

### User Benefits

- ◆ Phase analysis by quantitative mapping of iron oxide scale and identification of the types of iron oxide by Fe-L line state analysis are possible.
- ◆ Useful in research to improve the appearance quality of hot-rolled steel sheets.
- ◆ Useful in research on phase transformation behavior and control of the adhesion of iron oxide scale.

### ■ Introduction

In the hot-rolling process used in the manufacture of steel plates, wire rod material, and other steel products, an oxidized film (scale) with a thickness of approximately several mm forms on the steel surface because the material is heated to a high temperature of 800 to 1200 °C. This oxidized scale is removed by high pressure water or other methods before rolling, but if rolling is conducted without complete descaling, surface flaws will occur, causing a remarkable deterioration in the surface quality of the finished product. Moreover, because new oxidized scale with a thickness of several  $\mu\text{m}$  to several 10  $\mu\text{m}$  is formed by reoxidation immediately before rolling, the product is either shipped as mill scale steel or is descaled by acid treatment (pickling).

Because removal of the oxidized scale that forms on the surface of steel products has a large influence on the surface properties of the products, research and development have been conducted to clarify the relationship between the growth rate of oxidized scale and the surface properties, high temperature adhesion, and the peelability of the scale.

This article introduces an example of an analysis of oxidized scale using an EPMA-1720HT EPMA™ electron probe microanalyzer.

### ■ Iron Oxide Scale

In the hot-rolling process of steel products, three layers of lamellar iron oxide scale are formed on the steel surface. In order from the outermost surface typically, these are an outer layer of hematite ( $\text{Fe}_2\text{O}_3$ ), a middle layer of magnetite ( $\text{Fe}_3\text{O}_4$ ), and an inner layer of wustite ( $\text{FeO}$ ). Although the thickness ratio of the  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{FeO}$  layers varies depending on the oxidation temperature and time, the ratio at around 1000 °C is roughly 1 : 4 : 95, and the largest part of the iron oxide layer is  $\text{FeO}$ .

Fig. 1 shows the results of a mapping analysis of a cross-section where the three layers of lamellar iron oxide scale on the right side of the figure have formed of the steel material on the left side. From the quantitative elemental mapping of O and Fe, it can be understood that a  $\text{Fe}_2\text{O}_3$  layer (Fe, O : 70, 30 wt%), a  $\text{Fe}_3\text{O}_4$  layer (Fe, O : 72, 28 wt%), and a  $\text{FeO}$  layer (Fe, O : 78, 22 wt%) have formed from the outermost surface on the right side, and granular  $\text{Fe}_3\text{O}_4$  has precipitated in the  $\text{FeO}$  layer. The overlay display in Fig. 2 is an RGB overlay in which the mapping images of O and Fe in Fig. 1 are shown by red and green, respectively, and the existence of three layers from the surface is shown by the differences in the concentrations.

The scatter plot of O-Fe in Fig. 3 shows a representation of the three types of compounds ( $\text{FeO}$  [□],  $\text{Fe}_3\text{O}_4$  [▽],  $\text{Fe}_2\text{O}_3$  [○]) by their theoretical values. Since the theoretical values and point-sets (clusters) are in good agreement, the clusters were extracted as the three types of iron oxides. The phase diagram of the iron oxide scale in Fig. 4 shows that  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{FeO}$  layers have formed in order from the surface, and  $\text{Fe}_3\text{O}_4$  is mixed in the  $\text{FeO}$  layer, which is the inner layer. The distribution of compound states can be represented accurately if this type of phase analysis is used.

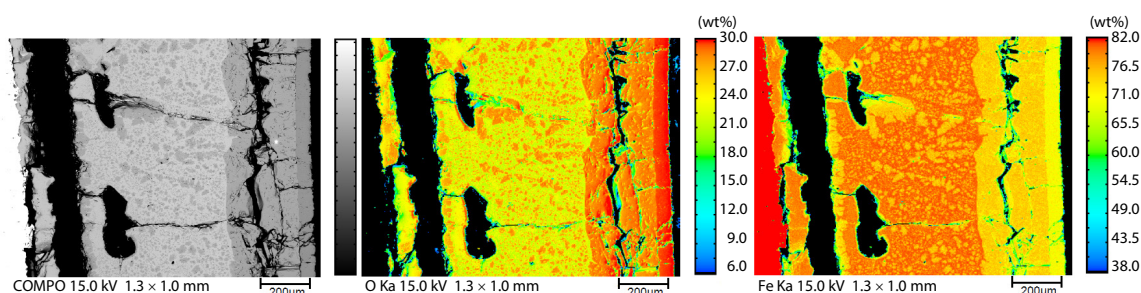


Fig. 1 Quantitative Mapping Analysis of Iron Oxide Scale

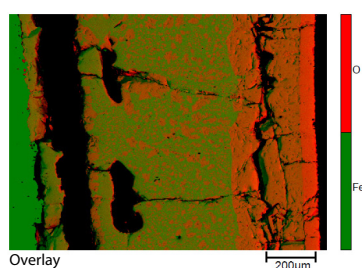


Fig. 2 Overlay

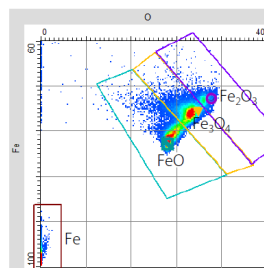


Fig. 3 Scatter Plot

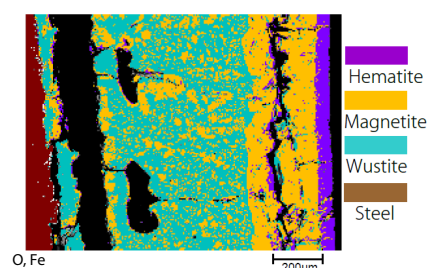


Fig. 4 Phase Map

## ■ State Analysis of Iron Oxide Scale

The wavelengths of the characteristic X-rays generated by the transition of orbital electrons are determined by differences in the energy levels of the orbits. Outer shell (valence shell) orbital electrons are easily affected by chemical bonds, and the wavelengths of the long-wavelength characteristic X-rays related to transition from the valence shell orbits easily change.

It is known that state analysis of iron (Fe) based on the peak wavelength shift, waveform, and other features is possible by using the Fe-L line spectrum. Fig.5 and Fig.6 show enlargements of the peak apex regions when the Fe-L line spectra of the standard samples and the three oxidized scale layers were normalized by the spectral intensities of Fe-La (Fig.5) and Fe-Lβ (Fig.6). The waveforms differ depending on the type of iron oxide, and the wavelength shifts to the short wavelength side as the proportion of oxygen (O) increases.

Table 1 shows the Fe-La wavelength shifts ( $\Delta\text{Fe-La}$ ) of the standard samples and each iron oxide scale layer against the wavelength shift ( $\Delta 0$ ) of the standard sample of Fe. Owing to the high wavelength resolution of EPMA, it is possible to capture the differences in the Fe-La wavelength of the iron oxides and show the oxidation states of the respective iron oxide scale layers.

Similarly, Table 2 shows the Fe-Lβ wavelength shifts of the standard samples and iron oxide scale layers against the Fe standard sample. It can be understood that differences in the Fe-Lβ wavelengths of the iron oxides are different from those of Fe-La.

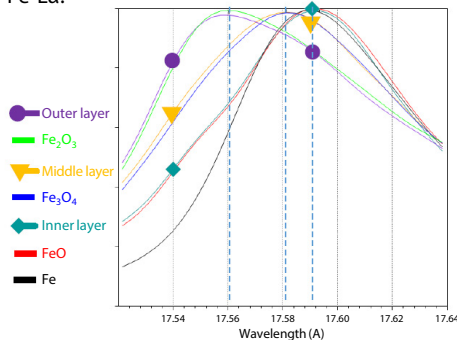


Fig. 5 Fe-La Line Spectrum of Iron Oxide Scale

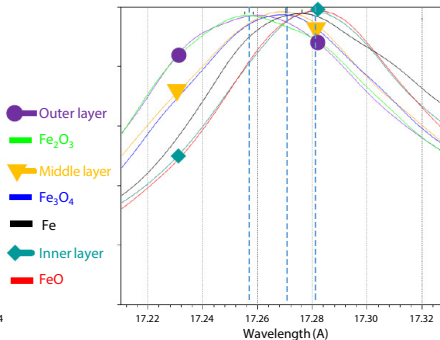


Fig. 6 Fe-Lβ Line Spectrum of Iron Oxide Scale

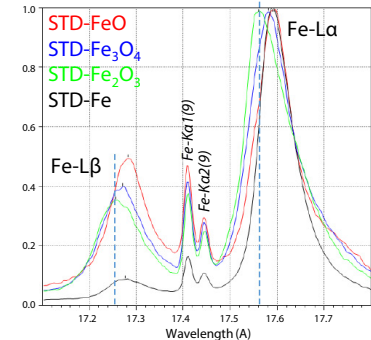


Fig. 7 Fe-L Line Spectra

Table 1 Wavelength Shift of Fe-La

Standard sample	$\Delta\text{Fe-La}$	Scale	$\Delta\text{Fe-La}$
FeO	0.003Å	Inner layer	0.003Å
Fe <sub>3</sub> O <sub>4</sub>	-0.008Å	Middle layer	-0.009Å
Fe <sub>2</sub> O <sub>3</sub>	-0.030Å	Outer layer	-0.030Å
Fe	$\Delta 0$		

Table 2 Wavelength Shift of Fe-Lβ

Standard sample	$\Delta\text{Fe-L}\beta$	Scale	$\Delta\text{Fe-L}\beta$
FeO	0.006Å	Inner layer	0.005Å
Fe <sub>3</sub> O <sub>4</sub>	-0.006Å	Middle layer	-0.006Å
Fe <sub>2</sub> O <sub>3</sub>	-0.021Å	Outer layer	-0.018Å
Fe	$\Delta 0$		

Table 3 Fe-Lβ/Fe-La Ratios at Wavelength of Fe<sub>2</sub>O<sub>3</sub>

Standard sample	Fe-Lβ/Fe-La	Scale	Fe-Lβ/Fe-La
FeO	58%	Inner layer	59%
Fe <sub>3</sub> O <sub>4</sub>	44%	Middle layer	44%
Fe <sub>2</sub> O <sub>3</sub>	36%	Outer layer	37%
Fe	12%		

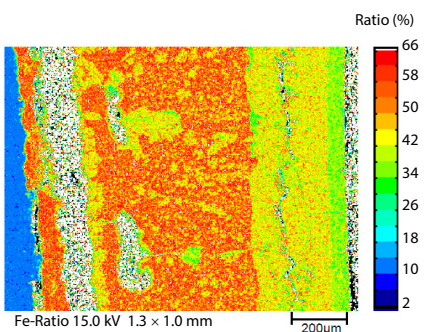
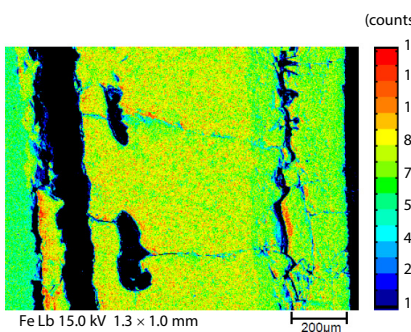
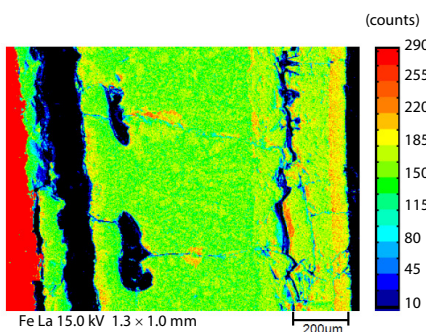


Fig. 8 Fe-L Line Mapping Analysis of Iron Oxide Scale

Fig. 9 Fe-L Line Ratio Display

### <References>

Hiroyoshi Soezima, Electron Probe Microanalysis, Nikkan Kogyo Shimbun, Ltd. (1987)  
J. Japan Inst. Met. Mater., Vol. 83, No. 11 (2019)

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## ■ Iron Oxide Scale Ratio Display

In the case of oxidation states of Fe, the distributions of Fe-La and Fe-Lβ mapped at a designated wavelength do not coincide because the wavelength shifts and waveforms of Fe-La and Fe-Lβ are different, as shown in Fig.7 and Tables 1 and 2. Fig.8 shows the result of a mapping analysis of Fe-La and Fe-Lβ by the wavelength of Fe<sub>2</sub>O<sub>3</sub>. Here, the color gradation is different in comparison with the Fe-Kα image in Fig.1, in which a wavelength shift was not recognized. Table 3 shows the ratio Fe-Lβ/Fe-La of the standard samples at the wavelength of Fe<sub>2</sub>O<sub>3</sub>. The Fe-ratio image in Fig.9 represents 100 \* (Fe-Lβ image/Fe-La image). Compared with the ratio values in Table 3, the ratio values are substantially in agreement, and the image is divided into four layers, which correspond to the distributions of Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, and FeO from the outermost layer of the iron oxide scale, and the Fe in the base metal.

## ■ Conclusion

By using phase analysis by quantitative mapping, state analysis based on the changes in the wavelength and waveform of the Fe-L line spectrum, and ratio display by Fe-L line mapping, it was possible to identify the distributions of iron oxides of different types. In addition to iron oxide scale, these techniques can also be applied to analysis of corrosion of steel.

# Related Products

Some products may be updated to newer models.



> EPMA-1720  
Electron Probe Microanalyzer

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