CHEMISTRY LETTERS, pp. 1263-1266, 1983.

STATE ANALYSIS OF STEEL SURFACES UTILIZING THE 9TH-ORDER $FeK\alpha_1$ LINE BY AN ELECTRON PROBE MICROANALYZER

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Chemical states of steel surfaces covered with iron oxides and fluorides were analyzed by a state analysis method utilizing the 9th-order $FeK\alpha_1$ line. The method was effective for the state analysis of iron compounds especially when the compounds were thicker than the detection depth of the $FeK\alpha_1$ line.

In a previous study,[1)] a state analysis method utilizing the 9th-order $FeK\alpha_1$ ($FeK\alpha_1^9$) line was proposed as a better way to identify iron compounds (Fe_2O_3, Fe_3O_4, FeO, FeF_3, or FeF_2) by an electron probe microanalyzer (EPMA). The usefulness of the $FeK\alpha_1^9$ line is that (1) its peak wavelength serves as a marker to measure the peak wavelength shift of the $FeL\alpha$ (or $FeL\beta$) line and that (2) the peak intensity ratio of the $FeK\alpha_1^9$ line to $FeL\alpha$ (or $FeL\beta$) line is available as a new state analysis parameter in addition to the conventional one, the peak intensity ratio of the $FeL\beta$ line to $FeL\alpha$ line. This letter reports results of the state analysis of steel surfaces covered with iron oxides and fluorides utilizing the $FeK\alpha_1^9$ line.

Two kinds of samples were prepared by using blades of Ni-Co alloy steel (50 mm x 10 mm x 0.4 mm). The main components of the steel were iron (64.3%), nickel (17.3%) and cobalt (12.8%). One kind of sample (SE) was a steel blade exposed to saturated steam at 500 °C for 5 h to produce an oxide film. The other kind of sample (HFE) was an SE specimen which had been further exposed to hydrogen fluoride gas at 90 °C and 26.6 kPa for 21 d to produce iron fluorides.

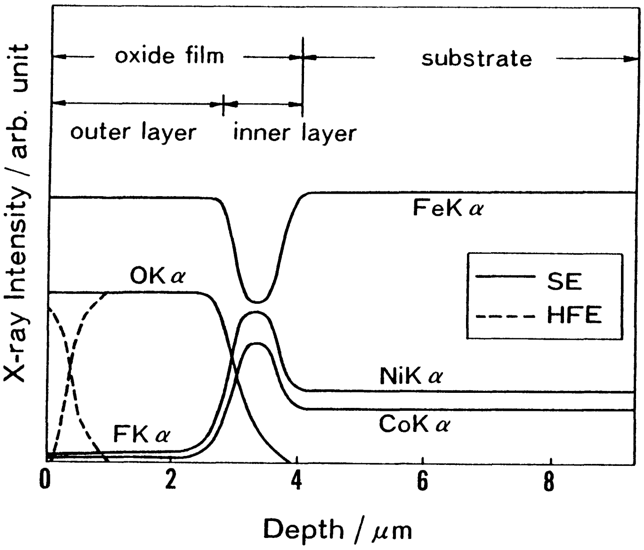

Fig. 1. Elemental distributions of steel cross sections.

Elemental distributions of

the sample cross sections were analyzed by a Hitachi X-560 EPMA (Fig. 1). The excitation voltage was 10 kV for the OKα and FKα lines and 20 kV for the FeKα, CoKα, and NiKα lines. In the SE specimen, the oxide film consisted of two layers. The outer layer (about 3 μm thick) was mostly iron oxide, while the inner layer (about 1 μm thick) was rich in nickel and cobalt. The same type of film structure of oxide has been reported for the stainless steel produced in saturated steam at 540-650 °C.[2)] In the HFE specimen, an iron fluoride layer of under 1 μm thickness was produced at the oxide film surface.

The X-ray spectra for the state analysis of the sample surfaces (Fig. 2) were measured by means of a Hitachi X-560 EPMA. The specimen current was 0.05 μA and the excitation voltage was set at 20 kV. The X-rays emitted from the sample were analyzed by scanning the analyzing crystal (rubidium hydrogenphthalate, 2d = 26.12 Å, Johansson type) at a speed of 0.5 mm/min. The X-rays analyzed were detected by a tandem type proportional counter which consisted of gas filled and gas flow ones with 1.0 mm slit width. The Rowland's circle radius was 125 mm. In the spectra of Fig. 2, the wavelengths were corrected against the peak wavelength of the $FeK\alpha_1^9$ line, 17.424 Å (nine times the wavelength of the $FeK\alpha_1$ line for metallic iron), and the X-ray intensities were normalized to the peak heights of the FeLα lines.

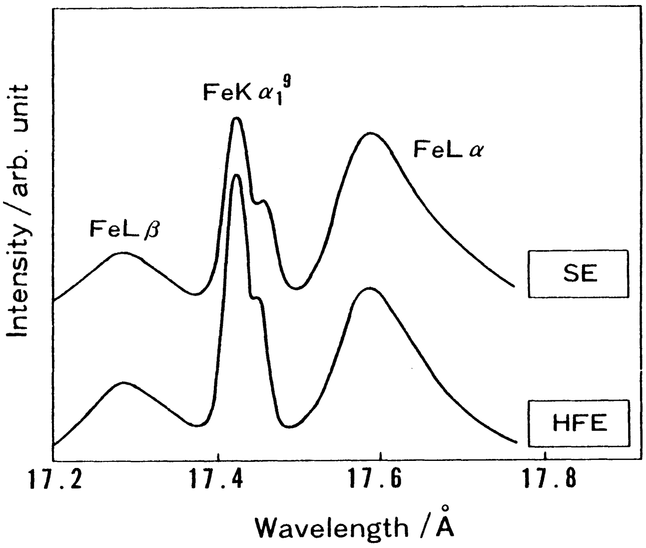

Fig. 2. X-Ray spectra of steel surfaces.

The state analysis parameters used in this study were the peak intensity ratio of the $FeK\alpha_1^9$ line to FeLα line, that of the FeLβ line to FeLα line, and the peak wavelength shift of the FeLα line (they were represented as $r(K\alpha_1^9/L\alpha)$, $r(L\beta/L\alpha)$, and $\Delta\lambda(L\alpha)$ respectively). The values of the parameters for the spectra of Fig. 2 are summarized in Table 1 along with standard sample values[1)] obtained under the same experimental conditions as used in this study. By comparing the three parameters of the SE surface with those of the standard samples (Fe_2O_3, Fe_3O_4, and FeO), it was seen that the iron oxide of the outer layer is Fe_3O_4. This is an expected result if the steam exposure condition[2)] and the phase diagram of the iron-oxygen system[3)] are considered. On the other hand, in the HFE surface, one parameter $r(K\alpha_1^9/L\alpha)$ did not coincide with those of the standard samples (FeF_2 and FeF_3), although the other two parameters, $r(L\beta/L\alpha)$ and $\Delta\lambda(L\alpha)$, agreed well with those of FeF_3. The discrepancies in $r(K\alpha_1^9/L\alpha)$ between the HFE surface and FeF_3 were considered to be attributable to the differences in detection depths of the FeLα, FeLβ, and $FeK\alpha_1$ lines. The detection depth of the

FeKα_1 line can be estimated from the depth of the X-ray generation[4] because of the small absorption coefficient for the FeKα_1 line, while the detection depths of the FeLα and FeLβ lines can be estimated from the depth of the X-ray transmission because of the large absorption coefficients for the latter lines. For the iron compounds listed in Table 1, estimated values of the detection depths of the FeLα and FeLβ lines are under 0.5 μm and that of the FeKα_1 line about 2-3 μm for the excitation voltage of 20 kV.[5] Consequently, the observed intensities of the FeLα and FeLβ lines of the HFE surface came mainly from the product layer (FeF_3) and those of the FeKα_1^9 line mainly from the unreacted oxide film (Fe_3O_4).

Table 1. State analysis parameters.[a]

Sample	r(Lβ/Lα) (error/%)	r(Kα$_1^9$/Lα) (error/%)	Δλ(Lα)/Å (error)
SE	0.36(8)	0.95(9)	0.014(0.004)
HFE	0.47(8)	1.4 (12)	0.016(0.004)
FeO	0.43(7)	1.1 (9)	0.001(0.003)
Fe_3O_4	0.38(6)	0.93(9)	0.016(0.003)
Fe_2O_3	0.36(7)	0.30(10)	0.031(0.003)
FeF_2	0.50(7)	1.7 (9)	0.0 (0.004)
FeF_3	0.48(7)	1.1 (8)	0.018(0.004)

a) Values of the parameters except for SE and HFE are from Ref. 1.

The spectral profiles of the OKα and FKα lines (the detection depths < 0.5 μm) of SE and HFE surfaces were also compared with those of the standard samples.[6] The results support the conclusion that the iron oxide of the SE surface is Fe_3O_4 and its product by the reaction with hydrogen fluoride gas (the product layer of the HFE surface) is FeF_3.

The above results revealed that the state analysis method utilizing the FeKα_1^9 line was useful to identify iron compounds by an EPMA. The method is considered to be effective especially when the layers of the compounds are thicker than the detection depth of the FeKα_1 line because the peak intensity ratio r(Kα_1^9/Lα) serves as a valid state analysis parameter. When the layers are thinner than the detection depth of the FeKα_1 line, the peak intensity ratio r(Kα_1^9/Lα) depends on the chemical states of both the compound and the substrate. In these cases, the FeKα_1^9 line is still effective for the state analysis because its peak wavelength remains a powerful marker to measure the peak wavelength shift of the FeLα line.

The authors are grateful to Mr. K. Fukuchi for his help in the sample preparation, and also to Mr. M. Akiba of Hitachi Works, Hitachi, Ltd., for his help in the spectral measurements.

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6) The experimental conditions of the spectral measuremnts were the same as those for the iron emission lines except for the excitation voltage (10 kV) and the analyzing crystal (lead stearate for the OKα line, 2d = 50.1 Å). The measured values of the asymmetry index$^{1)}$ of the OKα and FKα lines and the peak intensity ratio of the major satellite to diagram line of the FKα line (they were represented as γ(OKα), γ(FKα), and r(FKα'/FKα) respectively) were as follows; γ(OKα) = 0.47±0.04 (SE), 0.48±0.03 (Fe_3O_4); γ(FKα) = 0.79±0.04 (HFE), 0.80±0.04 (FeF_3); r(FKα'/FKα) = 0.48±0.04 (HFE), 0.49±0.04 (FeF_3).

(Received May 14, 1983)