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An iterative procedure for the correction of secondary fluorescence effects in electron-probe microanalysis near phase boundaries

G. F. BASTIN, F. J. J. VAN LOO, P. J. C. VOSTERS and J. W. G. A. VROLIJK

Lab. for Physical Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Abstract—A correction procedure is proposed to correct for the effects of characteristic fluorescence in EPMA near phase boundaries. The necessary equations for the simple case of two homogeneous alloys sharing a common interface are given. The equations have been tested in practice and it is shown that they are well suited to predict the apparent concentration of the element suffering from secondary excitation as a function of distance from the boundary. Based on these equations an iterative correction procedure is proposed for application to sloping concentration profiles. The procedure is illustrated on some practical examples and some of the factors connected with its performance are briefly discussed.

1. INTRODUCTION

It is well-known that the spatial resolution in quantitative electron-probe microanalysis can be badly affected by the occurrence of secondary fluorescence, i.e. when the primary excited (electron beam generated) X-radiation of some other element in the matrix is capable of exciting extra X-radiation of the element one is trying to analyse. In such cases the total volume of excitation, which is normally 2–4 μm in diameter, can be increased by one to two orders of magnitude, mainly because of the fact that matter is relatively transparent to X-rays as compared to electrons. The effect is most pronounced in matrices containing elements with atomic numbers differing by two (for $Z > 21$) like combinations of Fe–Ni, Co–Cu etc. While the established REED [1] fluorescence correction procedure, which has been incorporated in most matrix correction (ZAF) programs, is in general quite satisfactory in correcting for these effects, it is bound to fail when the electron beam approaches a phase boundary or when the size of a particle to be analysed drops below a certain limit. One of the basic assumptions in this model is namely that the primary and secondary production of X-rays as well as the subsequent absorption all take place in the same homogeneous matrix, which is evidently no longer the case in the above examples. Hence the need for a correction scheme which calculates the correction factor as a function of distance or of particle size. An attempt in this direction has previously been undertaken by MAURICE *et al.* [2] and HENOC *et al.* [3] for the simple case of two pure metals sharing a flat interface. In order to overcome the inherent limited applicability of their equations we have extended their approach towards various geometries thereby allowing variable concentrations on both sides of the interface [4]. The resultant equations enabled us to propose an iterative correction procedure and this is the object of the present paper.

2. THEORY

Although a number of equations have been derived [4] for various geometries, (including flat interfaces, like in diffusion couples, lamellae and epitaxial layers, as well as curved interfaces, like hemispheres) we will limit ourselves here to the frequently encountered model of two homogeneous alloys sharing a common flat interface (Fig. 1). Involved are the

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[3] J. HENOC, F. MAURICE and A. ZEMSKOFF, *Vth Int. Congr. on X-ray Optics and Microanalysis*, Tübingen (1968).

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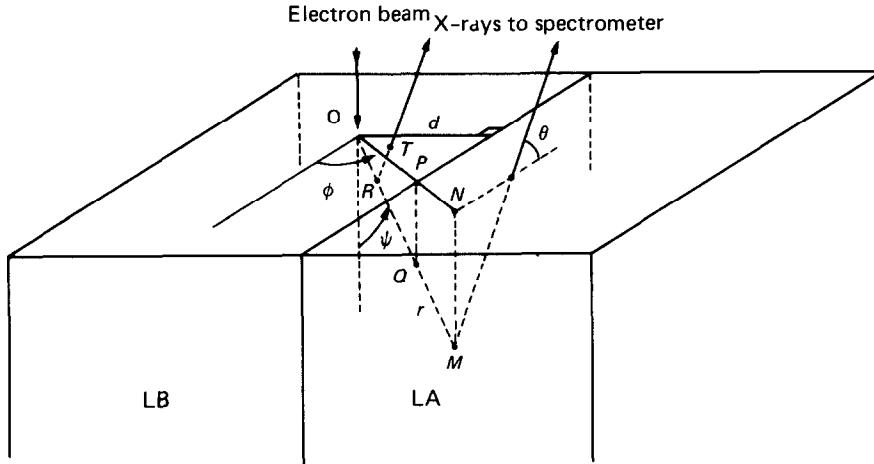


Fig. 1. Schematic drawing representing two alloys LB and LA , separated by a straight interface. It is assumed that LB is rich in B and LA is rich in A . $B-K_\alpha$ radiation is supposed to excite $A-K_\alpha$ radiation.

elements A and B with $Z_B > Z_A$, which implies that $B-K_\alpha$ radiation is capable of exciting $A-K_\alpha$ radiation.

The electron beam is located in O in alloy LB (richest in B , concentrations C_B^{LB} and C_A^{LB}) at a distance d from the interface separating it from LA (richest in A , concentrations C_A^{LA} and C_B^{LA}). Two restrictions are made:

- (1) All primary radiation is assumed to be emitted from a point source in O .
- (2) Contributions from continuum fluorescence (white X-radiation) are not taken into account.

Following Refs [2] and [3] we now consider the path of an X-ray travelling down towards M and crossing to boundary at Q , which means two distinct trajectories: one in LB (OQ), and one in LA (QM). We will briefly discuss the strategy followed for the trajectory OQ ; similar reasoning applies of course to QM .

The first step is to describe mathematically the absorption of B -radiation along OQ as a function of the spherical coordinates r , ψ and ϕ .

Next the fraction hereof absorbed specifically by A -atoms is calculated and this is subsequently partly transformed into *excited* fluorescent A -radiation. In order to be "seen" by the spectrometer the radiation has to emerge, e.g. from R in T , under an angle θ , which gives rise to an absorption term. The resultant mathematical expression gives us for each value of r , ψ and ϕ the intensity of *emitted* fluorescent A -radiation. The total amount emitted from LB between O and the boundary is obtained by integration over r , ψ and ϕ . In addition we have to take into account the contribution produced by B -radiation directed to the left hand side. As a result we get for the total amount of emitted fluorescent A -radiation (I_A^F) in relation to the primary emitted A -radiation (I_A) from LB the following expression:

$$\frac{I_A^F}{I_A}(LB) = S * C_B^{LB} * \int_{\phi=0}^{\pi} \int_{\psi=0}^{\pi/2} \frac{\sin \psi \, d\psi \, d\phi}{\mu_B^{LB} + \mu_A^{LB} \cos \psi \operatorname{cosec} \theta} * [2 - \exp\{-\{(\mu_B^{LB} \rho_{LB} + \mu_A^{LB} \rho_{LB} \cos \psi \operatorname{cosec} \theta) * d / \sin \psi \sin \phi\}\}] \quad (1)$$

with

$$S = \frac{\omega_B}{4\pi} * \left(\frac{r-1}{r}\right)_A * \frac{A_A}{A_B} * \mu_B^A * \left(\frac{U_B-1}{U_A^{-1}}\right)^{3/2}$$

in which μ denotes the mass absorption coefficient, with the subscript indicating the type of characteristic radiation and the superscript the type of alloy in which the absorption takes place and ρ represents the density. ω is the fluorescent yield $\left(\frac{r-1}{r}\right)$ the absorption edge jump ratio, A the atomic weight and U the overvoltage ratio (accelerating voltage/critical excitation voltage).

Along similar lines we get for the alloy *LA*:

$$\frac{I_A^F}{I_A}(LA) = S * \frac{C_B^{LB} * C_A^{LA}}{C_A^{LB}} * \int_{\phi=0}^{\pi} \int_{\psi=0}^{\pi/2} \frac{\sin \psi \, d\psi \, d\phi}{\mu_B^{LA} + \mu_A^{LA} \cos \psi \operatorname{cosec} \theta} * \exp - \{ (\mu_B^{LB} \rho_{LB} + \mu_A^{LA} \rho_{LA} \cos \psi \operatorname{cosec} \theta) * d / \sin \psi \sin \phi \} \tag{2}$$

with *S* having the same meaning as before.

The measured *k*-ratio (intensity from specimen divided by the intensity from the pure element standard) can now be corrected for characteristic fluorescence by multiplying it with $1 / (1 + I_A^F / I_A)$ in which I_A^F / I_A now represents the added contributions according to Eqns (1) and (2).

3. SOME TESTS OF THE DERIVED EQUATIONS

In Fig. 2 the results of measurements and calculations performed on an undiffused Cu–Co couple are shown. This case, in which two pure elements joined together are involved, can be considered as a limiting case of the geometry discussed in Section 2: the concentration terms in Eqns (1) and (2) drop out and instead of I_A^F / I_A we can write directly k_A (apparent *k*-ratio). Obviously, rather good agreement is obtained between calculations and measurements, as Fig. 2 shows, especially when estimated contributions from continuum fluorescence are added (solid circles). Note the distance over which fluorescence is noticeable. A similar test has been performed on a number of homogeneous Cu(Co) alloys which have been joined mechanically to a Co(4.1 wt% Cu) alloy. As Fig. 3 indicates very good agreement between theory and experiment is obtained.

4. THE SUGGESTED CORRECTION PROCEDURE

From the foregoing, the need for a correction procedure, which gives the correction factor as a function of distance, is obvious. Such a procedure, however, can only be devised for a given geometry and with a knowledge of the concentrations on both sides of the interface. As the latter are at the same time the quantities to be measured, the proposed correction procedure is inevitably iterative. It will now be described using the Co–Cu system as an

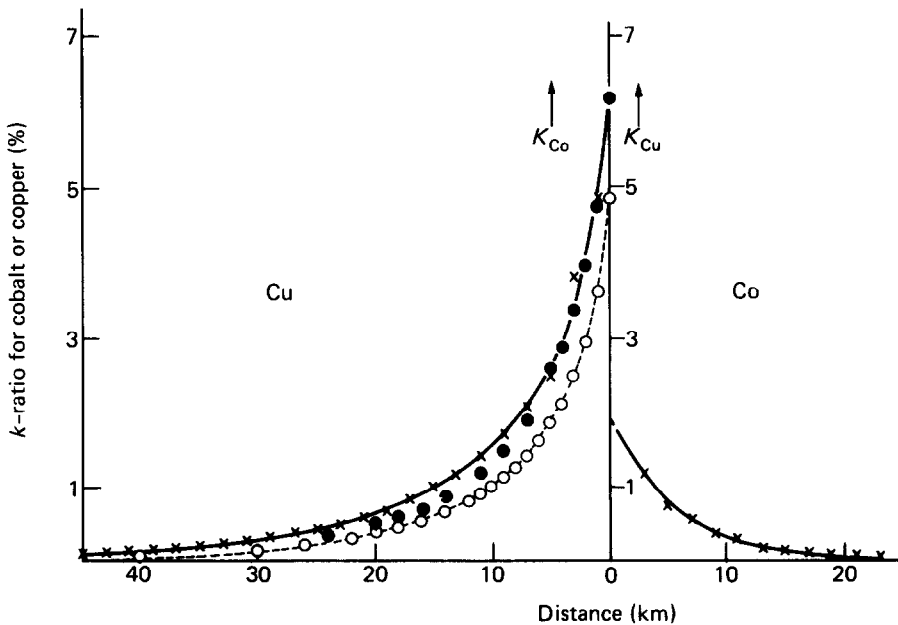


Fig. 2. Apparent *k*-ratio for Co in Cu (left hand side) as a function of distance in an undiffused Cu/Co couple; x measured; o calculated for *K*–*K* fluorescence only; ● calculated with additional estimates for continuum fluorescence included. There are obtained from the right hand side of the Figure.

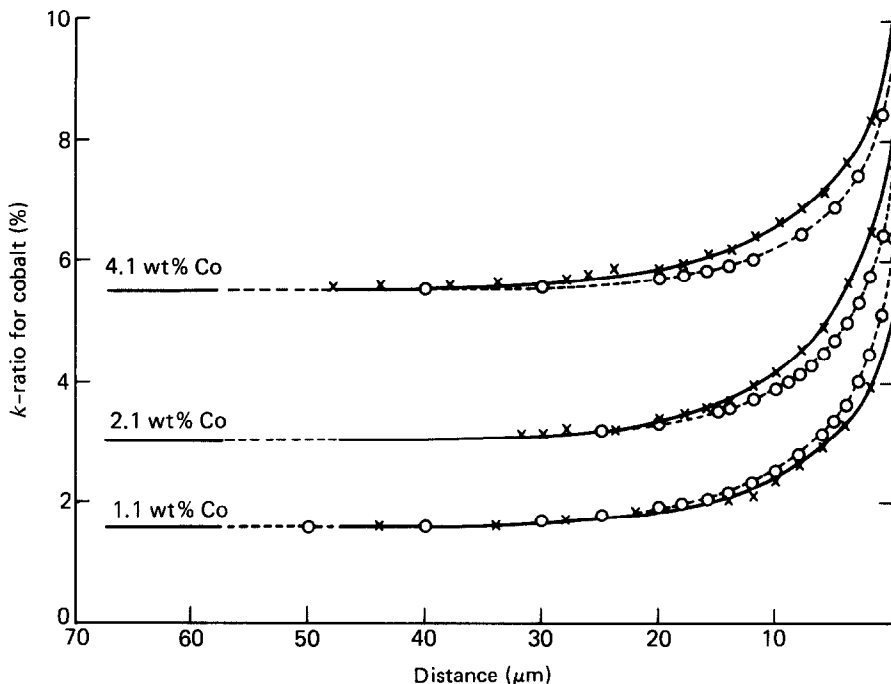


Fig. 3. Apparent k -ratio for Co in three different homogeneous Cu(Co) alloys as a function of distance from the boundary with a Co (4.1 wt % Cu) alloy; \times measured; \circ calculated (for K - K fluorescence only).

example. Essentially it comes down to the following steps:

(a) The initial microprobe measurements are used to make estimates of the average Co-concentrations C_A^{LB} and C_A^{LA} over the relevant (between 5 and 25 μm from the boundary) areas on both sides of the interface. As the value of C_A^{LA} will be quite reliable, because this is hardly affected by fluorescence, this will be kept fixed in the rest of the procedure. The value of C_A^{LB} , on the contrary, will invariably be too high initially.

(b) The original k -ratios for Co are corrected with calculated correction factors $F(d)$ as a function of d using Eqns (1) and (2).

(c) The fluorescence correction in the ZAF program is disabled and the corrected k -ratio for Co, together with the original k -ratio for Cu submitted to the rest of the ZAF program.

(d) The new concentration profile is used to generate a new estimate for C_A^{LB} after which the procedure is repeated.

The iterations are stopped as soon as the new estimate for C_A^{LB} differs less than, say, 0.05 wt % from the previous one, provided of course that convergence is obtained. According to our experience so far this has never failed and the stopping criterion is usually reached in 2 to 3 iterations.

5. RESULTS AND DISCUSSION

After a number of successful tests of the procedure on the undiffused couples shown in Fig. 3 in which cases the apparent Co-concentrations could be reduced almost to the actual levels in as few as 2 iterations, it was decided to test it on some real (annealed) diffusion couples. The first example is shown in Fig. 4 in which the measured initial concentration profiles (crosses) for the Cu-rich couple halves are shown after two different annealing times, together with the results for the successive iterations. In both cases the procedure is evidently able to reduce the initial apparent phase boundary concentration of approx. 8.5 wt % Co to approx. 6.35 wt % Co. The latter concentration is in close agreement with estimates based on so-called "measurements by difference", i.e. the Cu-concentration is measured only and the

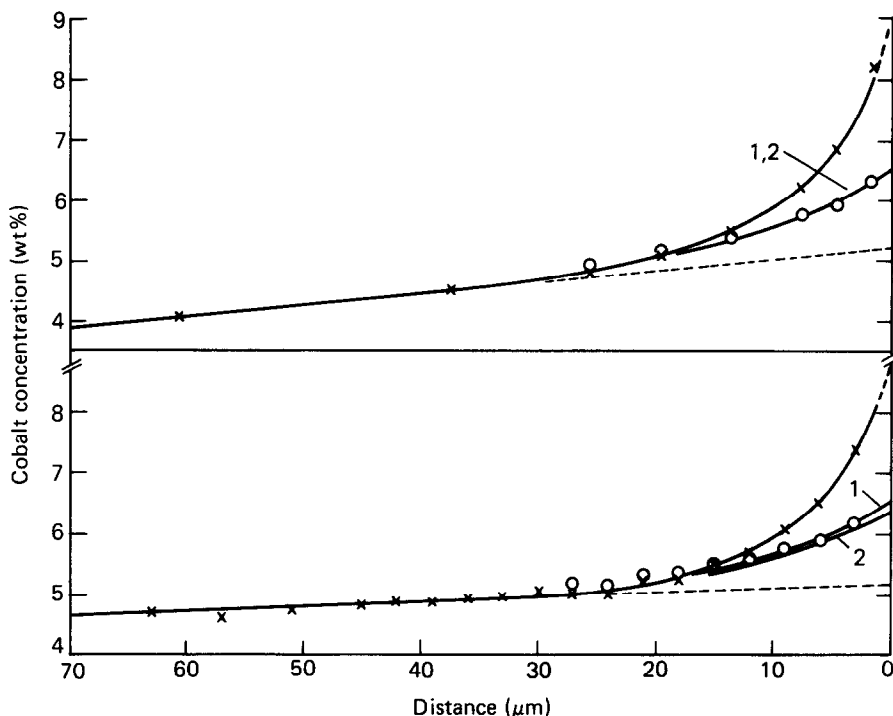


Fig. 4. Performance of the iterative correction procedure for two Cu/Co diffusion couples, annealed for 117 h (top) and 720 h (bottom) at 1000°C; × measured; o calculated after the first iteration.

Co-concentration is calculated as the balance. Unfortunately, the Cu–Co phase diagram [5] cannot be used as a guide in this case as the reported value of 3.65 wt % Co is evidently too low.

In order to answer the question of how critical the initial values of C_A^{LB} and C_A^{LA} are as well as the area over which C_A^{LB} is averaged, we have performed a series of calculations. The choice of C_A^{LA} was thereby found to be hardly critical: an absolute variation of 3.5 wt % Co to either side did not produce a noticeable effect for the last example. As far as C_A^{LB} is concerned, it turned out that a significantly too high initial value merely increases the number of iterations, the final results being the same. On the other hand, an evidently too low initial estimate leads to a higher value for the next iteration, thus showing again that convergence can be obtained. Apparently there is, in this example, no danger for overshoot in the correction. This must be attributed to the fact that the concentrations, outside the range where fluorescence effects from across the boundary can be expected, are still high enough to prevent C_A^{LB} from assuming very low (< 1%) values. In such cases the value of $F(d)$ is not too sensitive to small variations in C_A^{LB} . The danger for overcorrection is real, however, when the extent of the diffusion zone is very limited (< 25 μm) and C_A soon approaches zero. Then it is advisable to reduce the area over which C_A^{LB} is averaged and/or to take it closer to the boundary. This leads to slower convergence, of course, as was observed in a Cu₂O/Co couple (Fig. 5) in which, after diffusion, a layer of Cu adjacent to a CoO layer was developed. Here it was decided to take the average of C_A^{LB} over an area between 0 and only 10 μm from the boundary. As a result 6 iterations were necessary (see also the inset in Fig. 5). The final boundary concentration was again in agreement with measurements “by difference”. Summarizing it is apparent that the range over which C_A^{LB} is averaged should be adapted to the type of problem; the lower the expected end value of C_A^{LB} is, the more care should be exercised.

Nevertheless convergence can be obtained and the results so far indicate that a

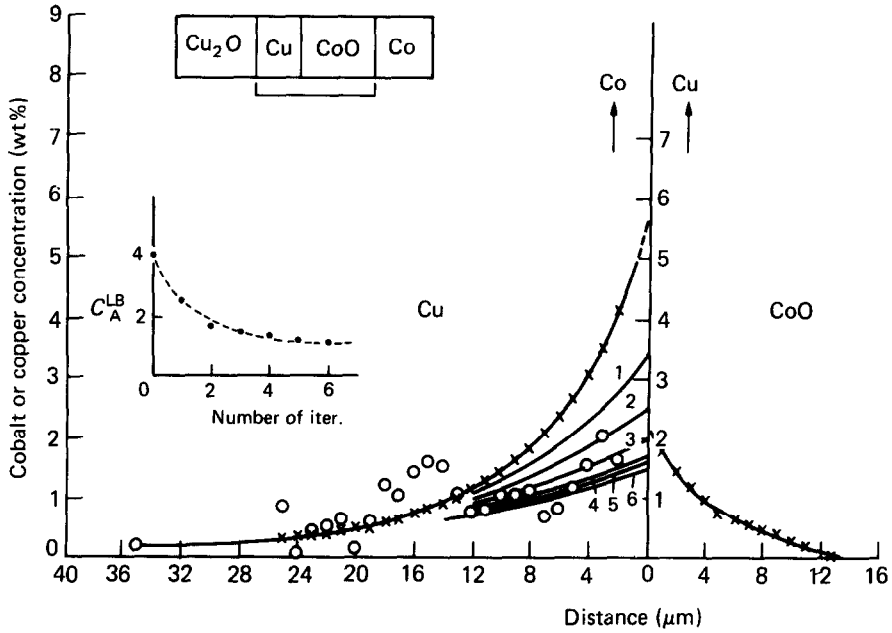


Fig. 5. Results of the correction procedure applied to a Cu_2O/Co diffusion couple annealed for 70 h at $1000^\circ C$; \times measured; o Co-concentration measured "by difference".

considerable improvement can be expected from the use of the proposed correction procedure.

It is to be expected that similar procedures can successfully be applied to small particles, lamellae etc. So far, however, no experimental work to this effect has been performed yet.