On the Estimation of Alloy Film Thickness by X-Ray Fluorescent Spectroscopy

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For the simultaneous determination of alloy film thickness and its composition, several methods in which experimental equations were employed have been proposed.[1-3] In the present report it shall be shown that thickness of a binary alloy film can be easily obtained with two experimental absorption parameters, when the composition of the film is known.

Usually the X-ray intensity from a film of thickness z is given by Eq. (1),

$$I_z=\int_{\lambda_{\min}}^{\lambda_{\rm edge}}\int_0^z\frac{I_0(\lambda)\rho_jQ(\lambda)}{\sin\beta}\cdot \exp\left\{-\left(\frac{\sum\mu^j{}_{(\lambda)}W_j}{\sin\alpha}+\frac{\sum\mu^j{}_fW_j}{\sin\beta}\right)z\right\}{\rm d}z\cdot{\rm d}\lambda \quad (1)$$

where α is the incident angle of primary X-rays; β is the emergent angle of fluorescent X-rays; $Q(\lambda)=\mu_j/\rho_jW_jK_jw_jR_p{}^j$ (μ_j/ρ_j is the mass absorption coefficient of element j; W_j is the weight fraction of element j; K_j is the term $(r_j-1)/r_j$ in which r_j is the ratio of absorption coefficient at the K discontinuity, *i.e.*, r_j is the K jump for j : w_j is the fluorescent yield of j; $R_p{}^j$ is the intensity ratio of the measured p line of element j, which belongs to the K series, to the total intensity of K lines, *i.e.*, the fraction of the measured p line in the characteristic X-ray series which the p line belongs to); $\mu^j{}_{(\lambda)}$ is the absorption coefficient of j for the incident ray of wavelength λ; $\mu_f{}^j$ is the absorption coefficient of j for the fluorescent beam; $I_0(\lambda)$ is the primary X-ray intensity; I_z is the X-ray intensity from a film of thickness z; ρ_j is the density of the element j.

To obtain an exact expression for fluorescent X-ray intensity, of course, Eq. (1) must be integrated with respect to the wavelength λ, together with respect to thickness z. However, if we assume that $I_0(\lambda)$ and $\mu_{(\lambda)}$ are constant at the definite experimental condition,[4] the approximate expression for the intensity ratio of X-rays from a film to that from the bulk sample with a constant composition A_j is given by Eq. (2):

$$-\ln\left(1-\frac{I_z{}^{A_j}}{I_\infty{}^{A_j}}\right)=\left(\frac{\sum\mu_i{}^{A_j}W_{A_j}}{\sin\alpha}+\frac{\sum\mu_A{}^{A_j}W_{A_j}}{\sin\beta}\right)z \quad (2)$$

The approximate X-ray intensity ratio of an element A in an alloy film to the pure element A can be also obtained by Eq. (3),

$$-\ln\left(1-\frac{\rho_{AA}}{\rho_{Aj}}\cdot\frac{1}{W_A}\cdot\frac{I_z{}^A}{I_\infty{}^A}\cdot\frac{\dfrac{\sum\mu_i{}^AW_A}{\sin\alpha}+\dfrac{\sum\mu_A{}^AW_A}{\sin\beta}}{\dfrac{\mu_i{}^A}{\sin\alpha}+\dfrac{\mu_A{}^A}{\sin\beta}}\right)=\left(\frac{\sum\mu_i{}^AW_A}{\sin\alpha}+\frac{\sum\mu_A{}^AW_A}{\sin\beta}\right)z \quad (3)$$

where ρ_{AA} is the density of pure element A, and ρ_{Aj} is the density of the alloy. When Eq. (3) is applied to an element A in a binary alloy AB, Eq. (4) can be derived:

$$-\ln\left\{1-\frac{I_z{}^A}{I_\infty{}^A}\cdot\frac{\rho_{AA}}{\rho_{AB}}\left[1-\frac{\left(\dfrac{\mu_i{}^B}{\sin\alpha}+\dfrac{\mu_A{}^B}{\sin\beta}\right)W_B}{\left(\dfrac{\mu_i{}^A}{\sin\alpha}+\dfrac{\mu_A{}^A}{\sin\beta}\right)W_A}\right]\right\}=\left\{\left(\frac{\mu_i{}^A}{\sin\alpha}+\frac{\mu_A{}^A}{\sin\beta}\right)W_A+\left(\frac{\mu_i{}^B}{\sin\alpha}+\frac{\mu_A{}^B}{\sin\beta}\right)W_B\right\}z \quad (4)$$

Equation (4) was applied to a nickel-iron alloy (81.5% Ni) film. The experimental conditions were the same as described in previous reports.[1,2] In this case it is necessary to get the $\mu_i{}^A$ and $\mu_i{}^B$ values. Fortunately, in this experiment the value of $\mu_i{}^{\rm Ni}$ or $\mu_i{}^{\rm Fe}$ could be obtained by the applica-

TABLE 1. EXPERIMENTAL AND CALCULATED VALUES OF X-RAY INTENSITY RATIO OF Ni AND Fe IN Ni-Fe ALLOY FILMS

Thickness	$I_z{}^{\rm Ni}/I_\infty{}^{\rm Ni}$		$I_z{}^{\rm Fe}/I_\infty{}^{\rm Fe}$	
μ	Exp.	Calcd.	Exp.	Calcd.
0.2	0.044	0.042	0.015	0.009
0.4	0.077	0.079	0.021	0.017
0.6	0.114	0.126	0.038	0.025
1.23	0.228	0.223	0.087	0.046
2.35	0.345	0.351	0.138	0.074

1) K. Hirokawa and H. Gotô, *Z. anal. Chem.*, **190**, 309 (1962).
2) K. Hirokawa and H. Gotô, *ibid.*, **193**, 346 (1963).
3) K. Hirokawa and H. Gotô, *ibid.*, **199**, 89 (1964).
4) a) H. T. Beattie and R. M. Brissey, *Anal. Chem.*, **26**, 980 (1954). b) J. Sherman, "Advances in X-Ray Analysis," Vol. 1, ed. by W. M. Mueller, Plenum Press, New York (1960), p. 244. c) K. Hirokawa and H. Goto, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 383 (1966).

tion of Eq. (2) to a nickel or iron film; the value of μ_i^{Ni} was 1750, and that of μ_i^{Fe}, 977. Using these values, the X-ray intensity ratios of nickel and iron were calculated with Eq. (4). These results were shown in Table 1 together with the experimental results. From this experiment it was recognized that the thickness of a binary alloy film could be easily obtained from the X-ray intensity ratio of an element in the film to that of the pure element.

However, for the element that receives inter-element effects from accompanying elements in the film, or from backing materials, of course, the correction for these effects must be considered, as for iron in the nickel-iron alloy film used in this experiment. For the normal case, the calculated results are in good agreement with experimental values, as nickel in this experiment.