Application of the Ion Microprobe Mass Analyzer to Problems in Steels

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Application of the Ion Microprobe Mass Analyzer to Problems in Steels

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Application of secondary ion analysis to iron and steel was investigated by using the ion microprobe mass analyzer. The spatial distribution of light elements was examined. The methods of various sample preparation were compared, and the surface polished with Al₂O₃ powder was found to be most suitable for in-depth analysis. This technique was applied to analysis of surface segregation of Al in Fe-0.1%Al alloys. In low alloy steels, it was found that the chemical composition of the sample could be determined with good accuracy by measuring the relative ion intensity ratios.

§1. Introduction

The development of the ion microprobe mass analyzer (IMMA) opened the way for micro-analysis of various solid materials. However, most of the application of IMMA to problems in steel were mainly concerned with analysis of alloy elements in steels. Nishimura and Okano reported the relative sensitivities of several elements in the NBS steels. Andersen and Hintorne developed an analytical method for quantitative analysis of sputtered ions and applied it to analysis of steels. Leroy et al. reported the method of quantitative analysis of ternary alloys using the calibration curves. They also studied the constituent elements in oxide films on steel surface. In the present study, spatial distribution, in-depth analysis and quantitative analysis have been investigated on several steels using IMMA.

§2. Spatial Distribution

In IMMA, it is possible to detect light elements with high sensitivity, because the secondary ions of the elements are analyzed by mass separation. Figure 1(a) shows the secondary ion image of H in an inclusion in the stainless steel. The inclusion was mainly composed of TiO₂, SiO₂ and Al₂O₃. In this complex inclusion, H was detected in aluminum silicate and not observed in TiO₂. This means that H is trapped in the silicate. The distribution of B was investigated in Fe-B alloys and boronized steels. Most of B precipitated as Fe₃B in hot-rolled Fe-B alloys. The secondary ion image of B in these steels showed that Fe₂B were formed along the austenitic grain boundaries. It was confirmed by X-ray diffraction that the surface of iron bornized in Na₂B₄O₇ consisted of two layers, and that the upper was FeB and the lower
Fe₂B. The existence of these layers were indicated clearly by ion imag of B, as shown in Fig. 1(b).

§3. In-depth Analysis

Since sputtering from the solid is a surface sensitive phenomenon, it is primarily important to establish the method of surface treatment adequate to in-depth analysis by IMMA.

First of all, the degree of surface contamination of pure irons was compared with the samples after polishing with Al₂O₃, CrO₃ and diamond paste. The surface of the sample was sputtered by restering the primary ion beam and the intensity of secondary ions from reduced rastering area was measured. The mass spectra of secondary ions showed that the main impurity elements on the surface were Na, Mg, Al, Si, K, Ca and Cr. The in-depth profile of Na, Mg, K and Ca which may be derived from water during polishing did not change with the method of polishing. The intensity of these elements became to be maximum at the surface, then rapidly decreased to an extremely low value. Figure 2 shows the in-depth profiles of Al, Si and Cr. The profiles of these elements changed with the method of polishing, i.e., large amount of Cr remained on the samples polished with CrO₃ powder, and Al and Si also remained on the surface polished with diamond paste. From these results, it was recognized that the surface of the sample polished with Al₂O₃ powder was suitable to obtain an exact in-depth profile. This superiority of Al₂O₃ powder may be caused by the fact that its size is relatively small (~0.05 μφ) and the powder is easily fallen off during ultrasonic cleaning.

Secondly, the contamination of surface after chemical polishing in the mixture of HF (3%) + H₂O₂ was examined in Fe-0.1% Al alloys. In this case, the specimen polished with Al₂O₃ was used as reference. The ion image of Al of the sample surface is shown in Fig. 3. The intensity of Al ions was enhanced at the grain boundaries on the surface. While, the intensity of Al ions of the surface polished with Al₂O₃ powder was considerably uniform. From the measurement of roughness of the sample surface polished chemically, it revealed that the grain boundaries were etched selectively. Thus, it is concluded that the apparent enhancement of Al ion inten-

![Image](attachment:image_url)

Fig. 2. In-depth profile of the sample polished with Al₂O₃, CrO₃ or diamond paste.

![Image](attachment:image_url)

(a) chemically polished

![Image](attachment:image_url)

(b) mechanically polished

Primary Beam  O⁺
Accel. Volt.    20kV
Beam Dia.      2μφ

Fig. 3. Ion image of Al on the surface of the sample polished chemically or mechanically.

Intensity may come from the increase of the sputtering yield due to the preferential oxidation and/or the edge effect at these sites.
the isotopic abundance $a_i$. If the transmission factor is constant for each ion, it is possible to deduce the following relation:

$$\frac{I_1}{I_2} = Y_1n_1a_1/Y_2n_2a_2$$

Figure 5 shows that the linear relationship exists between the intensity ratio of the ions of alloy element to Fe ions ($I_i/I_{Fe}/a_{Fe}$) and the atomic fraction of the element $n_i/n_{Fe}$. When the concentration of an alloy element exceeds solubility limit, phase change or precipitation

$\text{Fig. 4. In-depth profile of Al in Fe-0.1\%Al alloys.}$

From these preliminary examination, it is established that the sample polished with $\text{Al}_2\text{O}_3$ powder is most preferable in in-depth analysis. This technique was applied to the study of the surface segregation of alloy elements in steels. Figure 4 shows the in-depth profile of Al in Fe-0.1\%Al alloys. The distribution of Al was rather uniform before annealing. After annealing for 10 hr at 700°C in purified hydrogen atmosphere, Al segregated to the surface. The decrease of Al in the depth of 100～1200 Å may be explained as the formation of a denuded zone.

### §4. Quantitative Analysis

The secondary ion current at the collector $I_1$ is proportional to the secondary ion yield $Y_1$ of the element $i$, the atomic concentration $n_i$, and the isotopic abundance $a_i$. If the transmission factor is constant for each ion, it is possible to deduce the following relation:

$$\frac{I_1}{I_2} = Y_1n_1a_1/Y_2n_2a_2$$

Figure 5 shows that the linear relationship exists between the intensity ratio of the ions of alloy element to Fe ions ($I_i/I_{Fe}/a_{Fe}$) and the atomic fraction of the element $n_i/n_{Fe}$. When the concentration of an alloy element exceeds solubility limit, phase change or precipitation

$\text{Fig. 5. Calibration curves for alloying elements in the NBS steels.}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si</th>
<th>Mn</th>
<th>Al</th>
<th>Ni</th>
<th>Cr</th>
<th>V</th>
<th>Ti</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>620</td>
<td>0.18</td>
<td>0.41</td>
<td>0.053</td>
<td>0.097</td>
<td>0.010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>614</td>
<td>0.22</td>
<td>0.41</td>
<td>0.052</td>
<td>0.034</td>
<td>0.093</td>
<td>0.012</td>
<td></td>
<td></td>
</tr>
<tr>
<td>162-1</td>
<td>0.49</td>
<td>0.10</td>
<td>0.042</td>
<td>0.46</td>
<td>0.36</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The concentration of each element $C_i$ is deduced by the relation $C_i = c_i/(\sum c_i + 1)$, where $c_i$ is given by $c_i = (n_i/n_{Fe})(M_i/M_{Fe})$.**

**$M_i$ is the atomic weight of element $i$.**
occurs and the linear relationship fails to exist. Therefore, the calibration curves were obtained in dilute concentration range. The author applied the calibration curves to analysis of low alloy steels. The results of IMMA analysis of various steels were compared with those of chemical analysis (Table I). It was recognized that the concentration of alloying elements was determined with good accuracy by IMMA.

§5. Conclusion

The ion microprobe mass analyzer was applied to various problems in steels. The instrument was sensitive for analysis of light elements. For in-depth analysis, the method of polishing was established and applied successfully to analysis of surface segregation. It was also found possible to perform quantitative analysis by means of calibration curves.

References