1. Introduction

Steel is an essential material for manufacturing and infrastructure improvement, and it is expected to remain central to industry in the future. Therefore, the effective use of steel scrap is necessary to secure stable steel resources. The amount of steel scrap generated annually in Japan is estimated at approximately 20 to 25 million tons.\(^1\)

Many elements exist as impurities in steel scrap. Elements such as Cu and Sn, which cannot be removed by oxidation refining, are called tramp elements. Surface cracking caused by Cu and Sn during hot working\(^2,3\) is a problem. The highest permissible concentration of Cu in bar steel has been estimated at 0.4 wt\%.\(^4\) Additional predictions of this value have been conducted assuming various cases,\(^5\) and certain issues with the current steel recycling system have been identified that should be solved.

Measures against unintentional contamination by tramp elements include technical removal of contaminants and the prevention of contamination. Technical methods of tramp element removal include evaporation,\(^6-8\) sulfidation,\(^9-13\) and other routes. The Cu precipitates causing surface cracks are typically several micrometers in diameter.\(^14\) Additional predictions of this value have been conducted assuming various cases,\(^9\) and certain issues with the current steel recycling system have been identified that should be solved.

Contamination by tramp elements is attributed to Cu wires and motors in automobiles and electrical home appliances,\(^22\) but the details of contamination are not clear. In order to specify the source of tramp element contamination, the concentrations of many elements should be determined, even if the contaminant concentration is low or the element does not affect the recycled material. Current quantitative analysis by the dissolution of whole samples causes difficulties in obtaining accurate information on coexisting elements and the distribution states of tramp elements. LA-ICP-MS is an effective localized and microscale analytical method for elucidating the mechanism of tramp element contamination.

In this study, we conducted trace element analysis using laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)\(^16,18\) to quantitatively analyze the distribution and coexistence states of tramp elements with other elements in recycled steel materials. The concentration distributions of Cu, Sn, Pb, Ag, and Au in a 455 \(\mu\)m \(\times\) 270 \(\mu\)m region were measured using electric furnace steel as a sample by continuous line analysis. Although the concentration of Cu was the highest among the measured elements, the degree of variation in Cu concentration was the smallest. Meanwhile, not only were the degrees of variation of the Sn, Pb, and Ag concentrations large, but also the points of high concentration measurements tended to coincide. The coexistence states were investigated by determining the coefficient of correlation between the concentrations of two elements.

KEY WORDS: tramp element; steel scrap; LA-ICP-MS.
of each element were classified by level, and the concentration levels were compared. Furthermore, we investigated the coexistence states by determining the correlation coefficient of concentration between two elements.

2. Experiment

2.1. Sample and Pretreatment

A sample taken for Quantovac analysis during electric furnace steel refining was used as the sample material. Table 1 shows the impurity concentrations of the sample. The sample was processed to dimensions of 10 mm × 10 mm × 1 mm and sealed in resin. The surface of the sample was polished with abrasive paper (#800 and #1000), buffed with diamond paste, and corrosion-treated with 7% nital.

The surface of the sample was observed with an optical microscope (OLYMPUS BX51) and the region where precipitates were present was analyzed by LA-ICP-MS. Figure 1 shows an image from the optical microscope. In addition to the linear shape of ~500 μm in length from the lower left of the image to the center, a region containing many precipitates of several tens of micrometers in diameter was also analyzed. To prevent loss of the measurement areas and errors in the LA-ICP-MS analysis, the four corners of the target region were marked with a diamond indenter attached to a Micro Vickers Hardness Tester (Mitutoyo HM-103).

Three standard steel samples (Japan Iron and Steel Federation JSS 153-10, NIST 663, and NIST 1767) were used as standard samples. Table 2 shows the Cu, Sn, Ag, Pb, and Au concentrations of the standard samples.

2.2. LA-ICP-MS Measurements

2.2.1. Outline of the Apparatus and Measurement Method

An ICP-MS (Thermo Fisher Scientific, ELEMENT XR) and LA system (Teledyne CETAC Technologies, LSX-213 G2+) were connected by a resin tube with the inner diameter of 4 mm and length of approximately 2 m. An outline of the LA-ICP-MS system is shown in Fig. 2, and the operating conditions of each apparatus are shown in Table 3.

Figure 3 shows the laser scanning method on the sample surface. The sample is placed in the LA sample cell for line scanning analysis. Laser light with a spot diameter of 20 μm is irradiated downward with the scanning speed of 5 μm/s.

Table 1. Impurity concentrations of sample.

| Element | Concentration [mass%] |
|---------|-----------------------|
| Cu      | 0.37                  |
| Mn      | 0.33                  |
| C       | 0.16                  |
| Si      | 0.14                  |
| Ni      | 0.10                  |
| Cr      | 0.069                 |
| Mo      | 0.034                 |
| P       | 0.026                 |
| S       | 0.021                 |
| Sn      | 0.019                 |

Table 2. Cu, Sn, Ag, Pb, and Au concentrations of the standard samples.

| Element | JSS153-10 | NIST663 | NIST1767 |
|---------|-----------|---------|----------|
| Cu      | 3 000     | 980     | 14       |
| Sn      | 60        |         |          |
| Ag      |           |         | 8        |
| Pb      | 22        |         |          |
| Au      |           | 5       |          |

Fig. 1. Image from the optical microscope. (Online version in color.)

Fig. 2. Outline of the LA-ICP-MS system.
beginning at the upper left of the analysis region specified on the sample surface. The sampling interval and points are set to 2.6 s and 37, respectively. Thereafter, line scanning analysis of the second line was performed by irradiating laser light again from a point located 30 μm to the right of the starting point. In this study, line scan analysis was performed ten times in the vertical direction, yielding 370 analysis points. The signal intensity of each element was obtained by conveying the sample microparticles generated by the laser irradiation to the ICP-MS apparatus via carrier gas. The subjects of analysis were 361 of the 370 measurement points having Fe signal intensities of ≥1 × 10⁷ cps. The concentration of the sample was determined by the absolute calibration curve method; when the sample concentration exceeded the range of the standard samples, the value was obtained by extrapolation.

2.2.2 Analysis Method

In this study, a histogram of the measured element concentrations is prepared, as shown in Fig. 4, and the states of element concentration and coexistence were evaluated. The first quartile (Q₁) is defined as 25th percentile of the element concentrations. Also, the third quartile (Q₃) is 75th percentile. The second percentile (Q₂) is the median of them. After arranging the element concentrations, the normalized interquartile range (NIQR) was found. The state of element concentration was evaluated by creating a histogram of 14 classes with increments of 0.5 NIQR, using Q₂−3NIQR as the lower limit and Q₂+3NIQR as the upper limit. For the element concentration Cij (see Fig. 3) at a certain measurement point exceeding Q₂+3NIQR, the point is defined as a “high-concentration point,” and when multiple high-concentration points adjoin to form a region, it is defined as a “high-concentration region.” In addition, a contour diagram, created by classifying eight concentration levels with Q₂ as the lower limit value and Q₂+3NIQR as the upper limit, was used to evaluate the relative degrees of concentration of the elements, enabling evaluation of the coexistence states of multiple elements. Cases for which elements exceeding Q₂+3NIQR existed at

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**Table 3.** LA and ICP-MS apparatus operating conditions.

| ICP-MS conditions                  |       |
|------------------------------------|-------|
| RF power                           | 1.25 kW |
| Plasma gas flow rate               | 16 L/min |
| Intermediate gas flow rate         | 0.8 L/min |
| Carrier gas flow rate              | 1.35 L/min |

| LA conditions                      |       |
|------------------------------------|-------|
| Laser                              | ND: YAG |
| Wavelength                         | 213 nm |
| Pulse duration                     | 5 ns |
| Spot size                          | 20 μm |
| Repetition rate                    | 20 Hz |
| Fluence                            | 10 J/cm² |
| Sampling mode                      | 5 μm/s |
| Carrier gas flow rate              | 0.6 L/min |

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Fig. 3. Laser scanning method on the sample surface.

Fig. 4. Measured data analysis by histogram.
the same measurement point were considered “coexistence in a highly concentrated state.”

3. Result and Discussion

3.1. Element Concentration

Table 4 shows the average, median, maximum, minimum, normalized interquartile range, and average/median values of the Cu, Au, Sn, Ag, and Pb concentrations, respectively. The average concentration of Cu is the highest among the elements, measured at 2 137 mg/kg, approximately half of the bulk. The next-highest concentrations were, in order, Sn, Pb, Ag, and Au. For Au, which had the lowest concentration, the average concentration was 0.13 mg/kg. This indicates that precious metal incorporation with the steel recycled material is negligible. For Cu and Au, the average/median values are 1.0 and 1.1, respectively, whereas for Sn, Pb, and Ag they are 2.0, 3.8, and 1.9, respectively. These three elements are of clearly contrasting concentrations, and the average/median value of Pb is especially remarkable.

Table 4. Average, median, maximum, minimum, normalized interquartile range, and average/median values of Cu, Au, Sn, Ag, and Pb concentrations.

| Element | Cu [mg/kg] | Ag | Sn [mg/kg] | Au | Pb [mg/kg] |
|---------|------------|----|------------|----|------------|
| Average | 2 194      | 0.92 | 437        | 0.14 | 8.1        |
| Median  | 2 137      | 0.49 | 221        | 0.13 | 2.1        |
| Maximum | 3 971      | 33  | 17 670     | 0.40 | 328        |
| Minimum | 1 347      | 0.23 | 117        | 0.058| 0.81       |
| NIQR    | 373        | 0.33 | 191        | 0.044| 2.0        |
| Average/Median | 1.03 | 1.9 | 2.0 | 1.1 | 3.8 |

Figure 5(a) shows histograms of the Cu and Au concentrations, while (b) shows histograms of the Sn, Au, and Pb concentrations. The relative frequency of Cu is highest for the class \( Q_2 - 0.5\text{NIQR} \) to \( Q_2 \), but that of the classes before and after \( (Q_2 - \text{NIQR} \) to \( Q_2 - 0.5\text{NIQR} \) and \( Q_2 to Q_2 + 0.5\text{NIQR} \)) is approximately similar. That of Cu exceeding class \( Q_2 + 3\text{NIQR} \) is at most 1.8%, which is the lowest value among the five elements. Au shows a frequency distribution similar to that of Cu, although with some differences. Meanwhile, the shape of the histograms of Sn, Au, and Pb differ significantly from those of Cu and Au. Class \( Q_2 - 0.5\text{NIQR} \) to \( Q_2 \) has the highest relative frequency with large values of 41–47%. Furthermore, 7.3–13% exceed class \( Q_2 + 3\text{NIQR} \), verifying the contrast in concentrations among elements.

3.2. Concentration Distribution and Status of Coexistence of Elements

Figure 6 shows the concentration distribution of Cu, Au, Ag, Sn, and Pb. Most regions in which the concentrations of Ag, Sn, and Pb exceed the median values are in agreement. This tendency does not change even for high-concentration regions. Among these regions, some coincide with high-concentration regions of Cu and Au. Among the five elements, 49 points show high Pb concentrations, which is the greatest number of high-concentration points for a given element. These points often coincide with high-concentration regions of other elements. Figure 7 shows the relationship between the high-concentration points for each element and Pb high-concentration points. For Cu, 71% of its high-concentration points coincide with Pb high-concentration points, although the ratio of the existence of high-concentration points is low. For Ag and Sn, the rates of coexistence are further increased to 89% and 88%, respectively. Although the tendency for coincidence of high-concentration points and regions between pairs of elements is high, a clear rela-
with precipitate formation is not observed. Figure 8 shows the correlation plots between element concentrations and Table 5 shows the correlation coefficient between element concentrations. Excluding Au–Pb, the correlation coefficients are ≥ 0.5 or more, but the correlation coefficients are ≥ 0.75 for combinations of Pb, Ag, and Sn. Although these metals have more high-concentration points than Cu and Au and clear differences in concentration, the cause of their coexistence is unclear at present. Mixing as alloys or coexistence during melting may cause coexistence, but further study, including thermodynamic analysis, is necessary in the future.

4. Conclusion
In this study, we conducted quantitative analysis by LA-
ICP-MS of Cu, Sn, Pb, Ag, and Au in a 455 μm × 270 μm region of a characteristic surface of electric furnace steel sample, allowing quantitative analysis of the distribution and coexistence states of tramp elements with other elements present in recycled steel materials. For each element, the concentration was classified into eight levels centered on the median value, and the concentrations were compared among the elements. Although Cu showed the highest concentration among the measured elements, it showed the smallest variations in concentration level. For Sn, Pb, and Ag, the variations in concentration level were large, and the high-concentration points tended to coincide for these elements. In addition, for combinations of Sn, Pb, and Ag, the concentration correlation coefficient between the two elements was ≥0.75, indicating a strong coexistence correlation. Meanwhile, no clear relationship was recognized between surface structure formation and concentration changes for the analyzed elements. These results are one means enabling prediction of the routes and origins of elements unintentionally mixed in recycled steel materials.

Acknowledgement

This study was supported by JSPS KAKENHI Grant Number 15H02860.

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