Characteristics of the Calibration Curves of Copper for the Rapid Sorting of Steel Scrap by Means of Laser-induced Breakdown Spectroscopy under Ambient Air Atmospheres

Shunsuke KASHIWAKURA[†] and Kazuaki WAGATSUMA

Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba, Sendai, Miyagi 980-8577, Japan

For the rapid and precise sorting of steel scrap with relatively high contents of copper, laser-induced breakdown spectroscopy (LIBS) is a promising method. It has several advantages such that it can work under ambient air atmospheres, and specimens can be tested without any pretreatment, such as acid digestion, polishing of the surface of the specimens, *etc.* For the application of LIBS for actual steel scrap, we obtained emission spectra by an LIBS system, which was mainly comprised of an Nd:YAG laser, an Echelle-type spectrometer, and an ICCD detector. The standard reference materials (SRMs) of JISF FXS 350-352, which are Fe-Cu binary alloy and have certified concentrations of copper, were employed for making calibration lines. Considering spectral interferences from the emission lines of the iron matrix in the alloys, Cu I lines having wavelengths of 324.754 and 327.396 nm could be chosen. In five replicate measurements of each SRM, shorter delay times after laser irradiation and longer gate widths for detecting the transient emission signal are suggested to be the optimal experiment parameters. In the determination process, utilizing the calibration line from Cu I 327.396 nm was better because of less spectral interference. By using 200 pulsed laser shots for the measurement sequence, a limit of detection of 0.004 Cu at% could be obtained.

Keywords LIBS, steel scrap, tramp element, rapid sorting

(Received August 5, 2013; Accepted October 27, 2013; Published December 10, 2013)

Introduction

In recent years, the recycling of steel scrap has been energetically encouraged in order to comply with “Basic Act for the Promotion of the Recycling-Oriented Society”,¹ which has been enforced since 2000 in Japan. The amount of steel production in Japan has been around 100 million tons, and produced steels have been stocked and accumulated as infrastructures, cars, constructions, *etc.*² Around one-third of the steel production in amount has been conducted by electric arc furnaces (EAF), which is the major recycle route for steel scrap.³

When recycling various types of steel scrap, clarifying and controlling their characters is of great concern. The classification of steel scrap has been conducted in Japan according to specifications by The Japan Ferrous Raw Materials Association.⁴ Especially, copper in steel products has been well recognized as one of the so-called tramp elements,⁵ which adversely affects hot processing.⁶ The threshold concentration of copper in steel products is usually 0.2 wt%.⁷ Since copper in steel products is difficult to be thermodynamically removed, and it thus tends to contaminate into steel scrap,⁸ it must be deeply concerned with the concentration of copper in recycled steel products, the so called “cyclic concentration”.

In order to sort steel scrap according to the chemical compositions, we can apply laser-induced breakdown

spectroscopy (LIBS) as an encouraging and promising analytical tool.⁹⁻¹⁴ It can determine the chemical composition by remote-sensing without any pretreatment of the targeted steel scrap. The diameter of the spot formed by the laser irradiation is usually less than 1 mm; therefore, LIBS is classified as a non-destructive method. In LIBS, a pulsed laser beam that has a high power density is irradiated to the surface of a specimen. According to the laser irradiation, atoms located on the surface receive energy from the laser, and are then ablated from the surface. Some of the ablated atoms are excited/ionized, and then light emissions from a so-called “initial plasma” is generated. Released electrons in the initial plasma also receive energy from the laser, accelerate, and collide with the ablated atoms. The collision partner of the ablated atoms is also excited/ionized, and then emits characteristic radiation during expansion of the plasma, a so-called “expanded plasma”.

In determining chemical composition by LIBS, the precision and repeatability of the calibration line is very important for reliable sorting of the pieces of steel scrap. In our previous work, it was revealed that the calibration line of copper in a laser-induced plasma (LIP) using low-pressure argon gas is enough to be employed for the elemental analysis of copper in Fe-based alloys.¹⁵ In that study, a criteria was made that a relative standard deviation (RSD) of below 10% is acceptable, and linear calibration curves of chromium in Fe-Cr binary standard reference materials (SRMs) under a reduced argon atmosphere ($P_{Ar} = 2660$ Pa) could be obtained in the concentration range of 5 - 20 Cr at%.

The background emission from LIP would worsen the

[†] To whom correspondence should be addressed.

E-mail: shunsuke-k@imr.tohoku.ac.jp

Fig. 1 Schematic diagram of the experimental apparatus.

Fig. 2 Timing of the laser shots, LIP generation, intensifying, and detection.

precision of the calibration line due to: 1) recombination emission and 2) bremsstrahlung. Each effect can be described as follows:

$$1) G^+ + e^- = G + h\nu,$$

$$2) G + e^-(\text{fast}) = G + e^-(\text{slow}) + h\nu,$$

where $h\nu$ means the continuum radiation of the background emission. In recombination emission, energetic electrons combine with gas ions for neutralization, and extra energy is emitted. In bremsstrahlung, energetic electrons are re-accelerated by gas atoms, and lose their kinetic energy, which results in the continuum radiation. In LIBS at atmospheric pressures, nitrogen molecules play an important role in these collision processes because the nitrogen molecule has many vibrational/rotational excited levels in different electronic states, and therefore it can become a major source for background

spectra of LIBS. If these negative effects can be overcome, LIBS in air atmospheres can be a very powerful tool for the elemental analysis of varieties of steel scrap at a sorting site. Therefore, in this study we investigated precise calibration lines of copper for practical analysis by optimizing the experimental parameters in the open-air LIBS.

Experimental

The LIBS system utilized in this study comprised an Nd:YAG pulse laser (LS-2137, LOTIS TH), a three-dimensional sample stage, planoconvex lenses for collecting the laser and the emitted radiation, an optical fiber, an Echelle-type spectrometer (ME5000, Andor) and an ICCD detector (DH734-18F, Andor), as shown in Fig. 1. The wavelength, energy, duration, and frequency of the pulse laser were 532 nm (SHG mode), 80 mJ/pulse, 16 – 18 ns, and 10 Hz, respectively. A schematic

Fig. 3 Stacked LIP spectra of both FXS 352 and 4N-purity iron (delay time, 0.5 μ s; gate width, 500 μ s).

image of the timing of the laser irradiation, the formation of LIP, and detection is illustrated in Fig. 2. When a laser pulse having a width of 16–18 ns is irradiated onto the surface of specimens, the initial plasma was generated for *ca.* 0.5 μ s. And then the plasma was expanded upwards, and vanished. As a result of a preliminary experiment, we found that the emission signals from LIP in an air atmosphere was the most intensive at a time delay of 0.5 μ s; therefore, we made a synchronization between the laser shot and the start of the emission detection by using a triggering unit, so that the values of the time delay could be varied from 0.5 to 10 μ s. As another parameter for intensifying the emission signals, the gate width was adjusted from 0.5 to 500 μ s, according to the delay time in order to obtain spectra with larger intensities and higher signal-to-background ratios. The signals from the Echelle-type spectrometer were integrated on the ICCD; we set the exposure time of the ICCD for signal integration to 1.0 s, as the maximum value in the Andor measuring system, enough to obtain all of the integrated emission signals when the laser irradiation was repeated at 10 Hz. The amplification factor by a micro-channel plate photomultiplier in the ICCD detector, which could be varied from 0 to 250, was also adjusted by an Andor Solis software interface in order to prevent saturation of the emission signals arriving at the micro-channel plate photomultiplier. Under this condition, the total measurement time was around 2 s for 10 laser shots irradiated in 1 s, which was estimated at the interface.

For obtaining calibration lines, meaning the relationship between the time-integrated emission intensities and the contents of copper in the specimen, we adopted standard reference materials (SRMs) of FXS 350-352 certified by The Japan Iron and Steel Federation. The copper contents in FXS 350-352, were 0.2, 0.5, and 1.0 wt%. Assuming that these SRMs could be regarded as being a Fe-Cu binary alloy not containing any impurities, the copper concentration range could be converted to 0.18, 0.44, and 0.89 at%, respectively. All of the measurements were conducted for five replicates in each specimen to evaluate the degree of fluctuation for calculating the RSDs.

Result and Discussion

Figure 3 shows the LIP emission spectra from the FXS 352 alloy and 4N-purity iron plate. Although all of the spectra were taken in the wavelength range of 200 to 950 nm, the displayed

Table 1 A assignment of emission lines for making calibration lines

Wavelength/ nm	Upper/ eV		Lowerer/ eV	
Cu I 324.754	3.8116	$3d^{10}4p^2 \ ^2P_{3/2}$	0.0000	$3d^{10}4s \ ^2S_{1/2}$
Cu I 327.396	3.7858	$3d^{10}4p^2 \ ^2P_{1/2}$	0.0000	$3d^{10}4s \ ^2S_{1/2}$
Fe I 344.061	3.6025	$3d^64s4p \ ^5P_3$	0.0000	$3d^64s^2 \ ^5D_4$

range was enlarged from 320 to 350 nm. Since iron has a large number of atomic/ionic emission lines, emission lines of copper used for establishing calibration lines must be carefully selected so that the copper emission line has larger intensities without any spectral interferences with the iron emission lines. As a result, two lines of copper atomic emission, whose assignments are given in Table 1, could be selected. These copper lines marked with black circles are Cu I 324.754 nm and a Cu I 327.396 nm, and also Fe I 344.061 nm was marked with a black triangle in Fig. 3. The characteristics of the Fe I 344.061 nm line is also listed in Table 1, because we utilized this line as an internal standard line, expecting that emission lines with similar upper levels would have similar emission characteristics.¹⁵ Since we utilized an Echelle-type spectrometer and ICCD detector, continuum background by recombination emission or bremsstrahlung could be observed as the jagged shape in Fig. 3.

The selection of resonance atomic lines is not generally suitable for making calibration lines due to a self-absorption effect:^{16–20} emission related to a resonance transition would be predominantly absorbed by the same kind of atom in the ground state, resulting in a decrease in the observed emission intensity. However, under the experimental conditions described above, we had no choice but to use the two resonance lines of copper because of relatively low concentrations of copper in Fe-Cu SRMs as well as severe spectral interferences with a number of iron atomic/ionic emission lines; therefore, emission lines of iron that have a similar excited energy were considered to be favorable for the internal standard method.

In order to make calibration lines, peak areas of the Cu I emission lines were calculated by subtracting the linearly-approximated background and the sectional mensuration by trapezoidal rule. Since the transient response of the emission signals from LIP in air is generally unstable, due to differences of the laser energy in each shot, of the surface texture, of the convection, *etc.*, it is important to optimize the measuring parameters for ICCD detection. Figure 4 shows the RSDs for the Cu I emission lines for five-times measurements as a function of the gate widths. To obtain these plots, FXS 350 (Cu = 0.18 at%) was employed and the delay time was fixed at 1 μ s. It was clearly observed that the RSDs decreased with an increase in the gate widths. Our previous report²¹ suggested that the expansion of the LIP would be suppressed by the air surrounding the plasma body, resulting in that the emission from the plasma could continue to be observed for more than 30 μ s. The tendency shown in Fig. 4 implies that longer gate widths could average the fluctuation of the emission intensities by each laser shot. In Fig. 4, the RSDs estimated from the net peak areas and the peak area ratios are compared. The Fe I line was utilized as an internal standard to cancel out any difference in the emission intensity due to a difference in the ablation amounts from the specimens; however, the effect of the internal standard did not clearly appear. This phenomenon implies that the fluctuation of the net peak area of Fe I 344.061 nm are too high to cancel out those of the Cu I lines. When we consider the

sorting of various steel scrap, the concentrations of iron in them are not generally given. If the values of the peak-area ratios of the emission lines between copper and iron were adopted to make calibration lines, the discrepancy of the values between the SRMs and the pieces of scrap could be expected due to the difference of the iron concentrations in them; therefore, we utilized the net peak areas of the Cu I lines to make calibration lines, and the determination of copper in the pieces of scrap.

As described in the introduction, we should evaluate the background emission mainly by nitrogen molecules due to both the recombination emission and the bremsstrahlung. In Fig. 5, the spectra of FXS 350 with different delay times are stacked and displayed. As a background emission, a continuum is clearly observed in the wavelength range from *ca.* 322.5 to 327.5 nm, especially at a delay time of 0.5 μ s. The continuum tends to decrease with an increase in the delay time, while the Cu I peaks are clearly observed in all of the spectra in Fig. 5.

Figure 6 describes calibration curves along with increasing the delay time. All of the calibration lines bend downwards at higher copper contents in the FXS standards, which typically suggested the occurrence of self-absorption. While the peak area of Cu I 327.396 nm was almost zero in a 4N-purity iron sample, that of Cu I 324.754 nm was non-zero, which would derive from a slight interference by the emission line of the Fe I

324.742 nm line. We have also obtained linear calibration curves of copper in the same FXS standards under an evacuated atmosphere using argon gas,²² and such a difference of the calibration curves can be explained by the degree of self-absorption. That is, the expansion and decay of the LIP in a low-pressure atmosphere tends to proceed more easily,²³ whereas it is blocked in an ambient atmosphere by surrounding air gases. That results in a difference in the number density of ablated atoms in the ground level, and affects the probability of occurrence of self-absorption. In Fig. 6, the peak areas obtained in FXS 352 (Cu = 0.89 at%) tend to be smaller than those of FXS 351 (Cu = 0.44 at%) with an increase in the delay time, representing the progress of self-absorption. This can be reasonable because when the delay time is prolonged, the number of copper atoms in excited levels is reduced, while that in the ground level increases. Although the background emission became elevated in the early stage of emission, we adopted 0.5 μ s of the delay time because the degree of self-absorption effect was less than that for longer delay times.

The elemental for actual pieces of steel scrap primarily requires a rapid detection of copper contents; for this purpose, an LIBS measurement with fewer laser shots is recommended. In other words, the detection of 0.2 wt% of copper would be required by this LIBS measurement. As the next step, an improvement in the accuracy of the measurement could be

Fig. 4 Relationship between the RSDs from the peak areas or the peak area ratios and the gate widths at a delay time of 1 μ s.

Fig. 5 Stacked LIBS spectra from FXS 350 along with the delay time.

Fig. 6 Calibration curves of copper by FXS SRMs by changing the delay times, when the gate width was fixed at 500 μ s.

Fig. 7 Calibration curves of copper by FXS SRMs by changing the laser shots, when the delay time and gate width were fixed at 0.5 and 500 μ s, respectively.

Table 2 RSDs and limits of detection from the calibration lines listed in Fig. 6

Wavelength/ nm	Laser shots/ times	RSD, %	Fe	350	351	352	Limits of detection, at%
Cu I 324.753	10		20.3	11.6	7.7	7.5	0.094
	50		9.6	4.8	6.8	2.6	0.043
	100		5.6	2.2	2.6	4.1	0.035
	200		2.3	3.7	1.8	4.7	0.012
Cu I 327.396	10		89.7	16.4	2.6	13.3	0.084
	50		89.7	11.9	5.5	5.1	0.034
	100		46.7	6.5	5.9	2.5	0.030
	200		6.4	4.3	3.6	2.2	0.004

conducted by accumulating emission signals with the change in the laser shots from 10 to 200. The total measurement times varied from 2.1 to 42.6 s. The result is shown in Fig. 7, and it is obvious that the fluctuation of the measured peak area ratio drastically decreased with an increase in the repetition times. From the quadratic regression functions listed in Fig. 7, the limits of detection by the Kaiser 3-sigma criterion are listed in Table 2. In order to calculate the limit of detection, the intercepts of the quadratic functions were equally set to the average values of the peak area ratios in the 4N-purity iron. It was revealed that the RSDs as well as the limit of detections could be greatly improved by increasing the repetition times. It should be noted that the limits of detection from Cu I 327.396 nm are better than those of Cu I 324.753 nm, because the peak area of Cu I 324.753 nm includes the peak area of Fe I 324.742

nm as the spectral interference.

As a final step, LIBS under the ambient air condition was applied to measurements of the copper contents of three pieces of steel scrap named as scrap 1 – 3, which were obtained from a market for recycling. The copper contents in these pieces of steel scrap were measured by means of handheld-type X-ray fluorescence analysis (DP2000, Olympus). They were determined by a fundamental parameter method with two beams: 40 s of irradiation of a 40 kV beam and 20 s of irradiation of a 8 kV beam. The limit of detection of copper in a Fe-based alloy in this XRF is ensured below 10 ppmw, and the determined concentration of copper in the pieces of scrap are 0.031 wt% for scrap 1, and non-detected for scrap 2 and 3. The scrap 1 mainly consists of iron and zinc, and their compositions are 58.3 and 37.3 wt%, respectively.

The results of LIBS measurements are given in Table 3. It was conducted under the same conditions as described in Table 2. We could not detect the copper contents in scrap 2 and 3, which are consistent with the results by XRF measurements. The detection of copper contents in scrap 1 by the LIBS measurement was successful only in the 200-laser-shot condition due to the sufficient limit of detection. The determined values of copper contents in scrap 1 could be converted to 0.024 and 0.039 wt%, respectively, with the assumption that scrap 1 is Fe-Zn-Cu ternary alloy. Compared to the XRF analysis, it seems that the determination of copper contents in scrap 1 was successful; however, we could not the detailed accuracy of this determination due to a lack of variations of scrap specimens. Further investigation for targets of steels scrap with higher copper contents (e.g. more than 0.1 wt%) is needed for our future study.

Table 3 Determination of Cu contents in 3 types of steel scrap using the calibration lines listed in Table 2

Wavelength/ nm	Laser shots/ times	Limits of Detection, at%	Cu in Scrap 1, at%	Cu in Scrap 2, at%	Cu in Scrap 3, at%
Cu I 324.753	10	0.094	Not detected	Not detected	Not detected
	50	0.043	Not detected	Not detected	Not detected
	100	0.035	Not detected	Not detected	Not detected
	200	0.012	0.022	Not detected	Not detected
Cu I 327.396	10	0.084	Not detected	Not detected	Not detected
	50	0.034	Not detected	Not detected	Not detected
	100	0.030	Not detected	Not detected	Not detected
	200	0.004	0.037	Not detected	Not detected

Conclusions

The aim of this study was to optimize the experimental parameters for obtaining calibration curves of copper in Fe-Cu binary SRMs by laser-induced breakdown spectroscopy. The emission lines of Cu I 324.754 nm and Cu I 327.396 nm were found to be candidates for the detection of copper in the Fe-Cu alloy, though they were resonance lines that would suffer from self-absorption. Since prolonged gate widths are sufficient to detect the transient emission, and the decay of the LIP was effective for the reduction of fluctuation of the emission signals, the gate width was set to 500 μ s as an optimal parameter, because it could average the emission from the LIP by each laser shot. A shorter delay time was also favorable in order to suppress the self-absorption effect. The accuracy of the calibration curves could be improved by repeating the measurement sequence. A limit of detection of 0.004 Cu at% could be achieved by 200 laser shots, and these optimized experimental conditions might be applied for actual pieces of steel scrap.

Acknowledgements

This research is supported by a Grand-in-Aid from the Ministry of Education, Science, Sports and Culture of Japan (No. 23310049). Several parts of the setups were installed under support of the A-STEP program in Japan Science and Technology Agency (No. 241FT0286) and ISIJ Research Promotion Grant (Incl. Ishihara/Asada Grant) by the Iron and Steel Institute of Japan.

References

1. The Basic Law for Establishing the Recycling-based Society, The Ministry of Environment, Japan, **2000**, <http://law.e-gov.go.jp/htmldata/H12/H12HO110.html>.
2. The Japan Iron and Steel Federation, <http://www.jisf.or.jp/data/>.
3. Non-Integrated Steel Producers Association, http://www.fudenkou.jp/about_03.html.
4. Uniform Standards of Ferrous Scrap, The Japan Ferrous Raw Materials Association, <http://www.tetsugen.gol.com/kikaku/index.htm>.
5. The Society of Materials Science, Japan, <http://www.jsms.jp/word/index-kato.html>.
6. L. Savov, E. Volkova, and D. Janke, *RMZ - Mater. Geoenviron.*, **2003**, 50, 627.
7. T. Kajitani, M. Wakoh, N. Tokumitsu, S. Ogibayashi, and S. Mizoguchi, *Tetsu-to-Hagane* (in Japanese), **1995**, 81, 185.
8. K. Yamamoto, T. Toh, H. Hamatani, K. Tsunenari, K. Umetsu, Y. Maruki, S. Takeuchi, and Y. Yamada, *Engineering Report of Nippon Steel & Sumitomo Metal* (in Japanese), **2012**, 394, 69.
9. T. M. Naeem, H. Matsuta, and K. Wagatsuma, *ISIJ Int.*, **2002**, 42, 1318.
10. K. Kuzuya, M. Murakami, and N. Maruyama, *Spectrochim. Acta, Part B*, **2003**, 58, 957.
11. Y. Ushirozawa and K. Wagatsuma, *Anal. Sci.*, **2006**, 22, 1011.
12. Y. Iida, *Spectrochim. Acta, Part B*, **1990**, 45, 1353.
13. T. L. Thiem, R. H. Salter, J. A. Gardner, Y. I. Lee, and J. Sneddon, *Appl. Spectrosc.*, **1994**, 48, 4.
14. L. Fornarini, F. Colao, and R. Fantoni, *Spectrochim. Acta, Part B*, **2005**, 60, 1186.
15. H. Shimada and K. Wagatsuma, *Bunseki Kagaku*, **2011**, 60, 59.
16. V. Lazic, F. Brrbini, and R. Fantoni, *Spectrochim. Acta, Part B*, **2001**, 56, 807.
17. G. Gupta, B. Suri, and A. Verma, *J. Alloys Compd.*, **2011**, 509, 3740.
18. M. Garcimuno, M. Pace, and G. Bertuccelli, *Opt. Laser Technol.*, **2013**, 47, 26.
19. A. Sarkar, D. Alamelu, and S. Aggarwal, *Opt. Laser Technol.*, **2013**, 47, 30.
20. S. Beatrice, A. David, and A. Sylvestre, *Spectrochim. Acta, Part B*, **2005**, 60, 479.
21. S. Kashiwakura and K. Wagatsuma, *CAMP-ISIJ*, **2012**, 25, 1264.
22. L. Zhang and K. Wagatsuma, *ISIJ Int.*, **2013**, 58, in press.
23. L. Zhang, S. Kashiwakura, and K. Wagatsuma, *Key Eng. Mater.*, **2012**, 508, 331.