Uncertainty of the Analytical Values in Laser-induced Plasma Optical Emission Spectrometry for Element-based Sorting of Commercial Aluminum Alloys

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Abstract

This paper describes uncertainty ranges of the analytical values by laser-induced breakdown spectrometry (LIBS), in order to realize an element-based sorting of commercial Al alloys whose chemical compositions are varied in different kinds. For this purpose, calibration factors and their standard errors between the emission intensity and the content of major alloyed elements were estimated using a series of standard reference materials of Al alloys. From the result of LIBS analysis, Al alloy samples, labeled with A1050, A1100, A2017, A2024, A5052, A5083, and A6061, were actually classified into the kinds of Al alloy the chemical compositions of which were standardized by Japan Industrial Standards. The sorting was successfully conducted, although several of them could not be classified into a particular alloy type. This was not due to the analytical precision of LIBS but due to a similarity of the chemical composition between several types of the Al alloy. For comparison, a similar sorting procedure was carried out using the analytical result by ICP-OES, which gave the same conclusion as the LIBS. In fact, ICP-OES requires sample pretreatment and dissolution and thus cannot be applied to on-site/in-line analysis, whereas LIBS can provide a rapid response of analytical values. Accordingly, the LIBS analysis may be applied to put to the practical use for sorting Al alloy materials in details.

Key words:

Laser-induced breakdown spectrometry; element-based sorting; elemental analysis; recycling; Al alloys.
1. Introduction

A recycling-oriented society has become a worldwide challenge due to environmental conservation as well as the depletion of natural resources. For this purpose, Japanese government enacted the First Basic Plan for the Formation of a Recycling-Oriented Society in 2003, followed by the second in 2008, the third in 2013, and the fourth in 2018.\(^1\) While various efforts have been progressing, the recycling rate of resources as well as the amount of final disposals has been improved significantly; however, further activities are still required to achieve the recycling-oriented society based on the 3Rs (Reduce, Reuse, and Recycle).\(^2\) Metal materials are one of the important factors in building a recycling-oriented society, since it might be possible to be recycled completely. Aluminum materials are widely produced as plates, extrusions (including electric wires), castings, die casts, and forged products,\(^3\) due to its excellent properties such as light weight, thermal and electrical conductivity, and workability, so that it is widely used in various industrial materials like iron. Also, aluminum now becomes a metal with excellent recyclability due to the small amount of energy for recycling. Compared to the energy consumption when producing new aluminum ingots by electrolytic smelting from the raw material bauxite, the energy for dissolving and regenerating Al scrap is less than 3 to 5% of that. Therefore, the recovery and reuse of Al alloy scrap is expected to contribute to energy savings and effectively use limited resources.\(^4-8\)

There remains an important problem in recycling commercial aluminum materials. At present, they are generally treated by a cascade recycling method, in which the recovered scrap is totally dissolved and then used as a recycled mass for forgings and die-casting.\(^8,9\) This is because most of the Al materials are employed in a form of alloys to which various elements are added, and Al scraps of various compositions are mixed together. According to Japanese Industrial Standards (JIS), the upper limits of alloying elements contained in Al materials for extension, such as thin foil and sheet, are generally lower than the corresponding values for forgings and die casting.\(^10\) In the cascade recycling method, various Al alloys are re-melted without any separation to produce secondary Al ingot; however, in the process, the alloy concentration in the secondary ingot may exceed the specified value of a wrought material. In many cases, direct recycling to an Al alloy having a strict composition is difficult at present. As a result, new aluminum source has to be injected for the
production of the wrought materials, and thus, in Japanese Al industry, the ratio of recycled resources is less
than 60% of the domestic resource input. Therefore, there is a further need for improvement in the recycling
rate. If the Al alloy scrap before melting can be separated by the alloy composition, recycling between the
same kind of Al alloys, so-called ‘horizontal recycling’ becomes possible, and, accordingly, the recycling rate
of the Al alloy scrap would be greatly improved. For this purpose, it is important to use any analytical
method for directly monitoring the chemical composition in Al scrapped materials, when they are sorted
through the ‘horizontal recycling’.

At present, an analytical method by XRF (X-ray Fluorescence Analysis) have been employed for a
process control analysis in actual operation, including high-speed sorting of scrapped materials. However,
XRF cannot detect elements with lighter atomic numbers at ambient atmospheric pressure that is needed in the
actual operating environment, and it has a difficulty that some elements cannot be identified. In the 2010s, an
optical emission spectrometry by high-power laser plasma, generally called LIBS (Laser-Induced Breakdown
Spectrometry), began to be routinely applied to the sorting of scrapped materials. LIBS has several features
suitable for on-site/in-line analysis in the actual process of material production, in which an as-received sample
can be analyzed with little pre-treatment under ambient air atmosphere and thus the analytical result can be
obtained easily and rapidly. In steelmaking industry, it is now expected that LIBS can be applied to the ladle
analysis of steel products as an alternative to spark discharge plasma optical emission spectrometry. Also,
LIBS is a promising analytical method for sorting scrapped metallic materials because it can determine their
chemical compositions with a high response time. The first attempt of LIBS for sorting of Al alloys was
reported by Gesing et al., in which wrought and cast alloys could be separated from Al alloy family based on
elemental analysis of LIBS. Kuzuya published a report regarding a sorting of metal alloy scraps using
LIBS, and our previous paper investigated a LIBS application to a rapid sorting of stainless steels types. More recently, a LIBS apparatus has been commercially available for a use of scrap sorting.

As considering the previous reports, it is necessary to obtain more detailed and precise analytical
information of LIBS that can contribute to a ‘horizontal recycling’ of various Al alloy types, because some of
them have similar chemical compositions. Particularly, uncertainty of the analytical values in LIBS should be
evaluated so that a small difference in the chemical composition can be identified. This paper considers an analytical uncertainty, which includes the standard error of calibration curves as well as the standard deviation of emission intensities, for sorting various kinds of commercial Al alloys based on the contents of major alloyed elements (Si, Cu, Mn, Mg, Cr, and Zn) in them.

2. Experimental

A Q-switched pulsed Nd:YAG laser (SSL-330-50, EKSPLA, Lithuania) was operated at a pulse width of about 150 ps and an output wavelength of 1064 nm (fundamental frequency). A repetition rate of 50 Hz was applied with a laser power of about 20 mJ/pulse. The energy of the pulsed laser was measured using a power meter for lasers with a thermal sensor (3A-P, Ophir Photonics, Israel). The laser beam was focused on the sample surface with a plano-convex lens having a focal length of 150 mm. A digital single-lens camera (EOS KISS X9 L1855KBK, Canon, Japan) equipped with a long-range zoom lens (VH-Z50L, Keyence, Japan), whose magnification was 50-500, was incorporated in the optical system, to observe the sample surface during laser irradiation.

The plasma emission was focused on the entrance port of an optical fiber and collected on the entrance slit of a spectrometer, dispersed by a Czerny-Turner-type monochromator (MS7504i, SOL Instruments Ltd., Belarus) with a grating of 3600 lines/mm at an actual resolution of 0.02 nm, and detected by an intensified charge-coupled detector (ICCD) (DH734-18F-03, Andor, UK). The gate width and the delay time of the ICCD were important experimental parameters to be optimized, as described later. All the experiments were carried out under ambient air atmosphere and flow of the atmospheric gas was not controlled.

Nine certified reference materials (CRM) of aluminum alloy (Japan Aluminium Association, Tokyo) were prepared to investigate calibration relationships of seven alloyed elements (Si, Fe, Cu, Mn, Mg, Cr, and Zn). Their certified contents are listed in Table 1. Also, six samples of commercial Al alloy samples were used for optimizing measuring parameters of LIBS as well as evaluating the analytical performance, as described later. For a comparison use, the chemical compositions of these samples had been determined by inductively-
coupled plasma spectrometry (Arcos MV130, SPECTRO Analytical Instruments, Germany) using an external calibration method of standard solutions. Furthermore, an ingot sample melted from scrapped Al materials was prepared to investigate inclusion particles contained in them. All the measurements were carried out for their as-received surfaces without any pre-treatments before LIBS, such as polishing with emery paper.

These samples were set on a motor-driven X-Y-Z stage (SGSP26-200S, SIGMA Koki, Japan), which was controlled with a system controller (SHOT-304GS, SIGMA Koki, Japan), and could be precisely moved to the laser beam in three-dimensional directions. The X-Y-Z stage was first adjusted in the Z-direction (height direction) until the irradiation position of laser had been focused just on a target position of the sample surface. Then, a certain number of laser shots was irradiated on a measuring point while the point was moved step-wisely, to obtain calibration curves of the alloyed elements, or a single laser shot was irradiated on measuring points with a certain distance in the X and Y directions, to obtain the lateral distribution of inclusion particles on the sample surface.

3. Results and Discussion

3.1. Optimization of gate delay time and gate width

First of all, we investigated the most suitable conditions of the ICCD detector for the experimental parameters, the gate delay time and gate width, in LIBS measurement.

Figure 1 illustrates a schematic variation in the emission intensity from a laser-induced plasma (LIP) produced by a single laser shot. The emission intensity of the sample atoms emitted from the LIP has a feature that the maximum value will be reached immediately after the LIP is generated. This is because a large number of high-speed particles are generated in a condensed gas body at the initial stage of plasma generation (plasma breakdown), and the excitation collision with the sample atoms is actively repeated. However, although its emission intensity is high, there are still large amounts of fast electrons, which cause bremsstrahlung upon collision with gas particles, giving high background emission and thus hindering the measurement of the emission intensity from sample atoms. Therefore, it is not generally suitable for LIBS
analysis. An expansion of the plasma occurs subsequently, when the electron density and gas temperature decrease but light emission from the sample atoms is observed due to the excitation mechanisms such as collision with atmospheric gas. This is a temporal range suitable for optical emission analysis because a line spectrum is obtained with a relatively low background. In the LIBS method, it does not always give good analytical characteristics that the emission intensity, which has such a temporal variation, is integrated over the entire transient region. Therefore, the precision on the elemental analysis may be improved by appropriately selecting the transient response of the emission signal. Such a detection method is called time-resolved spectroscopy. In this case, two important experimental factors, the gate delay time and the measured gate width, as defined in Fig. 1, are considered. The behavior of LIP under atmospheric pressure is not understood completely; therefore, these parameters need to be determined experimentally for each measuring device and analytical emission line.

Figure 2 (a) and (b) show the relationship between the gate delay time and the intensities of two emission lines in an Al alloy when the gate delay time is varied from 0 to 1000 ns. A resonance line of Al atom, the Al I 309.271 nm, which is assigned to an optical transition from 4d \( ^{2}D_{5/2} \) (4.0216 eV) to 3p \( ^{2}P_{3/2} \) (0.0139 eV), and an resonance line of Mg ion, the Mg II 279.554 nm, which is from 3p \( ^{2}P_{3/2} \) (4.0216 eV) to 2s \( ^{2}S_{3/2} \) (0.00 eV), were selected as the analytical emission line. The emission intensity was averaged from ten replicate measurements, and the error range was estimated from the standard deviation of the averaged emission intensity. The emission intensities generally decrease with an increase in the gate delay time. This is considered to be due to the fact that the plasma expansion is observed at longer gate delay times, so that the emission intensity of the sample atoms is reduced. The error range takes relatively large values when the gate delay time is shorter than 500 ns, but the value rapidly decreases when the delay time is longer than 500 ns, improving the measurement precision. This is because the background emission, due to recombination and bremsstrahlung radiation of atmospheric gas species, becomes intense just after the laser breakdown (at shorter gate delay). It was found from the above result that the optimum gate delay time was 500 ns for the measurement of Al alloys, in which the emission intensity was stronger as well as the error range was relatively small for both Al and Mg. In all subsequent experiments, a gate delay time of 500 ns was used.
Figure 3 (a) and (b) show the relationship between the gate width and the intensities of the Al I 309.271-nm and the Mg II 279.554-nm lines in an Al alloy when the gate width is varied from 1 to 500 μs. In this measurement, the gate delay time was fixed at 500 ns. The emission intensity was averaged from 10 replicates and the error range was evaluated by the standard deviation of the emission intensity. The emission intensity increases as the gate width is prolonged. This is due to the fact that the gate of the ICCD opens for larger periods at wider gate widths, and thus the acquisition time of the emission is lengthened. Also, the emission intensity did not increase at the gate widths more than 50 μs and reached a maximum value. This was probably because the plasma expansion was almost terminated by a duration time of about 50 μs, and the emission intensity became almost zero after that. The error range increases as the gate width increases. This observation would be attributed to the fact that only the noise was integrated while the emission of the sample atoms was very faint at the prolonged gate widths. Therefore, the gate width was selected to be 50 μs for the following measurements, because the intensity was close to the maximum one with a relatively small deviation.

3.2. Analytical emission lines and the calibration curves

In this section, in order to prepare calibration curves for Si, Cu, Mn, Mg, Cr, and Zn, which are major alloyed elements in the Al alloy, we determined an analytical line for each element in the emission spectrum of the alloy samples. Aluminum has intense emission lines as the following: Al I 308.215 nm, Al I 309.271 nm, Al I 394.401 nm, and Al I 396.152 nm. In this measurement, emission lines of the alloyed elements were selected in the wavelength region of these Al I lines, because either of the Al lines had to be simultaneously measured as an internal standard line due to correcting for fluctuation of the ablation amount for a laser shot. Selected emission lines of Si, Cu, Mn, Mg, Cr, and Zn are listed in Table 2, together with their assignments.

A calibration curve was estimated for each alloyed element by using the CRM of Al alloy (see Table 1). For instance, calibration relations of the Mg I 285.211-nm and Mg I 383.829-nm lines are depicted in Figs. 4 and 5. The emission intensities were averaged from five replicates and the error bars were estimated by the standard deviation of their emission intensities. Here, the intensity ratio to the Al I 309.271 nm was calculated based on the internal standard method. Whereas a linear relationship of the calibration curve is found in the
Mg I 383.829 nm (Fig. 5), the emission intensity of Mg I 285.211 nm is not on a straight line over a wide range of the Mg contents (Fig. 4(a)). This is because the Mg I 285.211-nm line is a resonance atomic line and thus largely affected by self-absorption, in which the emitted light is absorbed by the ground state of Mg atom. It was found in Fig. 5 that the Mg I 383.829-nm line has a lower sensitivity but was applicable up to the higher contents, whereas the Mg I 285.211-nm line is more sensitive to the lower contents of Mg. Linear or quadratic regression analyses were performed for calibration curves of the Mg and Cu analytical lines. The result is also summarized in Table 2, which includes a fitted equation, the correlation coefficient ($r^2$), the standard error of fitting, and the applicable content range. These calibration relations were employed for actual analysis of commercial Al alloys and for element-based sorting of them.

3.3. Quantification of alloyed elements in commercial Al alloy samples

Using the calibration results in Table 2, we determined the chemical composition in seven different kinds of commercial Al alloys. Here, the contents of Si, Cu, Mn, Mg, Cr, and Zn were quantified.

In order to classify an unspecified sample into a particular kind of the alloys, it is necessary to obtain the lowest value of content that can be detected from a calibration result. The concepts of a limit of detection (LOD) and a limit of quantification (LOQ) are used as indices to evaluate the detection ability. According to JIS, LOD is defined as the minimum amount (value) that can be detected and LOQ as the minimum amount or concentration which can be quantified by a certain analytical method. Generally, LOD and LOQ can be defined to be several times as much as the standard deviation of a signal intensity in a blank sample. That is,

$$LOD = 3\sigma / a,$$  \hspace{1cm} (1)
$$LOQ = 10\sigma / a,$$  \hspace{1cm} (2)

where $\sigma$ and $a$ are the standard deviation value of the blank signal and the slope of the calibration curve, respectively. Also, there is a concept called a background equivalent concentration (BEC) especially in the field of atomic emission spectrometry. BEC is an idea to determine the concentration of an element to be measured that gives a signal intensity equal to the background intensity, and is determined by the following equation:

$$BEC = \frac{1}{a} \ln \frac{I}{I_{bg}}.$$
Based on the above concepts in Eqs. (1)-(3), LOD, LOQ, and BEC were estimated for determination of each alloyed element in Al alloys by using their calibrations (see Table 2), as summarized in Table 3. For this estimation, a pure aluminum rod (purity: >99 %) was employed as the blank sample, in which the standard deviations for each analytical line were determined from five replicated measurements.

Next, the alloy composition of the commercial Al alloys was determined, based on the calibration curve for the alloyed elements. The quantitative value was obtained from the averaged emission intensity over five measurements, and an error range was calculated from a geometrical mean of its standard deviation (σ) and a standard error (SE) of the linear regression for calibration curves: (σ x SE)\(^{1/2}\) (see Table 2). Here, it should be considered that the error range of the calibration relationship itself may be a critical factor for determining the Al alloy types because some of them have similar chemical compositions. The lowest determinable value in each measurement was estimated from ten-times as much as the error range, which followed the aspect of LOQ (Eq. (2)). Table 4 summarizes analytical results of the alloy composition of seven commercial Al alloys, labeled with A1050, A1100, A2017, A2024, A5052, A5083, and A6061. In addition, these alloy samples were also analyzed by ICP-OES, and the analytical result of two individual measurements is presented in Table 5. LIBS provided analytical results with a relatively high precision (lower error range). In comparison between LIBS and ICP-OES, the analytical values are similar to each other, while several of them were different in a digit of 0.01 mass %. The reason for this is that the detection sensitivity of ICP-OES is superior to that of LIBS in low concentration of the alloyed elements. In particular, LIBS could not determine the content of Zn in all the alloy samples due to the lower concentration.

### 3.4. Sorting of actual Al alloy type

Based on the alloy composition of the seven Al alloy samples, they were sorted into corresponding types of the Al alloy. At present, 68 different kinds of Al alloys are commercialized in Japan, and JIS standardizes their chemical compositions.\(^{10}\) As an instance, this element-based procedure is described in selecting an Al alloy labeled with A5052. Figure 6 shows a flow chart for this procedure. First, the analysis
result of Mg, which is the highest-content element in A5052, is compared with the reference value of 2.3 mass%, and then similar comparisons are carried out in the order of the amounts of alloyed elements to narrow down the alloy types. Table 6 indicates the result of sorting of the Al alloy samples tested in this study. The samples labeled with A1100, A2017, A5052, and A6061 could be completely separated into the corresponding alloy types. The sample labeled with A1050 was hardly classified into only one kind of Al alloys essentially, because it was almost pure Al. Further, the LIBS result indicated that the sample labeled with A2024 was an alloy type of either A2024 or A2124. This uncertainty is attributed not to the precision and accuracy of the LIBS but to a similarity in the chemical composition between A2024 and A2124, in which only one difference is the Si content (0 - 0.50 mass % in A2024 and 0 - 0.20 mass % in A2124). Further, a similar sorting procedure was carried out by using the analytical values of ICP-OES, and the same conclusion as the LIBS was obtained as indicated in Table 6. As a result, we can consider that the quantitative analysis by the LIBS generally provide useful information for sorting of Al alloy types.

4. Conclusions

The LIBS measurement generally provided the elemental composition of commercial Al alloys sufficient to carry out the element-based sorting of them. In this procedure, calibration factors and their standard errors between the emission intensity and the content of major alloyed elements were considered when using a series of standard reference materials of Al alloys. From the result of LIBS analysis, commercial Al alloy samples were actually classified into the kinds of Al alloy the chemical compositions of which were standardized by Japan Industrial Standards. The result of sorting was generally satisfactory, while several Al alloys having very similar chemical compositions were hardly identified. For comparison, a similar procedure for the sorting was conducted using the analytical result by ICP-OES, which gave the same result as the LIBS. In fact, ICP-OES is an analytical method that requires sample pretreatment and dissolution and thus cannot be applied to on-site/in-line analysis, whereas LIBS can provide a rapid response of analytical values. Accordingly, this merit of LIBS could contribute to recycling of Al resources.
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Table 1 Chemical composition of certified reference materials for Al alloys

| Desig. | Si   | Fe  | Cu  | Mn  | Mg   | Cr   | Zn  |
|--------|------|-----|-----|-----|------|------|-----|
| 1-A    | 0.10 | 0.37| 0.14| 0.03| 0.014| 0.002| 0.012|
| 5      | 0.063| 0.12| 0.003| 0.0015| 0.008| 0.0010| 0.003|
| 2011   | 0.35 | 0.45| 5.38|
| 2024   | 0.14 | 0.37| 4.64| 0.5 | 1.29 | 0.04 | 0.07|
| 5052   | 0.23 | 0.38| 0.108| 0.128| 2.8 | 0.42 | 0.13|
| 5083   | 0.093| 0.19| 0.028| 0.63 | 4.24 | 0.18 | 0.023|
| 6061   | 0.61 | 0.21| 0.28| 0.030| 0.97 | 0.056| 0.02|
| 601    | 0.60 | 0.17| 0.002| 0.002| 0.57 | <0.001| 0.008|
| 7N01   | 0.085| 0.18| 0.023| 0.43 | 1.38 | 0.11 | 4.6 |
| Analytical Line /nm | Assignment | Calibration relation |
|--------------------|------------|----------------------|
|                    | Upper level (eV) | Lower level (eV) | Fitted equation | \( r^2 \) | SE | Conc. Range /mass% |
| Si I 288.159       | 4s \(^1P\) \(_1\) (5.0822) | 3p \(^1D\) \(_2\) (0.7809) | y=0.0662x + 0.0172 | 0.9806 | 0.0020 | 0 - 0.61 |
| Cu I 327.395       | 4p \(^2P\) \(_{1/2}\) (3.7858) | 4s \(^2S\) \(_{1/2}\) (0.0000) | y=-0.0050x^2 + 0.0625x + 0.04 | 0.9919 | 0.0036 | 0 - 0.38 |
| Mn I 403.076       | 4p \(^6P\) \(_{7/2}\) (3.0750) | 4s \(^6S\) \(_{5/2}\) (0.0000) | y=0.095x + 0.0126 | 0.9989 | 0.0093 | 0 - 0.63 |
| Mg I 285.211       | 3p \(^1P\) \(_1\) (4.3457) | 3s \(^1S\) \(_0\) (0.0000) | y=-0.0282x^2 + 0.2392x + 0.06 | 0.9883 | 0.0275 | 0 - 4.24 |
| Mg I 383.829       | 3d \(^3D\) \(_{3,2,1}\) (5.9458) | 3p \(^3P\) \(_2\) (2.2716) | y=0.0613x + 0.0160 | 0.9910 | 0.0105 | 0 - 4.24 |
| Cr I 425.434       | 4p \(^7P\) \(_4\) (2.9134) | 4s \(^7S\) \(_3\) (0.0000) | y=0.1131x + 0.0146 | 0.9830 | 0.0020 | 0 - 0.42 |
| Zn I 334.502       | 4d \(^3D\) \(_3\) (7.7822) | 4p \(^3P\) \(_2\) (4.0778) | y=0.0111x + 0.0171 | 0.9867 | 0.0021 | 0 - 4.6 |

\( ^\text{*) correlation coefficient, } ^\text{**) standard error of calibration \)
Table 3 Limit of detection (3σ) and limit of quantification (10σ) for each calibration curve

| Analytical Line /nm | Limit of detection /mass % | Limit of quantification /mass % | Background equivalent concentration |
|---------------------|----------------------------|-------------------------------|------------------------------------|
| Si I 288.159        | 0.056                      | 0.190                         | 0.260                              |
| Cu I 327.395        | 0.020                      | 0.069                         | 0.085                              |
| Mn I 403.076        | 0.012                      | 0.040                         | 0.133                              |
| Mg I 285.211        | 0.026                      | 0.089                         | 0.197                              |
| Cr I 425.434        | 0.006                      | 0.021                         | 0.129                              |
| Zn I 334.502        | 0.740                      | 2.100                         | 1.55                               |
| Test specimen | Si   | Cu     | Mn     | Mg     | Cr  | Zn  |
|--------------|------|--------|--------|--------|-----|-----|
|    A1050     | <0.19| <0.063 | <0.040 | ND     | ND  | ND (*) |
|    A1100     | <0.19| 0.16±0.02| ND     | ND     | ND  | ND  |
|    A2017     | 0.47±0.04| 3.6±0.1 | 0.58±0.04| 0.60±0.1| <0.021| ND  |
|    A2024     | ND   | 3.8±0.2 | 0.35±0.02| 1.2±0.2| ND  | ND  |
|    A5052     | <0.19| <0.069 | 0.070±0.02| 2.3±0.1| 0.20±0.01| ND  |
|    A5083     | <0.19| <0.069 | 0.53±0.04| 4.1±0.2| 0.14±0.03| ND  |
|    A6061     | 0.43±0.02| 0.20±0.01| 0.073±0.03| 1.1±0.1| 0.18±0.01| ND  |

*) Signal not detected
Table 5 Analytical results of several commercial Al alloy determined by ICP-OES

| Test specimen | Si   | Cu    | Mn   | Mg   | Cr    | Zn   |
|--------------|------|-------|------|------|-------|------|
| A1050        | <0.05| <0.005| <0.001| <0.001| <0.003| 0.006|
| A1100        | <0.05| 0.14  | <0.001| <0.001| <0.003| <0.002|
| A2017        | 0.47-0.48| 3.6-3.7| 0.58-0.59| 0.52 | 0.017| 0.020|
| A2024        | <0.05| 3.9   | 0.39 | 1.3  | <0.003| 0.006|
| A5052        | <0.05| 0.053-0.054| 0.025-0.028| 2.2 | 0.17-0.19| 0.015|
| A5083        | 0.11-0.12| 0.041| 0.56 | 4.3  | 0.11  | 0.006|
| A6061        | 0.41-0.43| 0.26-0.27| 0.041-0.042| 0.94-0.95| 0.17  | 0.012-0.013|
Table 6  Sorting of several commercial Al alloys based on the analytical result of LIBS and ICP-OES

| Test specimen | Alloy type selected by LIBS | Alloy type selected by ICP-OES |
|---------------|-----------------------------|-------------------------------|
| A1050         | A1N90 or A1085 or A1080 or A1070 or A1060 or A1050 or A1100 or A1200 or A1230 | A1N99 or A1090 or A1080 or A1070 or A1060 or A1050 or A1200 or A1230 |
| A1100         | A1100                       | A1100                         |
| A2017         | A2017                       | A2017                         |
| A2024         | A2024 or A2124              | A2024 or A2124                |
| A5052         | A5052                       | A5052                         |
| A5083 or A5086 or A5183 | A5083 or A5086 or A5183 | A5083 or A5086 or A5183 |
| A5061         | A5061                       | A5061                         |
**Figure captions**

Figure 1 Schematic description of time-resolved measurement of the LIBS emission signal.

Figure 2 Variation in the emission intensities of Al I 309.271 nm (a) and Mg II 279.554 nm (b) as a function of the gate delay time.

Figure 3 Variation in the emission intensities of Al I 309.271 nm (a) and Mg II 279.554 nm (b) as a function of the gate width time.

Figure 4 Calibration curves of the Mg I 285.211-nm line in the LIBS measurement in the whole concentration range (a) and in the lower concentration range (b).

Figure 5 Calibration curve of the Mg I 383.829-nm line in the LIBS measurement.

Figure 6 Flow chart for element-based sorting of a type of commercial Al alloy labeled with A5052.
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