Spatial Distribution of Tramp Element Contents in Recycled Steel

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In this research, we analyzed electric furnace steel using the laser ablation inductively coupled plasma mass spectrometry (LA–ICP–MS) method with the objective of quantitatively evaluating the concentration distributions of tramp elements present in microdomains. Point analysis was carried out for nine microdomain locations (defined as Areas) measuring 500 µm (length) × 600 µm (width) for the elements Cu, Sn, Ni, Mn, W, Cr, Mo, Ag, Pb, and B.

The highest concentration of Cu found in Area 4 was 4 936 ppm, while the lowest was 674 ppm in Area 5. The correlations between Cu concentration and concentrations of other elements were analyzed for all measured points. Mo, W, Mn, Sn had correlation coefficients of more than 0.65, while Pb, Ag, Ni, B, Cr had correlation coefficients of −0.15 to +0.22. Furthermore, concentration distributions for the four elements with high correlations were analyzed for regions where the Cu concentration was more than 1.5-times the bulk concentration (5 490 ppm).

KEY WORDS: tramp element; copper distribution; steel scrap; LA–ICP–MS.

1. Introduction

Steel is an indispensable material for manufacturing and infrastructure construction; it will likely continue to be a material central to industry in coming years. For this reason, effective utilization of steel scrap is indispensable in order to secure a reliable supply of steel resources. Japan is believed that annual generation of obsolete scrap is from about 20 to about 25 million tons over the last several years, and most of this is believed to be recycled.

Steel scrap contains numerous elemental impurities, among which so-called tramp elements such as Cu and Sn cannot be removed via oxidative refining. Cu and Sn represent major barriers in the promotion of recycling of steel scrap because they cause surface cracking during hot working. If current processes are retained and steel scrap with high Cu concentrations continues to be recycled, there are fears that in the future recycled steel might not meet quality requirements. On this account, either tramp elements will have to be removed through technological means, or the contamination process elucidated in order to promote the recycling of steel scrap.

Technological methods include vaporization of Cu and Sn from molten iron and sulfidation. Addition of Ni is known to suppress crack formation during hot working. Further, mechanical separation prior to melting is another known method but an issue here is insufficient data related to the contamination routes of tramp elements. Quantification of co-existing elements is thought to be an effective means of elucidating the contamination route of tramp elements (Cu in particular) in the iron and steel recycling process. The diameters of precipitated Cu particles that cause surface cracking are of the order of several µm, meaning the required data cannot be obtained by analysis of tramp elements based on bulk melting.

Laser Induced Plasma Spectroscopy (LIPS) and LA–ICP–MS are effective tools for localized elemental analysis of sample surfaces. A highly precise calibration curve for analysis of iron samples using LIPS has been obtained with an iron-copper (0.2–1.0 mass%) alloy. LA–ICP–MS can be employed for both quantitative and qualitative elemental analysis on account of its high sensitivity. Besides iron and steel samples, this analytical method is also used for trace analysis of geological samples and for a wide variety of other areas. Resolution is of the order of several tens of micrometers, which is similar to the diameters of areas of high concentration of tramp elements. Consequently, one can assume the possibility of being able to identify co-existing elements on a localized basis. Further, eventually this leads to identification of the tramp element contamination process and in the future, potentially the ability to propose new recycling systems.

In this research, LA–ICP–MS analysis of electric furnace steel was carried out in order to quantitatively evaluate the concentration distributions of tramp elements existing in microdomains (500 × 600 µm) of recycled steel. Two types of standard steel samples were used for quantitative analy-
sis. Besides Cu and Sn; Ni, Mn, W, Cr, Mo, Ag, Pb, and B were also targeted. Based on the findings, we discuss tramp element enrichment levels and concentration gradients, as well as the behaviors of Cu and co-existing elements.

2. Experiment

2.1. Analytical Apparatus and Conditions

The ICP–MS apparatus was an Optimass 9500 (GBC Scientific). The ICP–MS apparatus was connected to the Laser Ablation (LA) apparatus (NWR–Femto from ESI) with a plastic tube measuring 2 mm in internal diameter and approximately 1 m in length. Figure 1 shows an overview of the LA–ICP–MS. Table 1 shows the operational conditions of each apparatus.

Table 1. LA–ICP–MS operational conditions.

| ICP–MS conditions |          |
|-------------------|----------|
| RF power          | 1.2 kW   |
| Plasma gas flow rate | 10 L/min |
| Intermediate gas flow rate | 0.5 L/min |
| Carrier gas flow rate | 0.85 L/min |

| LA conditions   |          |
|-----------------|----------|
| Laser           | Ti: Sapphire |
| Wavelength      | 263 nm   |
| Pulse duration  | ca. 180 fs |
| Spot size       | 45 μm    |
| Repetition rate | 250 Hz   |
| Fluence         | 0.4 J/cm² |
| Sampling mode   | Spotted raster (2 s/spot) |
| Carrier gas flow rate (He) | 0.8 L/min |

Table 2. Impurity element concentrations in sample.

| Element | Concentration [wt%] |
|---------|---------------------|
| Cu      | 0.366               |
| Mn      | 0.328               |
| C       | 0.138               |
| Si      | 0.128               |
| Ni      | 0.10                |
| Cr      | 0.070               |
| Sn      | 0.022               |

2.2. Samples

Electric furnace steel was cut into pieces (10 mm × 10 mm × 5 mm). An arbitrarily chosen piece was used as the experimental sample. Table 2 shows the bulk concentrations of the elemental impurities contained in the sample. Sample surfaces were polished with progressively finer sandpaper (#120, #220, #320, #500) and then ultrasonically washed in ethanol prior to LA–ICP–MS analysis. Two types of standard steel samples (Japan Steel Federation JSS152-10 and NIST SRM 176) were employed.

2.3. Measurement Procedure

Samples were placed in the sample cell of the LA apparatus and irradiated with laser beam with a spot diameter of 45 μm. Sample particles ablated by the laser irradiation were conveyed by the carrier gas to the ICP–MS apparatus and signal strengths for each element were obtained to quantitatively analyze Cu, Sn, Ni, Mn, W, Cr, Mo, Ag, Pb, and B. Laser beam reaches depth of 5–10 μm on the surface of sample in these experimental conditions.

2.4. Definitions of Measured Surface and Measured Area

Figure 2(a) shows the measured sample surfaces and Fig. 2(b) shows the measured sample areas. LA–ICP–MS analysis of a sample surface polished to a depth of around 1 mm was initially carried out (Fig. 2(a)). Analysis of a new surface exposed by polishing the sample surface once again to a depth of 1 mm was then conducted. In this research, Surface A is defined as the initial surface and Surface B is...
that obtained by further polishing. A series of 130 points were irradiated using a laser with spot diameter 45 μm at 50 μm intervals in the LA–ICP–MS analysis covering a grid measuring 10 vertical points by 13 horizontal points (see Fig. 2(b)). Each set of measurement points were enclosed within an area of 500 × 650 μm; hereinafter these are referred to as Areas. Four areas were analyzed for Surface A (Areas 1–4) and five areas for Surface B (Areas 5–9).

3. Results and Discussion

3.1. Comparison of Surface and Area Cu Concentrations

Table 3 shows the average Cu concentrations of Areas 1–9 and Surfaces A–B. The highest concentration, 4 936 ppm, was in Area 4; the lowest, 674 ppm, in Area 5. The average concentration of the entire measured surface was 2 077 ppm, which is lower than the bulk concentration of 3 660 ppm. Further, the average concentration of Surface A was 3 228 ppm, whereas that of Surface B was 1 156 ppm.

3.2. Correlation Coefficients of Elements Coexisting with Cu

Figure 3 plots Cu concentrations against those of the other measured elements and Table 4 shows the correlation coefficients between the concentrations of Cu and other measured elements. Mo, W, Mn, and Sn were strongly correlated with Cu, whereas there were almost no correlations for Pb, Ag, Ni, B, and Cr. Mo, W, and Sn increased exponentially with Cu, whereas only Mn increased linearly. Cr alone was negatively correlated with Cu; Cr concentrations peaked between Cu concentrations of 0–1 000 ppm, and remained almost constant for Cu concentrations over 2 000 ppm. Exponential increases imply that multiple contamination routes exist and that chemical reactions of co-existing metals occurring when the iron is in a molten state contribute greatly. Thermodynamic consideration is needed to determine the appropriateness for the elements that strongly correlated with Cu. From its result, the influence of raw material or process on co-existing behaviors should be discussed.

3.3. Cu Concentration Frequency Distribution over All Analysis Points

Figure 4 shows the Cu concentration frequency distribution. The most frequent Cu concentrations were between 1 000 and 2 000 ppm, accounting for 35.6% of total measured concentrations. The frequency of Cu concentrations of less than 2 000 ppm was 62.9% overall. The frequency of concentrations exceeding 4 000 ppm, which is higher than the bulk concentration of 3 660 ppm, was 13.9%.

Looking at individual Areas, the frequency of Cu concentrations of 4 000–5 000 ppm was highest for Area 4, which exhibited the highest average concentration. The frequency of Cu concentrations of 3 000–4 000 ppm was highest for Area 1, for which the average concentration was close to that of the bulk concentration. The frequency of Cu concentrations of 0–1 000 ppm was highest for Area 5, in which the average concentration was lowest. These rankings match the average Cu concentrations for the respective Areas. One can surmise that the variation in Cu concentration within a specific area is relatively small.

3.4. Cu Concentration Distribution in Three Areas

Figure 5 shows the Cu concentration distribution in Area
Table 4. Correlation coefficients between Cu concentration and measured elemental concentrations.

| Element | Correlation coefficient |
|---------|------------------------|
| Mo      | 0.85                   |
| W       | 0.80                   |
| Mn      | 0.79                   |
| Sn      | 0.65                   |
| Pb      | 0.22                   |
| Ag      | 0.18                   |
| Ni      | 0.10                   |
| B       | 0.10                   |
| Cr      | −0.15                  |

5. Regions with Cu concentrations of less than 458 ppm (one-eighth of the bulk concentration) account for 62% of the total area (enclosed by the dashed lines in the diagram). Regions with concentrations of 458–916 ppm (one-eighth to one-quarter of the bulk concentration) account for around 36% of the overall area.

Figure 6 shows the Cu concentration distribution in Area 1. Regions with Cu concentrations of 1 830–5 490 ppm account for 92% of the overall area. In contrast, regions with Cu concentrations of less than 1 830 ppm account for just 8% of overall area. Regions with concentrations less than 50% of the bulk concentration are defined as “low concentration regions,” those with concentrations of 50 to less than 150% of bulk concentration are defined as “bulk concentration regions” (except for enclosed by the black dashed line in the diagram), and those with concentrations of 150% or more are defined as “high concentration regions.” The low
3.5. Concentration Distributions of other Elements in Regions of High Cu Concentration

Figure 8 shows (a) Cu, (b) Mo, (c) W, (d) Mn, and (e) Sn concentration distributions in Area 4. Among regions of high Cu concentration, enriched domains with ascending Cu concentration gradients are labeled in Fig. 8 with a–i. In the case of Mo, these enriched domains coincide with all of the high Cu concentration regions. Similarly, the matching enrichment behaviors in b, c, d, f, and h are conspicuous in that they almost all coincide with enriched Cu domains. In the case of Mn, the enriched domains b, d, and h coincide with parts of A, and B and C, which are regions of high Cu concentration. Further, in the case of Sn, enrichment behavior in regions of high Cu concentration is quite similar to

Cu concentration region/bulk concentration region ratio is 8:92. Furthermore, high concentration regions do not exist within this area, indicating that low Cu concentration regions are very similar in state to the bulk concentration.

Figure 7 shows the Cu concentration distribution in Area 4. Of the overall area, low concentration regions accounted for 7%, bulk concentration regions for 79%, and high concentration regions for 14%. There were three high concentration regions (A–C in the diagram) with areas of 49 274, 35 895, and 14 987 μm², respectively. The straight line distances indicated by αα', ββ', and γγ' in the diagram are 258, 248, and 209 μm, respectively. Over such distances, the Cu concentration gradients were greater than 6 400 ppm.
that of Mn, but all enriched domains coincide with regions of high Cu concentration. In this manner, Mo, Mn, and Sn, which are correlated with Cu concentration, exhibit close relationships with the enrichment behavior of Cu, albeit to differing degrees. However, h is the only match in the case of W, with no correlations apparent for other enrichment regions and enrichment domains.

4. Conclusions

In this research, the concentration distributions in microdomains of tramp elements present in recycled iron and steel were quantitatively assessed through LA–ICP–MS analysis of electric furnace steel. Sample surfaces were consecutively irradiated with 45 μm diameter laser beam at intervals of 50 μm covering a 130-point grid measuring 10 vertical points by 13 horizontal points. These 130-point microdomains measuring 500 μm (length) and 650 μm (width) were defined as Areas; Cu, Sn, Ni, Mn, W, Cr, Mo, Ag, Pb, and B were quantitatively analyzed for nine such Areas.

The results indicate that the highest average concentration of Cu found in any of the Areas was 4,936 ppm, whereas the lowest was 674 ppm. In one instance, the concentration gradient was more than 6,400 ppm over a distance of just 250 μm. Correlations between Cu concentrations and concentrations of the other elements were analyzed for all measurement points. The correlation coefficients for Mo, W, Mn, and Sn were greater than 0.65, whereas those for Pb, Ag, Ni, B, and Cr ranged from −0.15 to +0.22. Furthermore, concentration distributions were analyzed for the four elements with the highest correlations in regions where the Cu concentration was more than 1.5-times the bulk concentration (or higher than 5,490 ppm). The concentration gradients of Mo matched those of Cu, even outside of high Cu concentration regions. Although not to the same extent as Mo, Sn and Mn followed similar tendencies. However, in the case of W, only one location coincided with a region with high Cu concentration.

It is thought multiple phases seem to exit in this experimental sample, in this case, expected the enrichment behaviors of elements differ from phases. Focusing this point, enrichment behavior from other standpoint through LA–ICP–MS analysis can be resolved.

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