Quantitative Electron Probe Microanalysis of Thin Films*

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A new method for analysis of thin films by electron microprobe technique is proposed. This method is characterized by the determination of the thickness of thin films together with its chemical compositions.

Results obtained to data through the use of this method have been fairly good; being the accuracy of the order of 10% in determination of film thickness and of the order of 5% in quantitative analysis of constituent elements.

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I. Introduction

Surface films thicker than a micron are usually analysed by conventional microprobe technique: the principle of quantitative analysis with the electron probe microanalyser is based on the assumption that the constituent element in a given sample is distributed randomly making solid solution. However, to make a quantitative analysis or estimate of the thickness of a film thinner than the electron penetration depth it is necessary to take account of the behavior of incident electrons and emitted X-rays in the specimen. Some researchers have tried to make use of calibration curves for thickness determination based on the electron excitation curves, and Colby proposed a method of quantitative analysis of thin film with known thickness. Reuter has calculated the ionization function with metals covering a wide range of primary energies, and determined their film thickness.

The purpose of the present study is to discuss the factors involved in quantitative analysis of thin film composed of multicomponents and to establish a method of obtaining its thickness together with the chemical composition.

II. Determination of the Film Thickness and Its Chemical Composition

The concentration of an element A in a given sample, C_A , will be deduced by the following relation:

$$k_A = g \cdot C_A \quad (1')$$

where $k_A = I_A^S/I_A^A$: the ratio of the intensity, I_A^S , of the characteristic radiation emitted from element A in the sample to the intensity, I_A^A , of the same characteristic radiation emitted from pure element A under the same condition, and g is a correction factor depending on the kind of element, the relative intensity of the characteristic radiation and the geometrical condition of measurement. In practice, it is convenient to use the following relation instead of eq. (1)':

$$C_A = G_A^S(k_A) \cdot k_A. \quad (1)$$

Correction factor $G_A^S(k_A)$ is considered to be composed of the main three terms, namely, absorption, atomic number and fluorescence corrections and is given as follows:

$$G_A^S(k_A) = G_A^a(k_A) \cdot G_A^Z(k_A) \cdot G_A^f(k_A), \quad (2)$$

where G_A^a , G_A^Z , and G_A^f , are the correction terms for absorption, atomic number and fluorescence, respectively.

The intensity of characteristic X-ray radiation emitted from a constituent element A declines due to the absorption by the sample

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itself. The correction term for the absorption was given by Castaing⁽³⁾ as:

$$G_A^a(k_A) = \frac{\int_0^\infty \phi(\bar{\rho}x) \cdot \exp(-\bar{\mu}_A \cdot \bar{\rho} \cdot x \cdot \operatorname{cosec} \theta) d(\bar{\rho}x)}{\int_0^\infty \phi(\rho_A x) \cdot \exp(-\mu_A^A \cdot \rho_A \cdot x \cdot \operatorname{cosec} \theta) d(\rho_A x)}, \quad (3)$$

where ρ_A : specific density of pure element A

x : depth from the surface

θ : X-ray take-off angle

μ_A^j : mass absorption coefficient of j for the characteristic radiation from element A

$$\bar{\mu}_A = \sum_{j=A}^N C_j \cdot \mu_A^j.$$

Castaing obtained experimentally the electron excitation function $\phi(\rho x)$ for various element at an operating voltage of 29 kV. According to his results, $\phi(\rho x)$ is a function of ρx but varies only slightly with the atomic number ranging from $Z=13$ to 79. In general, the average specific density of a given sample may approximately be given as $\bar{\rho} = \sum_{j=A}^N C_j \rho_j$, provided the sample is in the state of solid solution.

The correction term for the atomic number may be expressed as⁽⁴⁾⁽⁵⁾

$$G_A^n(k_A) = \frac{\bar{R}}{R_A} \cdot \frac{S_A}{\bar{S}}, \quad (4)$$

where R_A , $\bar{R}$: back scattering coefficient of A and sample, respectively

S_A , $\bar{S}$: stopping power of element A and specimen.

The fluorescence arises from both the continuous spectrum and the hard component of the characteristic radiation, the contribution of the former being generally smaller than that of the latter⁽⁵⁾. The correction for the fluorescence was given by⁽⁶⁾

$$G_A^f(k_A) = \frac{1}{1 + I_f/I_A^S}.$$

III. Characteristic X-ray Radiation Emitted from the Surface Film on the Substrate

Characteristic X-ray radiation emitted from the surface film may be divided into the following three groups: (1) those that are excited

directly by the incident beam, (2) those that are excited by electrons back-scattered from the substrate, and (3) those that are excited by X-rays from the coexisting heavier elements in the sample (fluorescence).

X-ray intensity emitted from element A in the surface film relating to the above items (1) and (2) is written from eqs. (3) and (4) as:

$$I_1(A) = C_A \cdot \frac{\bar{R}_F}{\bar{S}_F} \cdot \int_0^{\bar{\rho}_F t} \phi(\bar{\rho}_F x) \times \exp(-\bar{\mu}_A^F \cdot \bar{\rho}_F \cdot x \cdot \operatorname{cosec} \theta) d(\bar{\rho}_F x), \quad (5)$$

where $\bar{\rho}_F$: average specific density of the surface film. t : thickness of film. $\bar{R}_F$ and $\bar{S}_F$, back scattering coefficient and stopping power of the film, respectively, are obtained by Duncumb and Reed⁽⁴⁾ and Springer⁽⁵⁾ as functions of atomic number and over voltage ratio.

In general, the constituent elements of the substrate are different from those of the surface film. Therefore, it is necessary to take account of the effect of the electrons back-scattered from the substrate on the surface film. The correction for this is then given by integrating over the range from $\bar{\rho}_F t$ to $2\bar{\rho}_F t$ as:

$$I_2(A) = C_A \cdot \frac{\bar{R}_F}{\bar{S}_F} (\bar{\eta}_s - \bar{\eta}_F) \cdot \int_{\bar{\rho}_F t}^{2\bar{\rho}_F t} \phi(\bar{\rho}_F x) \times \exp\{-\bar{\mu}_A^F \cdot \bar{\rho}_F \cdot (2t - x) \cdot \operatorname{cosec} \theta\} d(\bar{\rho}_F x) \quad (6)$$

where $\bar{\eta}_F = \sum_{j=A}^N C_j \eta_j$ and $\bar{\eta} = \sum_{i=a}^n C_i \eta_i$ shows fraction of electron⁽⁷⁾ backscattered from film and substrate, respectively, and $A, B, \dots, N$ and $a, b, \dots, n$ denote constituent elements of film and substrate, respectively. X-ray radiation emitted from a given sample relating to the first two items is thus expressed as the sum of eqs. (5) and (6).

The excitation of element A by characteristic radiation from constituent element j which is related to item (3) may be given by multiplying the excitation efficiency, Q_A^x , by the intensity of X-rays as:

$$I_3(A) = C_A \cdot \sum_{j=A}^N \gamma_A^j \cdot Q_A^j \cdot I(j) + C_A \cdot \sum_{i=a}^n \gamma_A^i \cdot Q_A^i \cdot I(i) \quad (7)$$

$$I(x) = I_1(x) + I_2(x)$$

where $\gamma_A^x = 0.5^{(6)}$ when the energy of character-

istic X-rays in element A is lower than that of the constituent element j , and $\gamma_A^x = 0$ when the energy of characteristic X-rays in element A is higher than that of j . $I_1(x)$ and $I_2(x)$ is given by eqs. (5) and (6), respectively.

In practice, the thickness of the surface film is usually very thin so that the X-ray excitation function relating to item (3) may approximately be taken as a function of the absorption, because the energy of characteristic X-ray radiation is constant depending on the wave-length. Then, the contribution to the production of X-rays from the thin layer is written by

$$\frac{\int_0^{\bar{\rho}_F t} \exp(-\bar{\mu}_A^F \cdot \bar{\rho}_F \cdot x \cdot \text{cosec } \theta) d(\bar{\rho}_F x)}{\int_0^\infty \exp(-\mu_A^A \cdot \rho_A \cdot x \cdot \text{cosec } \theta) d(\rho_A x)} = \{1 - \exp(-\bar{\mu}_A^F \cdot \bar{\rho}_F \cdot t \cdot \text{cosec } \theta)\}. \quad (8)$$

By considering eqs. (7) and (8), the fluorescence X-rays from element A in the surface film is expressed as

where

$$k_A = \frac{C_A}{G_A^F(k_A)} = \frac{S_A}{R_A} \cdot \frac{\{I_1(A) + I_2(A)\} \times (1 + I_f^F)}{\int_0^\infty \phi(\rho_A x) \cdot \exp(-\mu_A^A \cdot \rho_A \cdot x \cdot \text{cosec } \theta) d(\rho_A x)} \quad (12)$$

IV. X-ray Radiation Emitted from the Constituent Element of the Substrate

X-ray radiation emitted from an element a in the substrate is considered to be composed of the following groups: (1) X-rays excited directly by incident electrons, (2) X-rays excited by electrons scattered by the constituent ele-

$$I_4(A) = C_A \left\{ \sum_{j=A}^N \gamma_A^j \cdot Q_A^j \cdot I(j) + \sum_{i=a}^n \gamma_A^i \cdot Q_A^i \cdot I(i) \right\} \times \{1 - \exp(-\bar{\mu}_A^F \cdot t \cdot \text{cosec } \theta)\}. \quad (9)$$

Then, the correction for the fluorescence is given by

$$I_f^F = \frac{I_4(A)}{C_A \cdot I(A)}. \quad (10)$$

The fluorescence effect is only an important factor when the coexisting elements are close to element A but larger in atomic number. However, even in such a case its intensity is only about 5% compared with that excited directly by the incident electrons. Therefore, the fluorescence effect would generally be neglected.

X-ray intensity to be measured practically is finally given as the following equation in comparison with the intensity obtained from pure element:

$$k_A = C_A \cdot \frac{1}{G_A^F(k_A)} \quad (11)$$

ments of surface film and (3) X-rays excited by the fluorescence X-rays.

Characteristic X-ray radiation emitted from element a of the substrate is diminished by the surface film as the radiation travels towards the surface by $\exp(-\bar{\mu}_a^F \cdot \bar{\rho}_F \cdot t \cdot \text{cosec } \theta)$. By assuming that the substrate is of a homogeneous structure the X-rays emitted from element a may be written by

$$I_1(a) = C_a \frac{\bar{R}_s}{\bar{S}_s} \cdot \exp(-\bar{\mu}_a^F \cdot \bar{\rho}_F \cdot t \cdot \text{cosec } \theta) \cdot \int_{\bar{\rho}_F t}^\infty \phi(\bar{\rho}_s x) \cdot \exp(-\bar{\mu}_a^s \cdot \bar{\rho}_s \cdot x \cdot \text{cosec } \theta) \cdot d(\bar{\rho}_s x), \quad (13)$$

where the constituent element a exists below the depth, t , from the surface.

The constituent elements of the surface film are usually different from those of the substrate.

Therefore, it is necessary to take account of the behavior of the incident electrons at their interface; the correction for this then given by

$$I_2(a) = C_a \frac{\bar{R}_s}{\bar{S}_s} \cdot (\bar{\eta}_s - \bar{\eta}_F) \cdot \exp(-\bar{\mu}_a^F \cdot \bar{\rho}_F \cdot t \cdot \text{cosec } \theta) \cdot \int_{\bar{\rho}_F t}^\infty \phi(\bar{\rho}_s x) \cdot \exp\{-\bar{\mu}_a^s \cdot \bar{\rho}_s \cdot x \cdot \text{cosec } \theta\} d(\bar{\rho}_s x). \quad (14)$$

The fluorescence effect of the element in the substrate is given in the same way as eq. (9):

$$I_4(a) = C_a \cdot \exp(-\bar{\mu}_a^F \cdot \bar{\rho}_F \cdot t \cdot \csc \theta) \times \left\{ \sum_{j=A}^N \gamma_a^j \cdot Q_a^j \cdot I(j) + \sum_{i=a}^n \gamma_a^i \cdot Q_a^i \cdot I(i) \right\}. \quad (15)$$

Then, the correction for the fluorescence is

$$k_a = \frac{C_a}{G_a^F(k_a)} = \frac{S_a}{R_a} \cdot \frac{\{I_1(a) + I_2(a)\} \times (1 + I_f^s)}{\int_0^\infty \phi(\rho_a x) \cdot \exp(-\mu_a^a \cdot \rho_a \cdot x \cdot \csc \theta) d(\rho_a x)} \quad (16)$$

where

$$\sum_{j=A}^N C_j = 1, \quad \sum_{i=a}^n C_i = 1. \quad (17)$$

Equations (11) and (16) correspond to the number of constituent element of the sample. Using these equations one can calculate the thickness of the surface film together with the concentration of each constituent element. These equations were evaluated for different thickness and chemical compositions in some alloy films, as shown later.

V. Comparison with Experimental Results

1. Estimation of thickness of Fe-Ni alloy films

The present method of estimating film thickness and its chemical composition was applied to Fe-Ni alloy vacuum-deposited on a silica plate.

The specimens were prepared by vacuum deposition of Fe and Ni on a silica plate preheated at 350°C, then annealed at 800°C for 30 min. Chemical analysis showed that the composition was Fe-6.1%Ni. The thickness of the film was previously determined by using a

given by

$$I_f^s = \frac{I_4(a)}{C_a \cdot I(a)}.$$

Finally, the total intensity emitted from element *a* in the substrate is obtained as the comparison with that of pure element *a*:

multiple beam interferometer, and the result obtained was used as a standard of comparison. The electron probe X-ray microanalyser was operated at 30 kV with 52.5° in X-ray take-off angle. The effective area irradiated was taken to be about 30 diameter.

Table 1 shows the result of the analysis together with the result obtained by using the multiple beam interferometer, in which the chemical compositions denoted by "measured" are values calculated directly from the raw data, and the values denoted by "corrected" are corrected values by applying the proposed method. It is seen from this table that the value of the film thickness estimated from the proposed method fits neatly to the result obtained from the interferometer.

2. Case of Ag-Cu alloy films produced by sputtering on plate of Fe-Ni alloy

A plate of Fe-Ni alloy polished mechanically was used as the substrate. The concentration of alloying element was determined by chemical analyses and turned out to be Fe-25%Ni, Ag-91.5%Cu and Ag-49.5%Cu, respectively. The homogeneity of the alloy was confirmed by using the electron probe microanalyser.

Table 2 lists the results of analyses, in which

Table 1 Thickness determination of Fe-Ni alloy film and its chemical composition.

Specimen	Chemical composition				Thickness	Thickness
	Measured		Corrected		EPMA	MBI
	Fe	Ni	Fe	Ni		
A	9.9%	0.5%	93.6%	6.4%	1200 Å	1100 Å

Table 2 Thickness determination of Cu-Ag alloy films on Fe-Ni alloy and their chemical compositions.

Specimen		Chemical composition				Thickness
		Ag	Cu	Fe	Ni	MBI
A	Measured	56.2%	6.1%	26.1%	8.6%	4800 Å
	Corrected I	62.9%	5.8%	26.2%	8.3%	EPMA
	Corrected II	90.8%	9.2%	75.3%	24.7%	4700 Å
B	Measured	2.3%	1.8%	76.8%	24.4%	MBI
	Corrected I	2.9%	2.3%	72.9%	29.3%	400 Å
	Corrected II	51.0%	49.0%	74.3%	25.7%	EPMA 420 Å

"corrected I" is the result corrected by using conventional microprobe technique and "corrected II" the result after the correction by using the proposed method. It is seen from this table that the results obtained agree well with those obtained by the interferometer, within the range of about 10%.

3. Thin layer of Sn in Al-Sn bearing metal

The proposed method may be applied to films as thin as several ten Å, depending on the kind of constituent elements. The present authors⁽⁸⁾ have investigated the surface film of Al-6wt%Sn alloy formed during friction. Solubility limit of Sn in Al is known to be 0.04% (weight)⁽⁹⁾. However, electron microprobe analysis of the surface after friction showed to turn out to be 0.18%, showing a homogeneous distribution. This result suggests a formation of thin film of Sn on the surface during the friction. The film thickness was determined by applying this method, and the result showed an existence of a very thin layer of Sn, the thickness being of the order of several ten Å.

VI. Summary

A new method for the determination of film

thickness together with its chemical composition has been developed.

This method was applied to analyse various thin metal and alloy films. It was shown that films thinner than the penetration depth of incident electrons could be analysed with sufficient accuracy: the relative error is written about 10% for their thickness determination and about 5% for the determination of their chemical composition.

REFERENCES

- (1) J. W. Colby: *Advance in X-ray analysis*, Plenum Press, New York., 11 (1967), 287.
- (2) W. Reuter: *X-ray Optics and Microanalysis*, University of Tokyo Press, (1972), p. 121.
- (3) R. Castaing: *Advance in electronics and electron physics*, Academic Press, (1980), p. 317.
- (4) P. Duncumb and S. J. B. Reed: *Quantitative electron probe microanalysis*, National Bureau of Standard Special Publication, (1966), p. 133.
- (5) G. Springer: *X-ray Optics and Microanalysis*, Boulerard Saint-German Paris, (1965), p. 296.
- (6) S. B. J. Reed: *British J. Appl. Phys.*, 16 (1965), 913.
- (7) H. E. Bishop: *Optique des Rayons-X et Microanalysis*, Herman, Paris, (1967).
- (8) Y. Oda, Y. Mizutani and K. Nakajima: *J. Japan Inst. Metals*, 36 (1972), 859.
- (9) R. P. Elliot: *Constitution of Binary Alloys*, First Supplement, McGraw-Hill Book Co., New York, (1965), p. 56.