by fast LIBS identification, In: Proceedings of the 7th Intl. Workskop in Progress in Analytical Chemistry in the Steel and Metal Industries, 2006, pp. 309–314.

[3] P. Werheit, C. Fricke-Begemann, M. Gesing, R. Noll, Fast single piece identification with a 3D scanning LIBS for aluminium cast and wrought alloys recycling, J. Anal. At. Spectrom. 26 (2011) 2166–2174.

[4] H.M. Solo-Gabriele, T.G. Townsend, D.W. Hahn, T.M. Moskal, N. Hosein, J. Jambeck, G. Jacobi, Evaluation of XRF and LIBS technologies for on-line sorting of CCA-treated wood waste, Waste Manage. 24 (2004) 413–424.

[5] G. Hubmer, R. Kitzberger, K. Mörvald, Application of LIBS to the in-line process control of liquid high-alloy steel under pressure, Anal. Bioanal. Chem. 385 (2006) 219–224.

[6] M. Kraushaar, R. Noll, H.-U. Schmitz, Multi-elemental analysis of slag from steel production using laser-induced breakdown spectroscopy, In: International Meeting on Chemical Engineering, Environmental Protection and Biotechnology, 2000, pp. 117–119.

[7] Y. Lu, J. Wang, D. Qiao, J. Zheng, Y. Tang, Analysis of metal elements in stainless steel by using laser-induced breakdown spectroscopy, Metall. Anal. 30 (2010) 10–15.

[8] V. Sturm, D. Eilers, P. Werheit, R. Noll, U. Chiarotti, V. Volponi, V. Moroli, U. DeMiranda, M. Zanforlin, M. Zani, J. Makowe, F. Vestin, A. Bengtson, Elemental monitoring of steel scrap loading an electrical arc furnace, In: Waste Management, 8th International Workshop on Progress in Analytical Chemistry & Materials Characterisation in the Steel and Metal Industries, Conference Proceedings, 2011.

[9] R. Grönlund, M. Lundqvist, S. Svanberg, Remote-imaging laser-induced breakdown spectroscopy and remote cultural heritage ablative cleaning, Opt. Lett. 30 (2005) 2882–2884.

[10] X. Zhou, K. Imasaki, H. Furukawa, S. Nakai, C. Yamanaka, Estimation of laser ablation surface cleaning efficiency, Int. J. Adv. Manuf. Technol. 19 (2002) 642–645.

[11] V. Sturm, J. Vrenegor, R. Noll, M. Hemmerlin, Bulk analysis of steel samples with surface scale layers by enhanced laser ablation and LIBS analysis of C, P, S, Al, Cr, Cu, Mn and Mo, J. Anal. At. Spectrom. 19 (2004) 451–456.