

any example in which these methods are applied to the analyses of trace components in steel at or below $\mu\text{g/g}$ level.

At JFE Steel, the development of a laser ICP atomic emission spectrometry was carried out in 1987 and this analysis method was applied to uses such as component analysis and defect analysis¹¹⁾. The basic principle of this method is a JFE-specific engineering element called "repeated laser irradiation to the same area," which is characterized by a beam scanning method. That is, an LA system that generates fine particles whose composition is the same as that of the base material sample was developed by combining a pulse laser having a high repetitive frequency and a galvanometer scanner. Also for LA-ICP-MS, in which this LA is applied to ICP-MS,

if thermal irradiation is repeated on the same area of a sample, this non-uniformity will be gradually eliminated.

For the sake of simplicity, the following assumptions are made. (1) The heated area is large enough to be able to neglect the effect of a side area (an area which is formed around a crater due to the pressure of the vapor generated during laser irradiation and in which a melted part deposits); and (2) during laser irradiation, the irradiation with thermal energy is uniformly performed in terms of time and place.

A sample initially consists of an element, S and a matrix element, m.

$C_S(0)$ is the initial concentration of S in a solid.

$$C_S(0) = \frac{m_0}{m_0 + m_0} \dots \dots \dots (1)$$

where m_0 is the quantity of the thermally-affected zone in the solid (= a vaporized part m_v + a melted part m_m), and m_0 is the quantity of the component to be analyzed S

in m_0 .

The vaporized part and the melted part are generated by the first irradiation. That is, m_0 is divided into m_v and m_m . m_0 is the quantity of the component to be analyzed S in the vaporized part m_v and m_m is the quantity of the component to be analyzed S in the melted part m_m . The value of

2.2. Analytical Precision and Sensitivity

To verify the analytical precision and sensitivity of LA-ICP-MS for steel samples, the correlation between the contents and ion intensities or intensity ratios of each element to ^{57}Fe was investigated using the steel standard reference materials NIST 1765, 1766 and 1767 (Table 2(a)). The results of the investigation are shown in Fig. 3. In the LA method, the ion intensity of Ar gas was used as a blank value, and the intensity ratio was found after the subtraction of the ion intensity of the Ar gas for each sample from the ion intensities of the elements to be analyzed and of ^{57}Fe . Although the repetitive analytical precision is indicated by an error bar (1, $n = 5$) in Fig. 3, the ion intensity ratio to Fe showed a smaller dispersion and the Fe internal standard method was effective.

For B, the coefficient of correlation between the concentration and ion intensity ratio in the trace concentration region of 4 to 10 $\mu\text{g/g}$ was 0.999 3 and a good linear relationship was thus obtained. RSD of 4% or less were obtained in the ion intensity ratio to ^{57}Fe , although some samples showed variations of 6% in RSD for ion intensity.

For As, the coefficient of correlation was 0.999 1 in the region of 5 to 40 $\mu\text{g/g}$ and the RSD of the ion intensity ratio was 2% or less.

For Sb, the coefficient of correlation between the certified value in the region of 5 to 20 $\mu\text{g/g}$ and ion intensity ratio was 0.989 and the linear relationship was somewhat poor compared to the other elements, although the repetitive measurement precision of the ion

intensity ratio was 2%, which is good in terms of poor compared

the accuracy of the LA method with respect to the determination and analysis on the order of $\mu\text{g/g}$. For this reason, the samples used in the LA method were chemically analyzed by the method described in paragraph 2.2.2 above, the analytical values were plotted as abscissa, and the correlation to these values was found.

In all of the elements, a good correlation of 0.995 or more in terms of the coefficient of correlation was observed between the two kinds of analytical values. This shows that the direct determination by this method is possible for elements that have hitherto been deter-

tion of 0.995 or more was obtained.

A technique for rapidly determining levels of trace elements in steel with high sensitivity was developed by introducing fine particles generated by the "repeated laser irradiation to the same area" that reduces the effect of fractionation into ICP-MS, which is a high-sensitivity technique. Particularly for B, As, Sb and Pb that have great analytic needs, the precision, sensitivity and accuracy of the LA method was evaluated and the following knowledge was obtained:

- (1) Analytical Precision: When the internal standard method that uses the ion intensity ratio to ^{57}Fe is adopted, in the trace concentration region of the level of $\mu\text{g/g}$ in steel, it is possible to analyze B with an RSD of 3% or so and the other elements with an RSD of 2% or so. For B, some samples showed large dispersions in the infinitesimal concentration region of $2\ \mu\text{g/g}$ or lower. However, because almost the same precision as in the JIS method was obtained by increasing the area radiated by the laser, it was judged that this is the effect of segregation.
- (2) Sensitivity: The lower limit of determination is on the order of several tens of nanograms/g for B and As and on the order of several nanograms/g for Sb and Pb, and high-sensitivity analysis is possible.
- (3) Accuracy of Analytical Values: A comparison was made between the measured values of the chemical analysis method and those of LA-ICP-MS and a high correlation with values of the coefficient of correlation

As described above, an investigation was made into the application of LA-ICP-MS to the determination of trace amounts of B, As, Sb, and Pb in steel samples and satisfactory results were obtained. JFE Steel consider that this method can contribute to the rapid evaluation of products and an improvement in productivity by shortening the analysis time thanks to the high sensitivity and rapidity of the method.

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