OVERVIEW

Quantitative X-ray Microanalysis in Analytical Electron Microscopy

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This paper presents an overview of the principles and procedures for the quantitative X-ray microanalysis of thin specimens using an analytical electron microscope (AEM) equipped with an energy dispersive X-ray spectrometer (EDS). The factors affecting the reliability of the quantification are also summarized. The quantitative X-ray microanalysis with the AEM-EDS system is effective for the composition determination, the thickness determination and the site-occupancy determination. For the compositional determination, the Cliff-Lorimer ratio method is introduced. A special emphasis is placed on the k -factor determination and the absorption correction to enhance reliability of the quantification. For the thickness determination, it is illustrated that there are two primary procedures with the AEM-EDS system: one is to make use of the proportionality between the X-ray intensity and the thickness and the other is to take advantage of the difference between the magnitudes of X-ray absorption in the specimen. For the site-occupancy determination, the ALCHEMI (atom location by channeling enhanced microanalysis) technique is described. A general form of an equation is presented, which can encompass various premises on the antisite occupation of host elements. It is shown that an error may be introduced from the delocalization effect in the quantification, and some correction procedures for this effect are suggested.

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I. Introduction

In 1963, Duncumb first reported combined use of X-ray microanalysis with transmission electron microscope by attaching a wave-length dispersive X-ray spectrometer (WDS) to a transmission electron microscope⁽¹⁾. It became then feasible to perform X-ray micro-chemical analysis along with microstructural observations and electron diffraction analyses in a single instrument. Later, the WDS was replaced by an energy dispersive X-ray spectrometer (EDS) for simultaneous detection of X-rays at different energy levels to enhance the efficiency of the microanalysis. The versatility of this analytical system thus established analytical electron microscopy (AEM), which has now developed with modern technology such that it is possible to achieve the microanalyses in a region as small as ~ 1 nm in diameter and occasionally to conduct such a high-spatial-resolution microanalysis with lattice image observations. Thus, the AEM is a powerful tool for detailed characterization of fine structures in the specimens and indispensable for the development of advanced materials.

With the AEM-EDS system, qualitative analysis is simply performed since the requirement is to identify the characteristic X-ray peaks from their energy levels in an acquired spectrum. This identification provides information of the elements involved in a region of interest. For

quantitative analysis, it is further necessary to measure peak intensities of the corresponding characteristic X-ray lines. A common application from the measurement of peak intensities is the quantitative determination of composition in a region of interest. When stated in the word "quantitative X-ray microanalysis using AEM-EDS", it is usually meant, without note, to indicate quantitative determination of composition. However, the AEM-EDS system also permits, from the measurement of peak intensities, the determination of specimen thickness at the beam position and the determination of the site occupancy of substitutional elements in an ordered structures. In this paper, an overview is presented for the quantification procedures of compositional determination, thickness determination and site-occupancy determination provided by the AEM-EDS system.

II. Composition Determination

In order to determine a composition in the region of interest, it is necessary to convert the composition from the peak intensities of characteristic X-rays measured with an EDS. However, the measured intensities are not equal to the intensities generated at the point of analysis. Among several reasons for inequality, X-ray absorption in the specimen is most significant and thus this effect should be corrected for reliable quantification. It is also necessary to determine the conversion factors from meas-

ured X-ray intensities to compositions: these factors are usually called the k factors or the Cliff-Lorimer factors⁽²⁾⁽³⁾.

This section begins by describing the generated intensity and the measured intensity of characteristic X-ray to illustrate the difference between the two intensities. The ratio method is then introduced as a convenient procedure for the conversion from X-ray intensities to a composition. Finally, this paper is devoted to describe the k -factor determination and the X-ray absorption correction which are the two important processes for the reliable determination of a composition.

1. Generated intensity

When a high-energy incident electron impinges on an atom in the specimen, X-rays may be generated which are characteristic of the element. For a thin specimen where the electron is fully transparent, the intensity of the characteristic X-ray is given by the following relationship:

$$(I_J)_g = (N\rho W_J / M_J) Q_J \omega_J a_J i s t \quad (1)$$

where $(I_J)_g$ is the intensity of the characteristic X-ray generated from element J in the specimen, N is the Avogadro's number, ρ and W_J are the density and weight fraction at the beam position, M_J is the atomic weight, Q_J is the ionization cross-section having a dimension of area, ω_J is the fluorescence yield, a_J is the ratio of K_α (or L_α , M_α) intensity to the total K (or L, M) intensity, i is the beam current density, s is the area of beam illumination, and t is the thickness at the beam position. The subscript J represents that the corresponding quantities are associated with element J or the characteristic X-ray of element J.

In eq. (1), $(N\rho W_J / M_J)$ represents the numbers of atom J in a unit volume and thus $(N\rho W_J / M_J) Q_J t$ is the numbers of atom J excited by a single incident electron across the thickness t . Then, the subsequent emission of characteristic X-ray J due to a single electron is given by $(N\rho W_J / M_J) Q_J t \omega_J$. Since si is the numbers of incident electrons in the area of s , the quantity $(N\rho W_J / M_J) Q_J t \omega_J si$ corresponds to the total numbers of characteristic X-ray emission from the specimen.

2. Measured intensity

The intensity which is measured with an EDS is not equal to the generated intensity presented in eq. (1). **Figure 1** illustrates the factors affecting the intensity of generated X-ray before measurement by a multichannel analyzer. The measured intensity is then given by the following form:

$$(I_J)_m = (I_J)_g (1 + F_J) A_J (\Omega / 4\pi) \varepsilon_J \xi_J \quad (2)$$

where F_J is the fluorescence factor and A_J is the absorption factor, Ω is the solid angle to the detector for X-ray collection, ε_J is the detector efficiency and ξ_J is the effective fraction of the peak intensity depending on the energy width of the characteristic X-ray peak. Here, the energy width is normally taken as 1.2 times of the full width at half maximum (FWHM)⁽⁴⁾.

Fig. 1 Factors affecting the intensity of generated X-ray: F is the fluorescence factor, A is the absorption factor, Ω is the solid angle to the detector for X-ray collection, ε is the detector efficiency and ξ is the effective fraction of the peak intensity.

3. Ratio method

From eqs. (1) and (2), the following relationship is derived

$$W_J / W_A = k_{JA} (I_J / I_A)_m \{ (1 + F_A) / (1 + F_J) \} (A_A / A_J) \quad (3)$$

where

$$k_{JA} = \{ (Q\omega a / M)_A / (Q\omega a / M)_J \} \{ (\varepsilon\xi)_A / (\varepsilon\xi)_J \} \quad (4)$$

When the effects of X-ray absorption and fluorescence are negligible, namely, $(1 + F_A) / (1 + F_J) \approx 1$ and $A_A / A_J \approx 1$, the quantification becomes straightforward. Equation (3) is reduced to the form

$$W_J / W_A = k_{JA} (I_J / I_A)_m \quad (5)$$

The composition is then determined with the combination of

$$W_A + \sum W_J = 1 \quad (6)$$

where $J = B, C, \dots$. The determination of composition using eqs. (3) and (6) or eqs. (5) and (6) is known as the Cliff-Lorimer ratio method⁽²⁾⁽³⁾. k_{JA} is called the k -factor of X-ray J with respect to X-ray A.

An advantage of using the ratio method is that it is possible to exclude the factor $\Omega / 4\pi$ in eq. (2) from the analysis. This factor is common to all X-rays and thus is eliminated when the intensity ratio is taken as eq. (3).

As will be described later in this section, the approximation $A_A / A_J \approx 1$ for the effect of X-ray absorption is not always valid. However, according to an evaluation given earlier⁽⁵⁾, the approximation $(1 + F_A) / (1 + F_J) \approx 1$ is mostly acceptable. The effect of X-ray fluorescence is less than 10% even at the maximum condition which occurred when the energy of a characteristic X-ray is just above the excitation energy of other characteristic X-ray line. Thus, the effect of X-ray fluorescence is regarded as negligible in this paper. For details of the X-ray fluorescence effect, see papers published earlier⁽⁴⁾⁽⁵⁾.

4. Determination of k -factor

The k -factor in eq. (3) or eq. (5) is determined in either of the experimental fashion (Cliff-Lorimer method)⁽²⁾⁽³⁾ or the theoretical fashion (Standardless method)⁽⁶⁾. For the former case, it is necessary to prepare thin standard specimens with known compositions. Then, by measuring characteristic X-ray intensities from the standards, the k -factor is determined from the relationship

$$k_{JA} = (W_J / W_A)_{\text{std}} (I_A / I_J)_{\text{std}} \quad (7)$$

where $J=B, C, \dots$ and the subscript "std" signifies that the weight fractions and the X-ray intensities are associated with the standard specimen. For the latter case, the k -factor is calculated through eq. (4) by putting the corresponding quantities from the literature and tables.

(1) Comparison between calculated and measured k -factors

Figure 2 compares the two types of k -factors, where the theoretical values are delineated from the calculation by Thomas⁽⁷⁾ for the Be window (BEW) type, the ultra-thin window (UTW) type and the windowless (WL) type detectors and the measured values are plotted from several published reports⁽³⁾⁽⁷⁾⁻⁽¹⁰⁾. The agreement is reasonable above the energy of ~ 2 keV but is poor below it except for the results of Thomas reported in 1985⁽⁷⁾. In the same report⁽⁷⁾, however, Thomas commented that this agreement was rather fortuitous. There are several other reports comparing the two types of k -factors⁽⁶⁾⁽¹¹⁾⁻⁽¹⁵⁾. All comparisons then concluded that the calculated values deviate significantly from the measured values for lighter elements than Si emitting the K-shell line and for heavy elements emitting the L- or M-shell line. The reasons for the discrepancy may be due to the ambiguity involved in the ionization cross section, relative intensity factor, fluorescence yield and the detector efficiency. These comparisons suggest that the measured k factors are more reliable than the calculated.

Fig. 2 Comparison between theoretical k -factors⁽⁷⁾ calculated using eq. (4) and measured k -factors using eq. (7)⁽³⁾⁽⁷⁾⁻⁽¹⁰⁾.

(2) Variation of measured k -factor

The measured k -factor may change from one measurement to the other. Figure 3 plots the values of $k_{\text{AlNi(K)}}$ measured over 2 years with the same AEM-EDS system⁽¹⁶⁾. The origin of the measured date was taken such that the k -factor measurement was initiated. The error bars arise from the X-ray counting statistics and represent the 95% confidence interval. The value of $k_{\text{AlNi(K)}}$ increases with the date of measurement to reach the value twice as large as the value at the initial stage of measurement. Thereafter, by the overhaul of the detector in the system, the value of $k_{\text{AlNi(K)}}$ is restored to the level at 10 months after the initiation of measurement. It is seen that the agreement with the calculated value, which is indicated by the shaded area, is restricted to a certain period of the measurement. In Fig. 3, the calculated value is given by a range and this is due to the uncertainty involved in the ionization cross-section required for the calculation.

The following reasons may be considered for the change in k factors with respect to the date of measurement: (1) deposition of contamination and buildup of ice on the detector window, (2) geometry change between the detector and specimen, and (3) inherent degradation of the detector. The aforementioned overhaul consisted of removing liquid nitrogen and thus of increasing the detector temperature to room temperature. This overhaul then suggests that the ice on the detector window may have a significant effect on the change in $k_{\text{AlNi(K)}}$. In eq. (4), no term is included to describe such a change of k -factor. Although a precise formulation may be difficult, it is important to include an extra term in eq. (4) for a reliable estimation of k factor.

Figure 3 includes one point obtained with the same

Fig. 3 Variation of $k_{\text{AlNi(K)}}$ with respect to the date of measurement. One point is included from the measurement using a different machine but with the same type of AEM-EDS system. (HVEM: High Voltage Electron Microscopy Laboratory of Kyushu University, RIAM: Research Institute of Applied Mechanics of Kyushu University)

type of an AEM-EDS system but installed later in the different division of Kyushu University. Despite the fact that the measurement was made on the same specimen in the same passage time, the two k -factors are significantly different. Figure 3 demonstrates that the k -factor should be measured before or after every series of microanalysis on the same AEM-EDS system.

(3) Optimization for k -factor determination

An advantage of using calculated k factors is that it is unnecessary to prepare a thin specimen for the standard and to measure characteristic X-ray intensities from it. Thus, with the calculated k factors, it is possible to anticipate a prompt determination of compositions and a release from the troublesome involved in the preparation of thin standard specimens. The latter point is significant specially when the fabrication of a thin standard specimen is difficult or impossible. However, the use of the calculated k factors does not guarantee reliability for the composition although they may be useful for the estimation of the relative magnitude of the composition with respect to other.

Currently, no equation is available to calculate reliable k factors because it is difficult to estimate the detector efficiency which may change day by day or machine by

machine as demonstrated in Fig. 3. Williams⁽¹⁷⁾ suggested a method where a few k -factors are measured from a standard and are used for an estimation of other k -factors. Figure 4(a) plots the three values of measured k -factors k_{MgFe} , k_{SiFe} and k_{CaFe} together with the k -factors calculated through eq. (4) for k_{AFe} ($A=\text{Mg-Zn}$). As the trend demonstrated in Fig. 3, the agreement is not satisfactory between the two types of k factors specially at lower atomic number elements. Figure 4(b) plots the two types of k factors but now the calculated values are changed to fit all measured ones by adjusting parameters in Q and ε in eq. (4). Thus, this adjustment can give a correct estimation of k factors without relying on the measurement of whole k factors.

5. Absorption effect

For thin specimens where electrons are fully transparent, the absorption factor A_J is expressed by the form⁽⁶⁾

$$A_J = \{1 - \exp [-(\mu/\rho)_s^J \rho t \csc \theta]\} / [(\mu/\rho)_s^J \rho t \csc \theta] \quad (8)$$

where $(\mu/\rho)_s^J$ is the mass absorption coefficient of X-ray J in the specimen and θ is the X-ray take-off angle. (See Fig. 1 for θ .)

If all X-rays are generated at one half the specimen thickness, the absorption factor A_J may be expressed by the following approximated form⁽⁶⁾.

$$A_J \approx \exp [-(\mu/\rho)_s^J \rho (t/2) \csc \theta] \quad (9)$$

Figure 5 shows the variation of A_J calculated as a function of t through eq. (8) for the Al K_α , Ni K_α , Mo K_α and Mo L_α lines in a Ni-11.2 mass%Al-7.2 mass%Mo alloy. The calculation has been made for two X-ray take-off angles, $\theta=20^\circ$ and $\theta=70^\circ$. Whereas the absorption of the Ni K_α and Mo K_α lines is small being less than 5% within the thickness of 1000 nm, that of the Al K_α and Mo L_α lines is large and this is more significant when the X-ray take-off angle is low. For example, the absorption of the Al K_α line becomes as large as $\sim 80\%$ and $\sim 50\%$ at the thickness of 500 nm for $\theta=20^\circ$ and $\theta=70^\circ$, respectively.

Fig. 4 (a) Three measured k -factors k_{MgFe} , k_{SiFe} and k_{CaFe} together with the calculated k factors through eq. (4) for k_{AFe} ($A=\text{Mg-Zn}$). (b) Plots of the two types of k factors but now the calculated k factors are changed to fit all measured ones by adjusting parameters in Q and ε in eq. (4)⁽¹⁷⁾.

Fig. 5 Absorption factor, A_J ($J=\text{Al } K_\alpha$, Ni K_α , Mo K_α and Mo L_α), calculated as a function of thickness, t , using eq. (8) for two X-ray take-off angles, $\theta=20^\circ$ and $\theta=70^\circ$.

6. Absorption correction factor

When the X-ray absorption is significant as the Al K_{α} line in the Ni–Al–Mo system shown in Fig. 5, it is necessary to correct the effect of absorption.

The factor for absorption correction, A_A/A_J , in eq. (3) is given using the form of eq. (8) as⁽⁶⁾

$$A_A/A_J = [(\mu/\rho)_s^J / (\mu/\rho)_s^A] \{1 - \exp [-(\mu/\rho)_s^A \rho t \csc \theta]\} / \{1 - \exp [-(\mu/\rho)_s^J \rho t \csc \theta]\} \quad (10)$$

or using the form of eq. (9) as⁽⁶⁾

$$A_A/A_J \approx \exp [-\{(\mu/\rho)_s^A - (\mu/\rho)_s^J\} \rho (t/2) \csc \theta] \quad (11)$$

As recognized from eq. (10) or eq. (11), the absorption correction requires knowledge of the thickness at the point of analysis. Although a number of methods are available for the thickness measurement, they are not always simple and occasionally a large error is involved in the measurement. Several methods were developed for the absorption correction without thickness measurement: they are the thin film approximation⁽⁶⁾, the extrapolation method^{(18)–(21)}, the differential X-ray absorption (DXA) method^{(22)–(23)} and the ζ -factor method⁽²⁴⁾. Principles of these methods are described below including advantages and disadvantages of the methods.

7. Absorption correction

(1) Thin-film approximation⁽⁶⁾

This procedure circumvents the problem of absorption by performing X-ray measurements in a region thin enough to neglect the absorption effect. The critical thickness is determined such that the decrease in characteristic X-ray intensity ratio due to absorption, $\{(I_J/I_A)_0 - (I_J/I_A)_m\}$, is within an experimental error of the measured intensity ratio, $\Delta(I_J/I_A)_m$. This condition can be expressed by the relationship as

$$(I_J/I_A)_0 - (I_J/I_A)_m \leq \Delta(I_J/I_A)_m \quad (12)$$

where $(I_J/I_A)_0$ is the intensity ratio without the effect of absorption and is given by

$$(I_J/I_A)_0 \equiv (I_J/I_A)_s \{(\epsilon_J \zeta_J) / (\epsilon_A \zeta_A)\} \quad (13)$$

Using eq. (11), thus, eq. (12) reduces to the following form to give the critical thickness t_c :

$$t \leq \log_{10} (1 + \Delta R_{JA}) / H_{JA} (\equiv t_c) \quad (14)$$

where ΔR_{JA} is the relative error of the measured intensities defined as

$$\Delta R_{JA} \equiv \Delta(I_J/I_A)_m / (I_J/I_A)_m \quad (15)$$

and

$$H_{JA} \equiv 0.217 \{(\mu/\rho)_s^J - (\mu/\rho)_s^A\} \rho \csc \theta \quad (16)$$

Estimating t_c for a standard of the Ni–11.2 mass%Al–7.2 mass%Mo alloy where the Al K_{α} line undergoes the largest effect of absorption as shown in Fig. 5, it follows that $t_c \approx 70$ nm for $\Delta R_{JA} = 0.1$ and $t_c \approx 20$ nm for $\Delta R_{JA} = 0.03$ at $\theta = 70^\circ$ and $t_c \approx 25$ nm for $\Delta R_{JA} = 0.1$ and

$t_c \approx 7$ nm for $\Delta R_{JA} = 0.03$ at $\theta = 20^\circ$. This estimation indicates that the critical thickness is fairly small and thus in practice it may be difficult to fabricate a thin region fulfilling the thin-film approximation. The estimation of t_c provided by Williams⁽⁴⁾ for several other materials also reveals that the application of the thin-film approximation is considerably restricted. It is likely that the minimum thickness reached by conventional specimen-thinning techniques such as the electropolishing and the ion-beam thinning exceeds the critical thickness.

(2) Extrapolation method^{(18)–(19)}

Using eq. (11), the measured intensity ratio, $(I_A/I_J)_m$, and the intensity ratio without the effect of absorption, $(I_A/I_J)_0$, are represented by the following form

$$\log (I_A/I_J)_m = \log (I_A/I_J)_0 + (H_{JA}/\psi)(I_x)_m \quad (17)$$

where ψ is a proportional constant defined in the relationship as

$$(I_x)_m = \psi t \quad (18)$$

Here, $(I_x)_m$ is the characteristic X-ray intensity from element X and this proportionality holds from eq. (1) and eq. (2) when the absorption of the corresponding X-ray is negligible. From eq. (17), it is possible to obtain $(I_A/I_J)_0$ by plotting the logarithmic $(I_A/I_J)_m$ against $(I_x)_m$ and extrapolating the relationship to $(I_x)_m = 0$.

The extrapolation method can be applied to the determination of k -factor using a standard specimen. The form of eq. (17) is then changed to

$$\log (k_{JA})_m = \log (k_{JA})_0 + (H_{JA}/\psi)(I_x)_m \quad (19)$$

where $(k_{JA})_m$ and $(k_{JA})_0$ are the absorption-involved and -free k factors, respectively.

A few conditions are required for the proper application of the extrapolation method. (a) At least one characteristic X-ray with negligible absorption should be available in the measured spectrum in order to use the X-ray intensity for $(I_x)_m$ in eq. (17) or eq. (19). (b) Beam current density should be kept constant during a series of X-ray measurements. (c) X-ray measurements should be made within a thickness range that the approximated form of the absorption correction factor given in eq. (11) is valid.

Despite such requirements, the extrapolation method provides important benefits that the method requires neither knowledge of thickness, density nor mass absorption coefficient for absorption correction. Thus, the errors arising from such quantities are eliminated and the reliability of microanalysis is enhanced. Because the extrapolation method requires X-ray measurements at more than two points with different thicknesses but an identical composition to allow extrapolation feasible, the method is used most efficiently when a sufficient region with a uniform composition is available in the specimen as in the determination of k factors from standard specimens. When the region for microanalysis is limited and comparable to the beam size, the method may be applicable by tilting the specimen at more than two different angles⁽²⁰⁾.

Fig. 6 Plots of $(k_{\text{AlNi}})_m$, $(k_{\text{Mo(L)Ni}})_m$ and $(k_{\text{Mo(K)Ni}})_m$ against $(I_{\text{Ni}})_m$ obtained from the standard of Ni-11.2 mass%Al-7.2 mass%Mo. The values at $(I_{\text{Ni}})_m = 0$ correspond to the absorption-free k factors⁽⁵⁾.

Figure 6 plots $(k_{\text{AlNi}})_m$, $(k_{\text{Mo(L)Ni}})_m$ and $(k_{\text{Mo(K)Ni}})_m$ against $(I_{\text{Ni}})_m$ in a semilogarithmic scale, where the data points were obtained using a standard of the Ni-11.2 mass%Al-7.2 mass%Mo as used in Fig. 5. The Ni K_{α} intensity was used in the abscissa because the reduction of the Ni K_{α} line due to absorption is negligibly small as shown in Fig. 5. The linear relationships hold well in a semilogarithmic scale. Thus, the absorption-free k factors are determined from the values at $(I_{\text{Ni}})_m = 0$.

(3) Differential X-ray absorption (DXA) method⁽²³⁾

This method was originally proposed by Morris *et al.*⁽²²⁾ and developed to a general form by Horita *et al.*⁽²³⁾ To determine the thickness required for absorption correction, the DXA method makes use of the difference in absorption between two characteristic X-rays emitted simultaneously from the specimen. The equation for the thickness determination is given by the following form.

$$\begin{aligned} (I_{Z(j)}/I_{X(i)})_o &= (I_{Z(j)}/I_{X(i)})_m A_{X(i)}/A_{Z(j)} \\ &= (I_{Z(j)}/I_{X(i)})_m [(\mu/\rho)_s^{Z(j)}/(\mu/\rho)_s^{X(i)}] \\ &\quad \times \{1 - \exp[-(\mu/\rho)_s^{X(i)} \rho t \csc \theta]\} \\ &\quad / \{1 - \exp[-(\mu/\rho)_s^{Z(j)} \rho t \csc \theta]\} \end{aligned} \quad (20)$$

where $I_{X(i)}$ and $I_{Z(j)}$ are the characteristic X-ray intensities of i line from element X and of j line from element Z, respectively, $(I_{Z(j)}/I_{X(i)})_m$ and $(I_{Z(j)}/I_{X(i)})_o$ are the measured and absorption-free intensity ratios, respectively, and $(\mu/\rho)_s^{X(i)}$ and $(\mu/\rho)_s^{Z(j)}$ are the mass absorption coefficients of X(i) and Z(j) lines, respectively. Equation (20) is essentially the same as the form for the absorption correction of $(I_{Z(j)}/I_{X(i)})_m$. Whereas the absorption correc-

tion calculates for $(I_{Z(j)}/I_{X(i)})_o$, this ratio is given initially using the k factor as

$$(I_{Z(j)}/I_{X(i)})_o = (W_Z/W_X) k_{X(i)Z(j)} \quad (21)$$

The thickness is then obtained from eq. (20) with $(I_{Z(j)}/I_{X(i)})_m$. However, inspection reveals that eq. (20) includes the terms of composition through $(I_{Z(j)}/I_{X(i)})_o$, $(\mu/\rho)_s^{X(i)}$, $(\mu/\rho)_s^{Z(j)}$ and ρ . Thus, the thickness obtained from eq. (20) involves an effect of absorption. This effect is eliminated by adopting iterative calculation between the compositional determination using eqs. (3) and (6) and the thickness determination using eq. (20). The composition and the thickness without the effect of absorption are then determined as the converged values in the iteration process.

The major limitation of the DXA method is that the specimen must contain at least one element which emits characteristic X-rays with different energies: for example, Ni emitting the Ni K_{α} and the Ni L_{α} lines. Thus, the method is not applicable if the specimen consists of only elements with the atomic numbers equal to 20 (Ca) or less than 20 (Ca). Furthermore, the DXA method requires density and mass absorption coefficients for the determination of composition and thickness, and thus it is susceptible to errors involved in these quantities in contrast to the extrapolation method. However, the DXA method is capable of determining a composition from a single measurement of X-ray intensities. Thus, the DXA method is applicable to the microanalysis of a region comparable to the beam size.

Figure 7 shows the variations of (a) C_{Al} and (b) thickness across the Ni/Ni₃Al diffusion-couple interface⁽²⁵⁾ where C_{Al} is the Al concentration in mol%. Both C_{Al} and thickness were determined simultaneously by the DXA method with absorption of the Al K_{α} line being corrected. The Ni K_{α} line and the Ni L_{α} line were used for X(i) and Z(j) in eq. (20) to determine the thickness for absorption correction of the Al K_{α} line. The results without the absorption correction are also plotted in Fig. 7(a). When the effect of absorption is not corrected, the level of C_{Al} is significantly lower than the expected level of $C_{\text{Al}} = 25$ mol%. This demonstrates that the absorption correction is important in order to determine a reliable diffusivity from the concentration profile.

(4) ζ -factor method⁽²⁴⁾

The following relationship holds from eq. (1).

$$\rho t = \zeta_X (I_X/W_X) \quad (22)$$

where ζ_X is the factor connecting the characteristic X-ray intensity to ρt and is defined as

$$\zeta_X \equiv A_X / N Q_X \omega_X a_{X,i} \quad (23)$$

This definition indicates that ζ_X is characteristic of element and X-ray energy concerned and is dependent on the accelerating voltage and the beam current. However, ζ_X is independent of the specimen composition.

Using eq. (22), it is possible to eliminate ρt in A_A/A_I given by eq. (10). Thus, if ζ_X is known, absorption correc-

Fig. 7 Variations of (a) Al concentration in mol%, C_{Al} , and (b) thickness, t , across the Ni/Ni₃Al diffusion-couple interface after annealing at 1173 K for 3 h⁽²⁵⁾.

tion is achieved without knowledge of ρt . It is important to note that the absorption of the characteristic X-ray from element X should be negligible as required for the extrapolation method. This requirement is to hold the proportionality between ρt and $(I_X)_m$ so that the measured intensity, $(I_X)_m$, can be used in eq. (22). The absorption correction of other characteristic X-rays is then made with the characteristic X-ray intensity of element X through eq. (10).

The determination of ζ_X is made together with k_{JA} using a standard specimen through eq. (3). First, the characteristic X-ray intensities are measured at more than two different thicknesses. A nonlinear least-square fitting procedure is then applied to eq. (3) with A_A/A_J in the form of eq. (10) to solve for ζ_X and k_{JA} . Once ζ_X and k_{JA} are determined from a standard specimen, microanalysis of an unknown specimen is achieved using eqs. (3) and (6) as described in Section II-3. In such microanalyses, it is important to use the same beam current density as used for the determination of ζ_X and k_{JA} . Furthermore, as in the DXA method, it is necessary to adopt an iterative calculation since eqs. (10) and (22) contains the composition-dependent terms such as W_X , $(\mu/\rho)_s^J$ and $(\mu/\rho)_s^A$.

The values of $\zeta_{Ni(K)}$ and $k_{Al(K)Ni(K)}$ determined from five different standards having compositions of Ni-8 mol% Al, Ni-24 mol% Al, Ni-26 mol% Al, Ni-45 mol% Al and Ni-50 mol% Al are plotted in Fig. 8 as a function of C_{Al} . The mass absorption coefficients required for this determination were taken from the tables given by Birks and Criss⁽²⁶⁾ and Heinrich⁽²⁷⁾. It is confirmed that the values of $\zeta_{Ni(K)}$ and $k_{Al(K)Ni(K)}$ are independent of C_{Al} within the scattering. Because the Heinrich's mass absorption coefficients are larger than those of Birks and Criss, they lead to the values invariably lower than those of Birks and Criss. Despite this difference, however, the values of

Fig. 8 (a) $\zeta_{Ni(K)}$ and (b) $k_{Al(K)Ni(K)}$ plotted against Al concentration in mol%, C_{Al} . The mass absorption coefficients required for the determination were taken from the tables of Birks and Criss⁽²⁶⁾ and Heinrich⁽²⁷⁾⁽²⁴⁾.

$k_{Al(K)Ni(K)}$ result in almost the same level and thus suggests that $k_{Al(K)Ni(K)}$ is insensitive to a change in $\zeta_{Ni(K)}$. In Fig. 8(b), the values of $k_{Al(K)Ni(K)}$ obtained by the extrapolation method are included for comparison. They are invariably higher than those determined by non-linear least square fitting in the ζ -factor method. The higher values arise because of the approximated form adopted for the extrapolation method.

When applying the ζ -factor method, it is necessary that the beam current density should be kept the same between the determination of k and ζ factors from a standard and the determination of composition and thickness in an unknown specimen. However, the ζ -factor method has features superior to both the extrapolation and the DXA methods. First, the ζ -factor method requires neither knowledge of the thickness nor the density and it is possible to measure thickness if the density is known. Second, although the mass absorption coefficients are required, it is possible to use the values from the combination of two K-shell lines emitted from different elements. It should be noted that the DXA method is applicable only with the mass absorption coefficients from the combination of K- and L-shell lines or of L- and M-shell lines. The mass absorption coefficients of K-shell lines are more reliable than those of the L-shell or M-shell lines because the former values are better established than the latter values. Third, the thickness range effective for the ζ -factor method is much greater than that for the extrapolation method because the ζ -factor method utilizes the form of eq. (10) rather than the approximated form of eq. (11) for the absorption correction factors. Fourth, as the DXA method, a single measurement of X-ray intensities is sufficient for the determination of composition and thickness, although it is necessary to measure X-ray intensities at more than two different thickness-

es for the determination of k -factors from standards.

Figure 9 plots (a) the variations of C_{Al} across the diffusion-couple interface with and without absorption correction and (b) the thickness variation at the corresponding positions⁽²⁸⁾ obtained by using the ζ -factor method. Without absorption correction, the level of C_{Al} cannot reach the expected level of $C_{Al} = 51.8$ mol% and the variation of C_{Al} was affected by the variation of thickness. Inspection of the concentration profile reveals that the Ni_3Al intermetallic phase (γ' phase) formed at the couple interface and there are abrupt changes in C_{Al} at the γ/γ' and γ'/β interfaces where γ is the Ni-rich solid solution phase and β is the $NiAl$ intermetallic phase. There is also an abrupt change in C_{Al} in the β phase which corresponds to the pseudo-boundary. The presence of such boundary arises because the interdiffusivity takes a minimum at $C_{Al} \approx 50$ mol%.

III. Thickness Determination

Several methods are available for the determination of thickness using transmission electron microscopy⁽²⁹⁾⁽³⁰⁾. When the determination relies on the AEM-EDS system, the two possible procedures are suggested from the forms of eq. (1) and eq. (2).

Inspection shows that the following relationship holds from eqs. (1), (2) and (22):

$$(I_J)_m / W_J = (\epsilon_J \zeta_J / \zeta_J) (\Omega / 4\pi) (1 + F_J) A_J \rho t \quad (24)$$

It is apparent that $(I_J)_m / W_J$ is directly proportional to t and it contains the term of t through F_J and A_J . Since $F_J \approx 0$ is generally applicable as mentioned in Section II-3, the thickness determination is anticipated either by using the proportionality between $(I_J)_m / W_J$ and t or through

the factor A_J . The two cases are now summarized below.

1. Use of proportionality

In order to make use of the proportionality between $(I_J)_m / W_J$ and t for the thickness determination, it is necessary that the effect of absorption is negligible and thus $A_J \approx 1$. Furthermore, this procedure requires calibration of the thickness with respect to the X-ray intensity. For this calibration, the thickness may be determined using the convergent beam electron diffraction method⁽³¹⁾ or other appropriate methods applicable to a given condition of the specimens. When the specimens with different compositions are used for the calibration, the X-ray intensities should be normalized as $(I_J)_m / W_J$ and the difference in specimen density ρ should be taken into account. Once the calibration is established, the thickness of other specimens is determined from the measurement of X-ray intensities through the calibrated relationship.

2. Use of absorption

When the absorption factor A_J is applied to the thickness determination, the form of eq. (24) may be modified so that it is used in the form of a ratio to other X-ray intensity as

$$\begin{aligned} & \{(I_J)_m / W_J\} / \{(I_A)_m / W_A\} \\ &= \{(\epsilon_J \zeta_J / \zeta_J) / (\epsilon_A \zeta_A / \zeta_A)\} (A_J / A_A) \end{aligned} \quad (25)$$

Here, the approximation has been made again as $(1 + F_J) / (1 + F_A) \approx 1$. The advantage of taking ratio is that it is possible to eliminate the terms such as $\Omega / 4\pi$ and ρt which are independent of element and X-ray. This procedure is based on the same idea as adopted for the ratio method introduced for the compositional determination in Section II-3. In fact, a comparison between eq. (3) and eq. (25) confirms the relationship as

$$(\epsilon_J \zeta_J / \zeta_J) / (\epsilon_A \zeta_A / \zeta_A) = k_{JA} \quad (26)$$

Hence, the thickness is determined from the difference in absorption between the two X-ray lines J and A through eq. (25). The thickness determination using X-ray absorption thus reduces to the procedures for the DXA method⁽²³⁾ or the ζ -factor method (24) described in Section II-7-(3) or Section II-7-(4), respectively.

First, it is necessary to determine a k factor. Then, when the specimen composition is known, the thickness determination is straightforward and is achieved by directly solving eq. (25) for t . When the composition is unknown, the thickness determination is combined with the compositional determination and an iterative calculation is adopted. The thickness is determined together with the composition from the converged values in the iteration. The thickness as an outcome of the iteration has been plotted in Fig. 7(b) when the DXA method is used⁽²⁵⁾ and in Fig. 9(b) when the ζ -factor method is used⁽²⁸⁾.

IV. Site-Occupancy Determination

When the incidence of electron beam is made almost

Fig. 9 Variations of (a) Al concentration in mol%, C_{Al} , and (b) thickness, t , across the Ni/Ni-51.8Al diffusion-couple interface after annealing at 1173 K for 2 h⁽²⁴⁾.

parallel to lattice planes or atom columns, the characteristic X-ray generation becomes sensitive to a change in the beam incident angle. Such X-ray generation occurs due to an effect of dynamical electron diffraction which gives rise to a localization of incident electrons on the lattice planes or the atom columns. For the determinations of composition and thickness described in Sections II and III, it is necessary to avoid measurements of X-ray intensities at such diffraction conditions. However, by making use of the dynamical diffraction conditions and by carefully controlling the incident angle, it is possible to determine the site occupancy of substitutional alloying elements in ordered structures. This quantification procedure is often called the ALCHEMI (atom location by channeling-enhanced microanalysis)⁽³²⁾. This terminology arises because the method utilizes the “electron channeling” which occurs along lattice planes or atom columns.

1. Electron distribution

Figure 10 shows the distributions of channeling electrons simulated along the thickness direction using the multislice calculation⁽³³⁾. The beam incidence is parallel to the $[111]$ zone axis in a Ni-21 mol%Al-4 mol%Ta alloy having the $L1_2$ ordered structure. The sectional plane corresponds to $(11\bar{2})$ so that the Al and Ni columns alternate in the $[1\bar{1}0]$ direction as illustrated in **Fig. 11**. The bright contrast indicates that the electron intensity is high. A periodic formation of intensity maxima is visible on the Ni columns but the formation of maxima is not periodic on the Al columns. It should be noted that the Debye-Waller factors and absorption coefficient are put zero in the simulation. When the Debye-Waller factors and absorption coefficient are taken into account, there are no appreciable channeling electrons beyond the depth of about 25 nm. **Figure 10** demonstrates that electrons localize on the Ni and Al columns although their intensities are different between the Ni and Al columns.

Figure 12 shows the thickness-average electron intensities at $[111]$ beam incidence in the same alloy as used for

Fig. 10 Distributions of channeling electrons simulated along the thickness direction using the multislice calculation⁽³³⁾. The beam incidence is parallel to the $[111]$ zone axis in a Ni-21 mol%Al-4 mol%Ta alloy having the $L1_2$ ordered structure.

Fig. 11 Atom arrangement projected onto the (111) plane, illustrating $(11\bar{2})$ sectional plane where the Al and Ni columns alternate in $[1\bar{1}0]$ direction⁽³³⁾.

Fig. 12 Thickness-average electron intensities at $[111]$ beam incidence in the same alloy as used for the simulation shown in Fig. 10⁽³³⁾. The Debye-Waller factors and absorption coefficient are not included in (a) but are included in (b).

the simulation⁽³³⁾. The Debye-Waller factors and absorption coefficient are not included in Fig. 12(a) but are included in Fig. 12(b). The averages have been taken at thicknesses of 25, 50, 75 and 100 nm. The electron intensity exhibits maxima at the Ni and Al columns and it is more intense on the Ni column than on the Al column. This trend holds irrespective of the use of Debye-Waller factors and absorption coefficient.

Figure 13 shows the X-ray intensities with respect to tilt angle where the zero tilt angle indicates the beam incidence parallel to the exact $[111]$ zone axis of the Ni-21 mol%Al-4 mol%Ta alloy. The X-ray intensities are highest at the zone axis but becomes low as the beam incidence angle is away from the zone axis by a few degrees. **Figure 13** confirms that the X-ray generation is sensitive to the incident angle around the zone axis condition.

2. Formulation for site occupancy

There are equations proposed for the site occupancy determination on the basis of the premises associated with the antisite occupation of host elements⁽³²⁾⁽³⁴⁾⁻⁽³⁹⁾.

Fig. 13 X-ray intensities with respect to tilt angle obtained in the Ni-21 mol%Al-4 mol%Ta alloy. The zero tilt angle corresponds to the beam incidence parallel to the exact [111] zone axis.

However, rather than reviewing these equations, this section presents a general form of an equation which can encompass all equations developed under different premises⁽⁴⁰⁾.

Consider the sample composed of elements A, B, C, ... where elements A and B represent the host elements and C, D, ... the alloying elements. Furthermore, the sample has a crystal structure consisting of sites α and β where site α is the preferential site of element A and site β is that of element B.

Denote $I_i^{(d)}$ the characteristic X-ray intensity of element i ($i=A, B, C, \dots$) at a dynamical (or channeling) diffraction condition. Thus, $I_i^{(d)}$ is expressed by the form of

$$I_i^{(d)} = k_i x_i \sum C_{i/r} I_r^{(d)} \quad (27)$$

where k_i is the factor representing the X-ray generation and absorption of element i , x_i is the atomic fraction of element i , $C_{i/r}$ is the fraction of element i on lattice plane or atom column r ($r=a, b, c, \dots$), and $I_r^{(d)}$ is the thickness-averaged intensity of incident electrons on plane or column r at a dynamical diffraction condition.

The fraction $C_{i/r}$ is represented as

$$C_{i/r} = \Phi_{i/\alpha} \phi_{\alpha/r} + \Phi_{i/\beta} \phi_{\beta/r} \quad (28)$$

where $\Phi_{i/\alpha}$ and $\Phi_{i/\beta}$ are the fractions of elements i on sites α and β , respectively, which are defined as the site occupancies, and $\phi_{\alpha/r}$ and $\phi_{\beta/r}$ are the fractions of sites α and β on plane or column r , respectively. Here, the following equalities are preserved:

$$\sum x_i = 1, \sum C_{i/r} = 1, \sum \phi_{\alpha/r} = 1, \sum \phi_{\beta/r} = 1, \quad \text{and} \quad \Phi_{i/\alpha} + \Phi_{i/\beta} = 1. \quad (29)$$

Table 1 shows the values of $\phi_{\alpha/r}$ and $\phi_{\beta/r}$ ($r=a, b$) for some lattice planes in B2, L1₀, L1₂ and Spinel types of crystal structures⁽⁴⁰⁾.

At the kinematical (non-channeling) diffraction condition, the distribution of incident electrons is homogeneous so that $I_r^{(k)} = I^{(k)}$ and the X-ray intensity is given as

$$I_i^{(k)} = k_i x_i I_r^{(k)} \quad (30)$$

Defining $R_i^{(d)} \equiv I_i^{(d)} / I_i^{(k)}$, the following equation is derived

$$\Phi_{i/\alpha} = \Phi_{j/\alpha} + (q_\alpha - \Phi_{j/\alpha})(R_i^{(d)} - R_j^{(d)}) / \sum x_m (R_m^{(d)} - R_j^{(d)}) \quad (31)$$

where $q_\alpha \equiv \sum x_m \Phi_{m/\alpha}$ and is the total fraction of site α in the unit cell. Table 1 includes the values of q_α for the corresponding crystal structures.

(1) No antisite occupation of host elements

When the host elements A and B are not presents at the antisites but at their own sublattices as considered by Spence and Taftø⁽³²⁾, it follows that $\Phi_{A/\alpha} = 1$ and $\Phi_{B/\alpha} = 0$. Based on this premise, eq. (31) reduces to

$$\Phi_{i/\alpha} = (R_i^{(d)} - R_B^{(d)}) / (R_A^{(d)} - R_B^{(d)}). \quad (32)$$

Equation (32) does not include q_α and thus, $\Phi_{i/\alpha}$ can be determined being independent of the crystal structure.

Goo⁽³⁵⁾ and Bentley⁽³⁶⁾ independently derived the same form as eq. (32). However, the equation derived by Spence and Taftø⁽³²⁾ contains the terms obtained at the two channeling conditions corresponding to positive and negative excitations other than a non-channeling condition. This is understood from the following relationship:

$$I_i^{(k)} = \{ I_i^{(d1)} (R_B^{(d2)} - R_A^{(d2)}) - I_i^{(d2)} (R_B^{(d1)} - R_A^{(d1)}) \} / (R_A^{(d1)} R_B^{(d2)} - R_A^{(d2)} R_B^{(d1)}) \quad (33)$$

Hence, Spence and Taftø⁽³²⁾ used the right hand side of eq. (33) for $I_i^{(k)}$ in eq. (32). Here, the superscripts d1 and d2 represent the positive and negative excitations.

(2) One host element occupying the antisite

Shindo *et al.*⁽³⁷⁾ considered the case where a host element with the fraction greater than the stoichiometry occupies the antisite but that with the fraction less than the stoichiometry does not occupy the antisite. If element A is the one with the fraction less than the stoichiometry, then $\Phi_{A/\alpha} = 1$ and eq. (31) reduces to

$$\Phi_{i/\alpha} = 1 + (q_\alpha - 1)(R_i^{(d)} - R_j^{(d)}) / \sum x_m (R_m^{(d)} - R_j^{(d)}). \quad (34)$$

Table 1 Fractions of given crystal structures.

Crystal structure	Plane parallel to beam direction			$\phi_{\alpha/a}$	$\phi_{\alpha/b}$	$\phi_{\beta/a}$	$\phi_{\beta/b}$	q_α	q_β
B2	(100)	(010)	(001)	1	0	0	1	1/2	1/2
L1 ₀	(001)	(110)		1	0	0	1	1/2	1/2
L1 ₂	(001)	(110)		1	0	1/3	2/3	1/4	3/4
Spinel*	(100)	(010)	(001)	1	0	0	1	1/3	2/3

* For cations only.

Fig. 14 Al site occupancy of Fe, $\Phi_{\text{Fe/Al}}$, in B2-type NiAl intermetallics where 5 mol% Fe is contained with varying fractions of Al to Ni concentration, $C_{\text{Al}}/C_{\text{Ni}}$.

It is now shown that $\Phi_{i/\alpha}$ can be determined with knowledge of q_α and by measuring $R_i^{(d)}$ ($i = \text{B, C, } \dots$). Although Shindo *et al.*⁽³⁷⁾ introduced an equation for the determination of $\Phi_{i/\alpha}$, it required formulation of an equation pertinent to a crystal structure concerned. It also required iterative calculation to obtain $\Phi_{i/\alpha}$.

Figure 14 shows the Al site occupancy of Fe, $\Phi_{\text{Fe/Al}}$, in B2-type NiAl intermetallics where 5 mol% Fe is contained with varying fractions of Al to Ni concentration, $C_{\text{Al}}/C_{\text{Ni}}$. Each specimen was illuminated nearly parallel to Al and Ni planes at (100) systematic diffraction conditions. The values of $\Phi_{\text{Fe/Al}}$ were obtained using eq. (34). For Ni-rich compositions ($C_{\text{Al}}/C_{\text{Ni}} < 1$), Fe tends to occupy the Al site, but the occupancy decreases to $\sim 50\%$ at the stoichiometric composition ($C_{\text{Al}}/C_{\text{Ni}} = 1$). For Al-rich compositions ($C_{\text{Al}}/C_{\text{Ni}} > 1$), it is to be anticipated that the occupancy further decreases below 50%. Thus, the results conclude that Fe can stay at both Al and Ni sites irrespective of the difference in site.

(3) No limitation on the antisite occupation

Matsumura *et al.*⁽³⁹⁾ introduced the structure factor into the site occupancy determination and thus, no limitation was placed on the antisite occupation of the host elements.

Denoting η_i as the long-range order parameter of element i , $\Phi_{i/\alpha}$ and $\Phi_{i/\beta}$ are related to η_i as $\Phi_{i/\alpha} = q_\alpha + \eta_i$ and $\Phi_{i/\beta} = q_\beta - \eta_i$. Here, q_β is the fraction of site β in the unit cell, fulfilling $q_\alpha + q_\beta = 1$ and $-q_\alpha \leq \eta_i \leq q_\beta$. Table 1 includes the values of q_β together with q_α . Equation (31) then reduces to the following form derived by Matsumura *et al.*⁽³⁹⁾

$$P_{ij} = 1 - (R_i^{(d)} - R_j^{(d)}) / \sum x_m (R_m^{(d)} - R_j^{(d)}). \quad (35)$$

where $P_{ij} \equiv \eta_i / \eta_j$. Since the structure factor contains the terms of η_j and P_{ij} , it is possible to solve for η_j by measuring a structure factor and by knowing P_{ij} from eq. (35).

3. Delocalization effect

The formulation of the equation for the site-occupan-

cy determination given above is based on the premise that the production of all characteristic X-rays occurs at the atom center⁽³²⁾. However, there is an effective range from the atom center for the X-ray production⁽³⁸⁾. This range is termed the impact parameter. Whereas the production occurs within a range close to the atom center for high-energy X-rays, the production range extends away from the atom center for low-energy X-rays.

Figure 15 shows the X-ray intensity ratios with respect to tilt angle obtained in a Ni-7 mol%Al-3 mol%Ti alloy having a disordered structure⁽⁴¹⁾. The zero tilt angle indicates the beam incidence parallel to the exact [111] zone axis. There are appreciable differences between the intensity ratios at the exact zone axis and a few degrees away from the zone axis. Since all elements are located randomly in the disordered structure, the X-ray intensity ratios should be the same for any diffraction condition. However, the intensity ratio is appreciably lower for the exact zone axis condition corresponding to the channeling diffraction condition than the other conditions corresponding to the non-channeling diffraction condition. Therefore, the change in the intensity ratio with orientation is due to the difference between the effective range of the X-ray production. This difference introduces an error in the site occupancy determination and should be corrected for reliable determination⁽³⁸⁾. This error is referred to as the delocalization effect. The effect is more significant when the beam incidence made along a zone axis than for lattice planes⁽⁴²⁾⁽⁴³⁾.

In order to take the delocalization effect into account in the formulation for the site-occupancy determination, it was shown⁽⁴⁴⁾ that the term $R_i^{(d)}$ in all equations presented in Section IV-2 should be replaced by $(R_i^{(d)} - 1) / \lambda_i$. Here, λ_i is the factor representing the extent of delocalization effect. This factor is equivalent to the delocalization correction factor introduced by Pennycook⁽³⁸⁾. It was suggested that this correction factor can be determined by comparison with the site occupancy obtained from ion-channeling experiments⁽³⁸⁾, by measuring two characteristic lines emitted from the same element⁽³⁶⁾⁽³⁸⁾ or by calculating an electron density distribution around the atom core⁽³⁸⁾⁽⁴⁵⁾.

Fig. 15 X-ray intensity ratios with respect to tilt angle obtained in a Ni-7 mol%Al-3 mol%Ti alloy having a disordered structure⁽⁴¹⁾.

There are also other attempts to correct or minimize the delocalization effect. First, the effect was corrected through correction factors obtained from the ratios of two characteristic X-ray lines from the different elements in a disordered structure⁽⁴¹⁾. Second, the effect was minimized by reducing the operating voltage⁽⁴⁶⁾ as the low energy electron involves less delocalization effect⁽³⁸⁾. Third, an alternative method called a multivariate statistical analysis technique was proposed for the site occupancy determination^{(47)–(49)}, which was claimed to suffer from a less delocalization effect⁽⁴⁷⁾. However, none of the correction procedures seems general and further development is required for the delocalization correction.

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REFERENCES

- (1) P. Duncumb: *Proc. Symp. on X-ray Optics and X-ray Microanalysis*, Stanford, (1963), p. 431.
- (2) G. Cliff and G. W. Lorimer: *Proc. 5th European Congr. on Electron Microscopy, Manchester, 1972*, Inst. Phys., London-Bristol, (1972), p. 140.
- (3) G. Cliff and G. W. Lorimer: *J. Microscopy*, **103** (1975), 203.
- (4) D. B. Williams: *Practical Analytical Electron Microscopy in Materials Science, Chapter 4*, Philips Electron Optics Publishing Group, Mahwah, New Jersey, (1984), p. 55.
- (5) Z. Horita, T. Sano and M. Nemoto: *ISIJ International*, **29** (1989), 179.
- (6) J. I. Goldstein, J. L. Costley, G. W. Lorimer and S. J. B. Reed: *Scanning Electron Microscopy/1977*, Vol. I, Ed. by O. Johari, IITRI, Chicago, IL, (1977), p. 315.
- (7) L. E. Thomas: *Ultramicroscopy*, **18** (1985), 173.
- (8) J. E. Wood, D. B. Williams and J. I. Goldstein: *J. Microscopy*, **133** (1984), 255.
- (9) L. E. Thomas: *Proc. 38th Ann. Meeting of the Electron Microscopy Society of America*, Ed. by G. W. Bailey, Claitor's Pub. Div., Balton Rouge, (1980), p. 90.
- (10) G. Cliff, D. M. Maher and G. W. Lorimer: *J. Microscopy*, **136** (1984), 219.
- (11) D. B. Williams, J. I. Goldstein and C. E. Fiori: *Principles of Analytical Electron Microscopy*, Ed. by D. C. Joy, A. D. Romig, Jr. and J. I. Goldstein, Plenum Press, New York, (1986), p. 123.
- (12) S. Mehta, J. I. Goldstein, D. B. Williams and A. D. Romig, Jr.: *Microbeam Analysis*, Ed. by D. E. Newbury, San Francisco Press, San Francisco, (1979), p. 119.
- (13) G. Wirmark, T. Thorvaldsson and H. Norden: *Electron Microscopy and Analysis 1983*, Inst. Phys. Conf. Ser. No. 68, Ed. by P. Doig, Inst. Physics, Bristol and London, (1983), p. 71.
- (14) E. Metcalfe and J. P. Broomfield: *Electron Microscopy and Analysis 1983*, Inst. Phys. Conf. Ser. No. 68, Ed. by P. Doig, Inst. Physics, Bristol and London, (1983), p. 75.
- (15) A. D. Romig, Jr.: *J. Microscopy*, **135** (1984), 191.
- (16) Z. Horita, T. Sano and M. Nemoto: *Bull. Japan Inst. Metals*, **28** (1989), 742.
- (17) D. B. Williams: Abstract of the Asian Science Seminar in Kyushu University, March 16–22, (1997).
- (18) Z. Horita, T. Sano and M. Nemoto: *J. Electron Microsc.*, **35** (1986), 324.
- (19) Z. Horita, T. Sano and M. Nemoto: *Ultramicroscopy*, **21** (1987), 271.
- (20) Z. Horita, T. Sano and M. Nemoto: *Ultramicroscopy*, **35** (1991), 27.
- (21) Z. Horita, M. R. McCartney and J. K. Weiss: *Ultramicroscopy*, **45** (1992), 263.
- (22) P. L. Morris, M. D. Ball and P. J. Statham: *Electron Microscopy and Analysis 1979*, Inst. Phys. Conf. Ser. No. 52, Ed. by T. Mulvey, Inst. Physics, Bristol and London, (1980), p. 413.
- (23) Z. Horita, K. Ichitani, T. Sano and M. Nemoto: *Phil. Mag.*, **A 59** (1989), 939.
- (24) M. Watanabe, Z. Horita and M. Nemoto: *Ultramicroscopy*, **65** (1996), 187.
- (25) M. Watanabe, Z. Horita, T. Sano and M. Nemoto: *Acta Metall. Mater.*, **42** (1994), 3389.
- (26) L. S. Birks and J. Criss: *Handbook of Spectroscopy*, CRC Press, Boca Raton, Florida, (1981).
- (27) K. F. J. Heinrich: *Proc. 11th Int. Congr. on X-Ray Optics and Microanalysis*, Ed. by J. D. Brown and R. H. Packwood, University of Western Ontario, Canada, (1986), p. 67.
- (28) M. Watanabe, Z. Horita and M. Nemoto: *Proc. 54th Annual Meeting of MSA, 30th Annual meeting of MAS and 23rd Annual Meeting of MSC*, Ed. by G. W. Bailey, J. M. Corbett, R. V. W. Dimlich, J. R. Michael and N. J. Zaluzec, San Francisco Press, San Francisco, (1996), p. 580.
- (29) P. B. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley and M. J. Whelan: *Electron Microscopy of Thin Crystals*, Butterworths, London, (1965), p. 415.
- (30) V. D. Scott and G. Love: *Mater. Sci. Technol.*, **3** (1987), 600.
- (31) P. M. Kelly, A. Jostsons, R. G. Blake and J. G. Napier: *Phys. Status Solidi (a)*, **31** (1975), 771.
- (32) J. C. H. Spence and J. Taftø: *J. Microsc.*, **130** (1983), 147.
- (33) Z. Horita, M. R. McCartney and H. Kuninaka: *Phil. Mag.*, **A 75** (1997), 153.
- (34) J. Taftø: *J. Appl. Crystallogr.*, **15** (1982), 378.
- (35) E. Goo: *Appl. Phys. Lett.*, **48** (1986), 1779.
- (36) J. Bentley: *Proc. 11th Inter. Cong. Electron Microscopy*, Vol. 1, Ed. by T. Imura, S. Maruse and T. Suzuki, Japanese Society of Electron Microscopy, Tokyo, (1986), p. 551.
- (37) D. Shindo, M. Hirabayashi, T. Kawabata and M. Kikuchi: *J. Electron Microsc.*, **35** (1986), 409.
- (38) S. J. Pennycook: *Ultramicroscopy*, **26** (1988), 239.
- (39) S. Matsumura, T. Morimura and K. Oki: *Mater. Trans.*, **JIM**, **32** (1991), 905.
- (40) Z. Horita, S. Matsumura and T. Baba: *Ultramicroscopy*, **58** (1995), 327.
- (41) Z. Horita, H. Kuninaka, T. Sano, M. Nemoto and J. C. H. Spence: *Phil. Mag.*, **A 67** (1993), 425.
- (42) J. C. H. Spence, M. Kuwabara and Y. Kim: *Ultramicroscopy*, **26** (1988), 103.
- (43) K. M. Krishnan: *Mater. Sci. Eng.*, **B 3** (1989), 397.
- (44) Z. Horita: *Ultramicroscopy*, **66** (1996), 1.
- (45) Y. Ma and J. Gjønnes: *J. Mater. Res.*, **7** (1992), 2049.
- (46) P. R. Munroe and I. Baker: *J. Mater. Res.*, **6** (1992), 943.
- (47) C. J. Rossouw, P. S. Turner, T. J. White and A. J. O'Connor: *Phil. Mag. Lett.*, **60** (1989), 225.
- (48) M. G. Walls: *Microsc. Microanal. Microstruct.*, **3** (1992), 443.
- (49) I. M. Anderson and J. Bentley: *Proc. 13th Inter. Cong. Electron Microscopy*, Vol. 1, Ed. by B. Joffrey and C. Colliex, Les Editions de Physique, Les Ulis, (1994), p. 609.