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A STATE ANALYSIS METHOD OF TRANSITION-METAL ELEMENTS BY AN ELECTRON PROBE MICROANALYZER

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It was shown that the chemical state of nickel or cobalt could be identified by the state analysis method utilizing the 9th-order Kα_1 line. Probable factors of the X-ray intensity variation with chemical state were the self-absorption, the $L_2L_3M_{4,5}$ Coster-Kronig process, and the pseudo Lβ emission.

In previous studies,[1,2] a state analysis method for iron utilizing the 9th-order FeKα_1 (FeKα_1^9) line by an electron probe microanalyzer (EPMA) was proposed and applied to steel surface analysis. In the method, the peak wavelength of the FeKα_1^9 line was utilized as a marker to measure the peak wavelength shift of the FeLα line and the peak intensity ratio of the FeKα_1^9 line to FeLα line was used as one of the state analysis parameters.[1] The same method is also applicable to state analysis by an EPMA of elements having an atomic number near 26. This letter reports on extension of the state analysis method utilizing the 9th-order Kα_1 line to cobalt and nickel. Possible mechanism of the X-ray intensity change by the chemical state is also discussed.

The samples were metallic manganese, iron, cobalt, nickel, and their compounds (NiO, NiF_2, Co_3O_4, and CoF_2). The purity of all the samples was over 99.9%. The samples of the compounds were coated with a carbon film after the powder was pelletized. The X-ray spectra were measured by a Hitachi X-650 EPMA. The X-ray spectra were analyzed by using a Johansson type analyzing crystal (rubidium hydrogen phthalate, 2d = 26.12 Å) and a proportional counter.[1] The specimen current was about 0.05 μA and the excitation voltage 5-40 kV.

The principle of the Kα_1^9 line method requires that the Lα and Lβ lines are sensitive to chemical state and that the Kα_1^9 line appears near the Lα and Lβ lines.[1] Previous studies[1,2] showed that iron was one of the most suitable elements for the method because the FeLα and FeLβ lines are emitted in relaxation from the outermost shell $M_{4,5}$ and the FeKα_1^9 line appears between the FeLα and FeLβ lines. Figure 1 shows the Lα, Lβ, and Kα_1^9 line spectra of metallic nickel, cobalt, and iron. These spectra indicate that these elements satisfies the above conditions. The CoKα_1^9 and CoLα lines, which were overlapped each other, could be separated by using the pulse height analyzer of the EPMA.

In the Kα_1^9 line method, the excitation voltage is an important experimental factor because the peak intensity ratio of the Kα_1^9 line to Lα (or Lβ) line changes significantly with it.[1] Figure 2 shows the effects of the excitation voltage for the observed peak intensities of the Lα and Kα_1^9 lines. The Lα line intensities decreased with the excitation voltage after reaching maxima at about 15-20 kV. The decrease is attributable to the strong self-absorption in the sample.[4,5] These trends for the $L\alpha$ line were observed for the $L\beta$ line. On the other hand, the $K\alpha_1^9$ line intensities increased monotonously with the excitation voltage because the self-absorption effect was much smaller than for the $L\alpha$ and $L\beta$ lines.[1] The higher excitation voltage degenerates the spatial resolution of analysis[3] and the lower one attenuates the $K\alpha_1^9$ line, so that the value of 20-30 kV is an appropriate excitation voltage for the $K\alpha_1^9$ line method.

The peak intensity ratio of the $L\beta$ line to $L\alpha$ line, that of the $K\alpha_1^9$ line to $L\alpha$ line, and the peak wavelength shift of the $L\alpha$ line (they were represented as $r(L\beta/L\alpha)$, $r(K\alpha_1^9/L\alpha)$, and $\Delta(L\alpha)$, respectively) obtained for nickel and cobalt are summarized in Table 1. The exciting voltage was 30 kV. Changes of $r(L\beta/L\alpha)$, $r(K\alpha_1^9/L\alpha)$, and $\Delta(L\alpha)$ by the chemical state of nickel or cobalt were small compared with that of iron.[1] However, Table 1 shows that the $K\alpha_1^9$ line method can be used for the state analysis of nickel or cobalt by EPMA as well as iron.

The observed values of $r(L\beta/L\alpha)$ in Table 1 differed from the value expected statistically, 0.5(the ratio of the production probability of the L_2 hole to L_3 hole),[6] and showed distinction between metals and the compounds. The same characteristics have been obtained for iron.[1] Factors of these differences are considered to be (1) the difference of the self-absorption effect between the $L\alpha$ and $L\beta$ lines owing to the L_3 absorption edge,[1] (2) the depletion of the L_2 hole by the $L_2L_3M_{4,5}$ Coster-Kronig process,[7,8] and (3) the relaxation from the excited orbitals with 3d character[8,9] to the L_3 hole.

Table 2 summarizes the observed values of $r(L\beta/L\alpha)$ and $r(K\alpha_1^9/L\alpha)$ for nickel, cobalt, and iron[1] with their absorption corrected values. The absorption

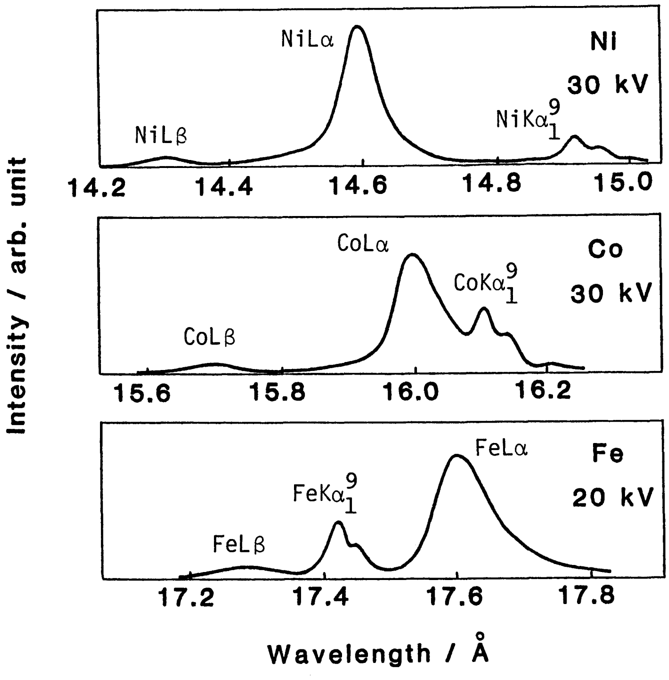

Fig. 1. X-Ray spectra of transition-metals.

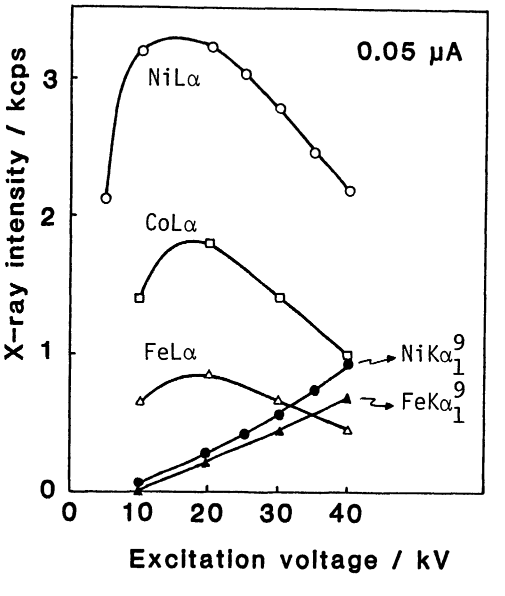

Fig. 2.
Effects of the excitation voltage on X-Ray intensity.

correction was performed by using the full Philibert method1,3) which is used for the quantitative elemental analysis of EPMA.10) The peak intensity ratio of the Lη line to Lℓ line (r(Lη/Lℓ)) for nickel and iron are also shown in Table 2. These values were calculated from the Lℓ and Lη X-ray spectra measured by Wood and Urch.8) While r(Lη/Lℓ) is not sensitive to the self-absorption because of no absorption edge between the lines, it is affected by the $L_2L_3M_{4,5}$ Coster-Kronig process as well as r(Lβ/Lα).11) The absorption corrected r(Lβ/Lα) for metallic iron and nickel were close to the observed r(Lη/Lℓ). This result suggests that the self-absorption and the $L_2L_3M_{4,5}$ Coster-Kronig process are major factors which make the observed r(Lβ/Lα) smaller than 0.5 for metallic nickel and iron.

On the other hand, the absorption corrected r(Lβ/Lα) for the nickel and iron compounds were much larger than their observed r(Lη/Lℓ) and also larger than 0.5

Table 1. State analysis parameters

Sample	r(Lβ/Lα)a)	r($K\alpha_1{}^9$/Lα)a)	Δ(Lα)/Åb)
Ni	0.068(7)	0.21(6)	-
NiO	0.23(6)	0.33(8)	0.003(0.003)
NiF_2	0.22(6)	0.18(9)	0.003(0.003)
Co	0.060(8)	0.43(7)	-
Co_3O_4	0.31(8)	0.68(9)	0.012(0.004)
CoF_2	0.34(8)	0.42(9)	0.008(0.004)

a) Value in brackets is error in %.
b) Value in brackets is error in Å.

Table 2. Observed and absorption corrected X-ray peak intensity ratio a)

Sample	r(Lη/Lℓ) b)	r(Lβ/Lα)		r($K\alpha_1{}^9$/Lα)	
	observed	observed	corrected	observed	corrected
Ni	0.24	0.068	0.25	0.21	0.022
NiO	0.28	0.23	0.65	0.33	0.030
NiF_2	-	0.22	0.46	0.18	0.012
Co	-	0.060	0.23	0.43	0.036
Co_3O_4	-	0.31	0.86	0.68	0.049
CoF_2	-	0.34	0.59	0.42	0.022
Fe	0.16	0.068	0.25	0.40	0.060
FeO	-	0.43	1.2	1.1	0.15
Fe_3O_4	-	0.38	1.0	0.93	0.12
Fe_2O_3	-	0.36	0.93	0.30	0.039
FeF_2	-	0.50	1.1	1.7	0.17
FeF_3	0.27	0.48	0.89	1.1	0.099

a) Values for metallic iron and iron compounds are from Ref. 1 except for r(Lη/Lℓ).
b) From Ref. 8.

(except for NiF_2). A possible explanation is that the observed Lβ line includes the emission by the relaxation from the excited orbitals with 3d character to the L_3 hole in addition to the intrinsic Lβ emission. That is, the former emission (the pseudo Lβ emission) is assumed to have an energy comparable with the intrinsic Lβ emission.[8,11)] If the pseudo Lβ emission occurs, the observed Lβ line intensity will increase and the Lα line intensity will decrease, so that the absorption corrected r(Lβ/Lα) and $r(K\alpha_1^9/L\alpha)$ will also increase. The above mechanism can explain the change of r(Lβ/Lα) and $r(K\alpha_1^9/L\alpha)$ by the chemical state for nickel and iron. The same mechanism will act on cobalt.

The above results revealed that the $K\alpha_1^9$ line method was applicable to the state analysis of nickel and cobalt as well as iron. The appropriate exciting voltage for the method was 20-30 kV. The observed values of r(Lβ/Lα) and $r(K\alpha_1^9/L\alpha)$ are considered to be affected by the self-absorption effect, the depletion of the L_2 hole by the $L_2L_3M_{4,5}$ Coster-Kronig process, and the pseudo Lβ emission by the relaxation from the excited orbitals with 3d character to the L_3 hole.

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10) If the sample is not homogeneous in the electron diffusion range (a few µm), the absorption correction becomes complex.[2,3)]
11) The doubly ionized 3d state by the $L_2L_3M_{4,5}$ Coster-Kronig process will give slightly different effect on r(Lη/Lℓ) from r(Lβ/Lα).

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