Short Communication

TWO CALCULATION PROCEDURES FOR THE DETERMINATION OF COMPOSITION AND MASS THICKNESS OF THIN SAMPLES BY X-RAY SPECTROMETRY

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Summary. Two procedures are described for calculating the composition and mass thickness of thin samples from measured x-ray intensities. One procedure is suitable for use with a programmable hand calculator but gives correct results only for very thin samples. The other procedure utilizes the NRLXRF program and produces correct results for thin and thick films.

There is a growing interest in the determination of composition and mass thickness of thin alloy films. Usually the thickness is measured interferometrically whereas the composition can be determined after dissolution, e.g., by atomic absorption spectrometry (a.a.s). A major contribution in this field was made by Laguitton [1] and Laguitton and Parrish [2] who described a new method for the simultaneous determination of composition and thickness by x-ray fluorescence (x.r.f.) measurements. Unfortunately, their computer program (LAMA) is not generally accessible. In the present communication, two procedures are described based on the same principle. One procedure can be applied with a programmable hand calculator, provided that no matrix effect corrections are necessary, i.e., for very thin films; the second procedure makes use of the commercially available NRLXRF program [3, 4]. This procedure allows for interelement effects and is therefore applicable for films of intermediate thickness as well.

Theory

The ratio of the intensity for the spectral line in a thin film of the pure element i to the intensity measured for the pure bulk can be represented by the general formula

$$\frac{I_{d,i}}{I_{b,i}} = w_i \frac{\int_{\lambda_0}^{\lambda_{\text{edge},i}} \frac{\tau_i(\lambda)}{X_d \sin \psi_1} [1 - \exp(-X_d \rho D)] I_o(\lambda) d\lambda}{\int_{\lambda_0}^{\lambda_{\text{edge},i}} \frac{\tau_i(\lambda)}{X_b \sin \psi_1} I_o(\lambda) d\lambda} \quad (1)$$

(The meanings of the symbols are listed in Table 1. Subscripts d and b refer to the thin sample and the pure bulk element, respectively.)

For very thin films the exponential function can be expanded in a series, which, truncated after the second term, leads to the simplified equation

$$\frac{I_{d,i}}{I_{b,i}} = w_i \rho D \int_{\lambda_0}^{\lambda_{\text{edge},i}} \tau_i(\lambda) I_o(\lambda) d\lambda \left/ \int_{\lambda_0}^{\lambda_{\text{edge},i}} \frac{\tau_i(\lambda)}{X_b} I_o(\lambda) d\lambda \right. = w_i \rho D G_i \quad (2)$$

Since G_i is a function of the spectral distribution of the x-ray tube, the mass photoabsorption coefficient and the value of $X_{b,i}$ only, values of G_i can be calculated once for each individual element.

For alloy films consisting of n components, the intensities $I_{d,1}, I_{d,2}, I_{d,3} \dots I_{d,n}$ as well as the intensities of pure element bulk standards ($I_{b,1}, \dots I_{b,n}$) have to be measured. From the n equations

$$w_i \rho D = I_{d,i}/I_{b,i} G_i \quad (i = 1, 2, \dots, n) \quad (3)$$

together with the condition $w_1 + w_2 + \dots + w_n = 1$, the n unknown weight fractions and the product ρD can be calculated.

Incorrect results are obtained with the method described above when it is applied to films of intermediate thickness or to films in which the inter-elemental effects cannot be neglected. In these cases, a more sophisticated procedure has to be adopted. The program NRLXRF, developed by Criss et al. [3, 4] offers interesting possibilities. Although this program does not contain a routine for the calculation of film thicknesses, it has two interesting features: (i) it can calculate the composition from values of the relative intensities when the film thickness is known; (ii) it can simulate relative intensities for films of known composition and thickness. These parts of the

TABLE 1

Definition of symbols

I_i	Count rate for line of element i
w_i	Weight fraction of element i in thin matrix
λ_0	Minimum wavelength of the primary radiation
$\lambda_{\text{edge},i}$	Wavelength of the considered edge of element i
$\tau_i(\lambda)$	Mass photoabsorption coefficient of element i for wavelength λ
X	$= [\mu(\lambda)/\sin \psi] + [\mu(\lambda_i)/\sin \psi_i]$
$\mu(\lambda)$	Mass absorption coefficient for wavelength λ
λ_i	Wavelength of the measured line of element i
ψ	Angle between central beam of tube radiation and surface of the sample
ψ_i	Take-off angle of measured radiation from the sample
ρ	Density of the thin sample
D	Thickness of the thin sample
$I_o(\lambda)$	Spectral distribution of primary radiation

program can be used in an iteration procedure in which they operate alternately; in between, the mass thickness is corrected until the calculated intensities correspond to the experimental ones. In this way a program is obtained that calculates the composition as well as the mass thickness.

Experimental

Instrumentation and samples. The experimental data were obtained with a Philips universal vacuum x-ray spectrometer (PW 1410), a Philips tungsten x-ray tube (PW 2184/00) and a Philips chromium x-ray tube (PW 2188/00). The geometry of the specimen chamber was $\psi_1 = 66^\circ$ and $\psi_2 = 35^\circ$; the analyzing crystal was LiF (220); the detector was a flow counter in connection with a single-channel pulse-height analyzer. All measurements were made in vacuum. The intensities measured for the sample were transformed to net intensities by subtracting the corresponding intensities of a blank specimen. Dead-time loss corrections were also applied.

Most of the thin alloy films under study consisted of two components on a substrate of glass or silicon. These films were prepared by vacuum evaporation and sputtering. The film thicknesses varied, in general, from 50 to 1000 nm (a mass thickness of about 40–800 $\mu\text{g cm}^{-2}$). For the x-ray measurements, a sample holder with an aperture of 1-cm diameter was used. The complete aperture was filled with samples 1×1 cm square.

For comparison, some of the films were also analyzed by wet chemical methods. To this end, the samples were washed with toluene and acetone, dried, weighed, treated with hydrochloric acid and/or nitric acid (1 + 1) in order to dissolve the alloy film, washed with water and washed again with acetone before the final weighing. These sample solutions were diluted to the mark in calibrated flasks and measured by a.a.s.

Calculations. For the calculation of factor G_i , a programmable hand calculator (Texas Instruments TI 59) was used. The values of $\tau_i(\lambda)$, $\mu_i(\lambda)$ and $\mu_i(\lambda_i)$ were calculated from the tabulated information presented by McMaster et al. [5]. To facilitate the calculation of G_i , the spectral distribution of the continuous x-ray tube radiation was expressed as a continuous function: $I_o(\lambda) = A \exp(-B\lambda^C) (1 - \lambda/\lambda_o)^D$. By trial and error the constants A, B, C and D were adapted to get the best fit with the experimental values of $I_o(\lambda)$ tabulated by Loomis and Keith [6]. On the two sides of a jump in the continuous spectrum, different values of A had to be used. The contribution of the continuous spectrum to the integrated intensity was obtained by means of a Simpson routine provided by the manufacturer of the calculator. The contributions of the characteristic lines were taken directly from Loomis and Keith's tables. (A copy of the complete program is available on request.)

For the more sophisticated procedure, the NRLXRF program was utilized. This program was implemented on a DEC-10 computer, and extended with a routine that executes the following iteration procedure: weight fractions are calculated starting with the measured intensities and an estimated value of the film thickness. Subsequently, these weight fractions and the estimated

value of the thickness are used to calculate relative intensities (RI). A new value of the mass thickness is calculated according to the formula

$$(\rho D)_{\text{new}} = (\rho D)_{\text{old}} (\sum RI_{\text{meas.}}) / (\sum RI_{\text{calc.}})$$

The iteration procedure is continued until the values of the calculated relative intensities and the measured relative intensities as well as the values of $(\sigma D)_{\text{new}}$ and $(\sigma D)_{\text{old}}$ show a difference of less than 0.1%. (For very thin samples values of 1% are taken.)

Results and discussion

Similar results for the composition and the mass thickness were obtained with the hand calculator method and the NRLXRF method for thin samples, as shown in Table 2. Tables 2 and 3 show that the results of the two methods differ more and more for increasing thickness of the samples. The conditions for preparing the iron/nickel-on-glass samples were such that identical compositions could be expected. The results of the NRLXRF method fit in with this. The a.a.s. method is not always accurate enough to determine which of the concentrations found with the two calculating methods is the correct one; but it is accurate enough for a decision about the correct mass thickness. It turned out that the glass used as substrate was attacked slightly by the strong acids used for dissolving the sample. In these cases, the loss in weight of the substrate gave no indication of the sample thickness. The silicon substrate was stable in the strong acids used and the mass thickness could be determined from the loss in weight.

In the case of the iron—nickel samples, a Cr-target x-ray tube was used; the measured radiation was excited by a large wavelength region of the tube

TABLE 2

Iron and nickel on glass

"Hand" method			NRLXRF method			A.a.s.		
%Fe	%Ni	Mass thickness ($\mu\text{g cm}^{-2}$)	%Fe	%Ni	Mass thickness ($\mu\text{g cm}^{-2}$)	%Fe	%Ni	Mass thickness ^a ($\mu\text{g cm}^{-2}$)
18.9	81.1	31	18.8	81.1	32			
18.8	81.2	57	18.5	81.4	60			
19.0	81.0	99	18.6	81.4	104	18.6	81.4	109
19.1	80.9	135	18.6	81.4	143	19.6	80.4	147
19.4	80.6	196	18.8	81.2	210			
19.4	80.6	234	18.6	81.4	252			
19.8	80.2	315	18.6	81.4	344			
19.9	80.1	342	18.7	81.3	375			
19.8	80.2	374	18.5	81.5	416			
20.2	79.8	430	18.6	81.3	479	19.0	81.0	493

^a Determined from the sum of Fe and Ni found.

TABLE 3

Cobalt and chromium on silicon

"Hand" method			NRLXRF method			A. a. s.	
%Co	%Cr	Mass thickness ($\mu\text{g cm}^{-2}$)	%Co	%Cr	Mass thickness ($\mu\text{g cm}^{-2}$)	%Cr	Mass thickness ^a ($\mu\text{g cm}^{-2}$)
82.0	18.0	613	85.8	14.2	717	14.8	700
82.7	17.3	418	85.8	14.2	470	14.3	455
82.9	17.1	419	86.1	13.9	471	14.3	467
84.8	15.2	324	87.5	12.5	358	12.7	368

^aDetermined from the loss in weight of the sample.

spectrum. For the cobalt—chromium samples, a W-target x-ray tube was used; most of the measured radiation was excited by the characteristic tungsten lines. Small differences in the intensity of the characteristic lines in the tube spectrum used by the NRLXRF program, those measured by Loomis and Keith (for a General Electric EA 75 Cr/W dual-target x-ray tube), and those in the x-ray tube used here, could cause deviations between the various results. It seems that the W-tube actually used is well simulated by the NRLXRF W-tube spectrum.

In the case of gadolinium and iron not much mutual influence was expected because the measuring wavelengths were both on the low side of the mass absorption coefficient jump. Table 4 indeed shows that the compositions found by both methods correspond up to fairly high mass thicknesses. The mass thicknesses obtained, however, differ just as in Tables 2 and 3.

Conclusions

The hand-calculator method and the NRLXRF method give similar results in the case of very thin alloy films for the composition as well as for the mass thickness.

TABLE 4

Iron and gadolinium on glass

"Hand" method			NRLXRF method		
%Fe	%Gd	Mass thickness ($\mu\text{g cm}^{-2}$)	%Fe	%Gd	Mass thickness ($\mu\text{g cm}^{-2}$)
53.6	46.4	75	53.4	46.1	79
54.7	45.3	136	54.9	45.1	145
55.5	44.5	348	55.5	44.5	393
56.7	43.3	529	56.7	43.3	632
55.8	44.2	595	55.7	44.3	724
56.1	43.9	822	56.1	43.9	1092

When there is little mutual influence of the elements present, even samples that are not very thin give similar results for the composition but not for the mass thickness found. But when there is a high mutual influence between the elements present, different results for both the composition and the mass thickness are obtained by the two methods. The results found by the NRLXRF method match those found by wet chemistry.

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