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X-RAY STUDIES RELATED TO COATING THICKNESS MEASUREMENTS

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Résumé - Des mesures d'intensité des rayons X sont faites sur une série de substrats avec des couches soigneusement calibrées. On propose une formule pour la détermination de l'épaisseur des couches ; elle peut être aussi utilisée pour donner la profondeur maximale de génération des rayons X.

Abstract - X-ray measurements are carried out on a series of substrates with carefully prescribed coatings. An equation is developed for determining coating thickness and can also be used to give values for the x-ray range.

1. INTRODUCTION

It is often necessary to know the depth in the sample from which x-rays are being generated, especially when carrying out electron-probe microanalysis on specimens having an abrupt change of chemical composition within a micrometre or so of the surface, e.g. precipitates, surface reaction products and coatings on substrates. Moreover, if the depth of x-ray generation, i.e. the x-ray range, can be formulated in terms of such parameters as mean atomic number of the specimen (Z), incident electron energy (E), and critical excitation energy of the measured x-ray line (E_0), it then becomes feasible to obtain quantitative data on coatings. In principle this means that if the thickness is known, the chemical composition can be determined or, alternatively, if the composition is known, the thickness may be established. Although, however, various formulae for the x-ray range have been proposed which embody the above parameters, many give widely diverse results which, in extreme cases, may differ by a factor of two (1).

2. PRINCIPLE OF THE PROPOSED METHOD

Our method involves the development of an equation which may be applied to any coating/substrate combination. The procedure may be summarised as follows.

(i) X-ray intensity measurements are made on the coated substrate and a standard of the same composition as the coating. The beam energy is then determined at which the generated x-rays are just confined to the coating material. In this situation the coating thickness (pt) will equal the x-ray range (pz) appropriate for these experimental conditions. Such an approach has been used previously by Reuter et al (1) in studies of the x-ray range.

(ii) We choose then to express pt in terms of the mean depth of x-ray generation (pZ) rather than pz for two reasons. Firstly, as indicated by the tails of Bishop's (2) normalised x-ray depth distributions, (figure 1) it appears that a simple proportional relationship may exist between pz and pZ. Secondly an expression for pZ is already available (3) which has been shown to work well for a very wide range of experimental conditions.

The method has the advantage that the results are not influenced by the substrate. Thus, atomic number corrections are not required because any electrons backscattered from the substrate will have insufficient energy to excite the x-ray line from the coating which is being measured. Furthermore, since no energetic x-rays are
generated in the substrate a characteristic fluorescence correction is unnecessary, whilst a continuum fluorescence correction is likely to be very small because continuum contributions will be almost identical in specimen and standard. This leaves us with possible errors due to x-ray absorption. These may arise in heavily absorbing systems because the depth in the target from which x-rays are emitted will then be somewhat less than the x-ray range (the depth in which x-rays are generated). For present purposes, however, absorption will be ignored and referred to again at the end of the paper.

3. EXPERIMENTAL

Coating/substrate combinations used in the investigation were aluminium/magnesium, copper/iron and gold/lead, all materials being of high purity. Samples of each coating/substrate combination were mounted together in bakelite and polished down to a mirror finish. After thorough degreasing, the polished mount was positioned on the platform in a vacuum evaporation unit together with two glass cover slips, one of which was partially masked. Care was taken to ensure that all items were equidistant from the metal evaporation source, the platform being rotated during evaporation to achieve uniformity of deposit. As a guide to the amount of material being deposited a quartz crystal monitor was included within the vacuum chamber but the actual coating thickness was determined from the amount deposited on the glass cover slips. Interferometric measurements were carried out on the partially masked cover slip to give the thickness directly, while atomic absorption spectroscopy was used to determine the mass of material deposited on the second cover slip. Mass thickness given by these two methods agreed to within a few percent for all systems studied.

X-ray intensity measurements were carried out using a JEOL JXA-50A electron-probe microanalyser fitted with wavelength-dispersive and energy-dispersive x-ray spectrometers. The energy-dispersive spectrometer was used primarily for measuring accurately the probe voltage, i.e. recording the short-wave length cut-off of the x-ray continuum.

X-ray intensity measurements were obtained from coated specimen and respective standard and plotted as a function of beam energy. The beam energy ($E_d$) at which the x-ray range coincides with the coating thickness was given by the value where the intensity ratio started to depart from unity.

4. RESULTS AND DISCUSSION

A typical series of x-ray intensity measurements from aluminium layers of different thickness deposited upon magnesium are shown in figure 2, plots of $I/I_s$ versus beam energy ($E_d$), where $I$ and $I_s$ are x-ray intensities from coating and standard respectively. The points lie on a series of straight lines, the intersection of each with the axis giving the beam energy ($E_d$) at which x-rays are just confined within the particular coating thickness. Similar data were obtained for all three substrate coating combinations.

Using these values of $E_d$, the mean depth of x-ray generation ($\overline{\rho z}$) was calculated from (1)

$$\overline{\rho z} = \rho_m \left(0.49269 - 1.09871 \eta + 0.78557 \eta^2\right) \ln U$$

where $U$ is given by $E_d/E$ and $E$ is the critical excitation energy; $\rho_m$ is the mean depth of x-ray generation calculated from

$$\rho_m = AZ^{-1} \left(0.787 \times 10^{-5} J^{1.5} 0.735 \times 10^{-6} E_d^{2.7} \right)$$

where $Z$ is atomic number and $A$ the atomic weight of the coating material; $J$ is the mean ionisation potential and equals 0.0135Z.

These calculated values for $\overline{\rho z}$ were then compared with the respective coating thicknesses as determined directly by optical interferometry and/or atomic
absorption spectroscopy. The sets of data for the aluminium coatings are plotted in figure 3 and the points lie on a straight line with gradient $2.84 \pm 0.06$, i.e. we may write

$$\rho t = kpz = (2.84 \pm 0.06)pz.$$ 

Values of $k$ were calculated for all systems studied and also for the coatings investigated by Reuter et al (1). The results indicate that $k$ is relatively independent of atomic number but is strongly influenced by $U=\frac{E_d}{E_c}$. This effect is illustrated in figure 4; above $U \approx 5$, $k$ remains approximately constant at 2.7, but below $U \approx 3$ it rises rapidly.

Least-squares analysis of the compiled data gives

$$k = 2.68 + 4.4 \exp(-0.725U),$$

from which we obtain

$$\rho t = pz (2.68 + 4.4 \exp(-0.725U))$$ \hspace{1cm} (2)

Values of $\rho t$ were calculated and compared with those obtained by optical and atomic absorption measurements. By including Reuter's systems with our own, some fifty data points were provided with coating thicknesses ranging from 50 to 800nm. It was found that our equation performed well when $U > 2.5$, with a root mean square (RMS) error of 6.7%; below $U = 2.5$, however, the error was significantly higher at 15%.

Before concluding, it is of interest to compare our method for determining coating thickness with the equation proposed by Reuter (1), viz

$$\rho t = 5.2(z^{1.3} - z_{c}^{1.3})A^{-0.9}$$

This expression is a little simpler than our own but gives RMS errors of 22% and 36% respectively, indicating that its performance is significantly less satisfactory.

5. CONCLUSIONS

An equation has been developed for calculating coating thickness which gives satisfactory results when applied to systems covering a wide range of atomic number. To use the method a standard consisting of the coating material is needed and then the beam energy is determined at which the generated x-rays are just contained within the coating; these measurements need only take ten minutes to carry out in practice. Best accuracy is achieved when the beam energy exceeds 2.5 times the critical excitation energy of the measured x-ray line and, if this criterion is to be met, low energy x-ray lines (say 1 to 3keV) must be recorded. Present results suggest that absorption effects are not serious, especially for coatings less than 500nm thick. However, with multi-element coatings these effects may no longer be negligible and it could prove necessary to extend equation 2 by introducing an absorption term correction.

Finally, the equation may be readily used to provide values for the x-ray range appropriate to any set of experimental conditions.

Acknowledgements

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REFERENCES

Fig. 1. Normalised x-ray depth distributions after Bishop. Horizontal axis scaled in terms of the mean depth and all curves normalised to the same total area.

Fig. 2. X-ray intensity ratios (I_c/I_g) plotted as a function of electron beam energy for six different coating thicknesses.

Fig. 3. Plot of coating thickness (pt) versus mean depth (\bar{\rho}z) for aluminium coatings.

Fig. 4. Graph of k (\rho_t/\bar{\rho}z) versus U (=Ed/E_c) for all systems studied.