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HIGH PRECISION MICROPROBE ANALYSIS BY THIN METALLIC FILM CALIBRATION

by

J. LEMAITRE and R. THEISEN

1963

Joint Nuclear Research Centre
Ispra Establishment (Italy)
Metallurgy and Ceramics Department

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PROCEEDINGS OF THE Xth COLLOQUIUM
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HIGH PRECISION MICROPROBE ANALYSIS BY THIN METALLIC FILM CALIBRATION

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INTRODUCTION

With the increasing availability of electron microprobes, the theory of quantitive microanalysis has been the object of new investigations.

Starting from the calculations published by R. Castaing in his thesis [1], it has been attempted to establish experimental and theoretical correction formulae for local microprobe analysis.

The effects of diffuse penetration of electrons and mass absorption of X-rays in the anticathodes [2-7], the effects of fluorescence excited by characteristic radiations [8-10] and of enhancement by the continuous spectrum [11] have been evaluated.

Measured X-ray intensities and calculated values of binary alloys are in reasonable agreement except:

a. At low concentration,
b. for great atomic mass difference of components combined with secondary fluorescence emission,
c. for analysis of inclusions (direct emission and fluorescence enhancement of matrix).

For high precision analysis of these alloys (no limitation in number of components) in the absence of calibration standards homogeneous on a $1/\mu$ scale, the use of thin films, 0.01 to $0.1/\mu$, obtained by ultramicrotomy permit high resolution analysis with negligible absorption and fluorescence corrections.

THEORY

Suppose, an electron beam of intensity I_o impinges perpendicularly on a metallic film of thickness z cm. The intensity

of the characteristic radiation I_t collected from a constant area at an emergent direction θ will be [6]:

$$I_t = K \frac{M_t}{A_t} I_o \int_{z=0}^{z} e^{-\alpha \rho z} e^{-(\mu/\rho) \csc \theta} \, dz, \qquad (1)$$

where

K = constant depending on the voltage ratio V/V_k,

M_t/A_t = number of atoms T per unit volume,

$\alpha = K/V^2$ (V being the accelerating voltage),

$\rho = \Sigma M_i$ = density,

M_t = mass of element T per volume unit,

A_t = atomic weight of element T,

μ/ρ = mass absorption for characteristic radiation in analysed alloy.

A considerable simplification is obtained when z and α become so small that the exponential term approaches unity. The physical significance of this simplification is that absorption effects are negligible.

By using sufficiently thin samples ($0.01\,\mu$) and a highly accelerated electron beam (35 KV and more if possible), it is possible to assume a direct proportionality between the characteristic X-ray emission and the masses per unit area of the analysed elements.

$$\frac{I_A}{I_{(A)}} = M_A \, . \qquad (2)$$

$I_A/I_{(A)}$ is the ratio of X-ray intensities emitted respectively in the K α (A) line, under the same experimental conditions by the pure element A and the analysed alloy. Similarly

$$\frac{I_B}{I_{(B)}} = M_B \, , \qquad (2')$$

$$\frac{I_C}{I_{(C)}} = M_C \, . \qquad (2'')$$

Considering

$$\rho = \Sigma M_i = M_A + M_B + M_C , \tag{3}$$

$$C_A = \frac{M_A}{\Sigma M_i} = \frac{M_A}{M_A + M_B + M_C + \ldots\ldots}, \tag{4}$$

$$C_B = \frac{M_B}{\Sigma M_i} . \tag{4'}$$

Using equation (4) the chemical composition of a sample is obtained by the determination of the superficial masses of all the elements being present in the sample.

EXPERIMENTAL PROCEDURE

The thin films 0.01 μ thick (samples and pure elements) should be of identical thickness, condition which can be most easily fulfilled by the automatic advance of an ultramicrotome after Fernandez Moran [12], followed by an interferometric thickness control of the films.

Films of about 2500 μ^2 were collected on standard electron microscope grids and inserted into a special probe holder (Figure 1).

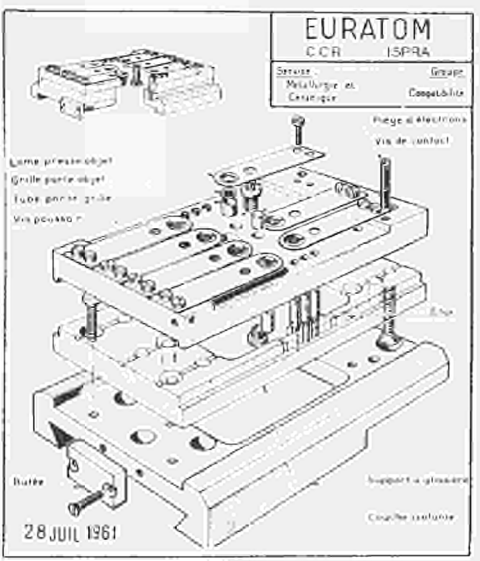

Figure 1. Special sample holder for French Microanalyser.

The highest available accelerating voltage (35 KV) of a CAMECA Microanalyser was used in order to avoid a notable deceleration of electrons in the anticathodes, to diminish the absorption effect of superficial oxide or contamination layers, as well as to increase the peak-to-background ratio of the analysed radiation.

APPLICATIONS

Quantitive microanalysis of small inclusion is a very difficult task because it is impossible to predict the direct emission and fluorescent contribution of the matrix. The thin film technique resolves this problem as it is possible to localize the inclusion on both surfaces of the thin sample. This method permitted the identification of 3 phases of an iron rich inclusion of SAP (sintered aluminum powder) (Figure 2). Several applications are listed in Table 1.

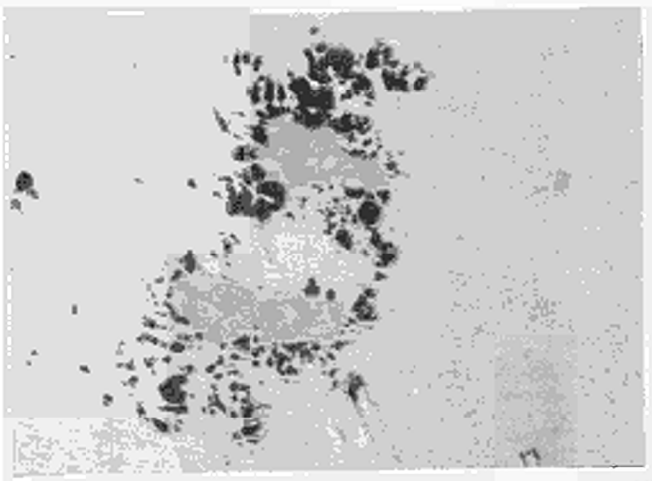

Figure 2. Iron rich inclusion in SAP 980. Electron image X700.

In microanalysis of infinitely thick samples, the diffuse penetration of electrons limits the resolution power of the method to about 0.5μ [13].

A considerable improvement of the volume resolution can be obtained by the thin film technique, as this limitation is no longer valid.

For additional information the use of the special sample holder transforms the French Microanalyser into a projection X-ray microscope with a typical Cosslet-Nixon [14] X-ray microfocus (Figure 3).

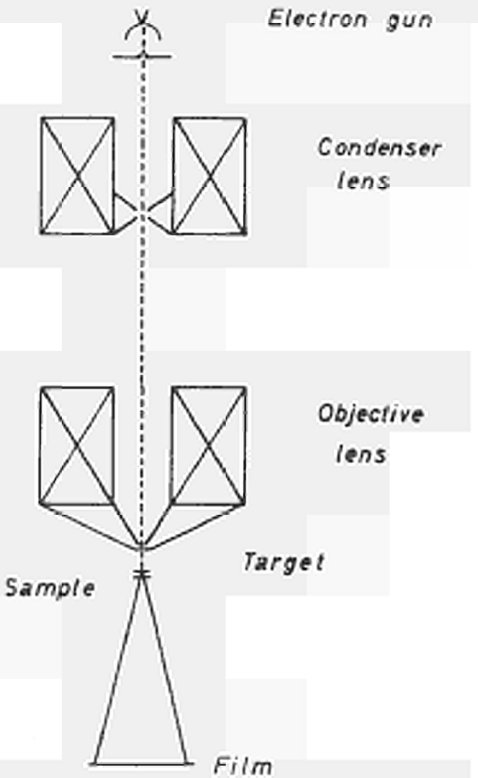

Figure 3. Projection Microradiography.

Table 1

Results of Chemical Analyses and Microanalyses

Alloy	Chemical Analyses	Microanalyses	$\frac{\Delta c}{c}$
	Al W% Theoretical Concentration	Experimental	
UAl_3	25.37	25.12	-0.99%
Sol × Sol × Al-Ni	5.0	4.99	-0.02%
SAP Inclusion $Fe\,Al_3$	59.1	59.63	+1.06%
SAP Inclusion $FeO \times Al_2O_3$	31.0	31.58	+1.88%

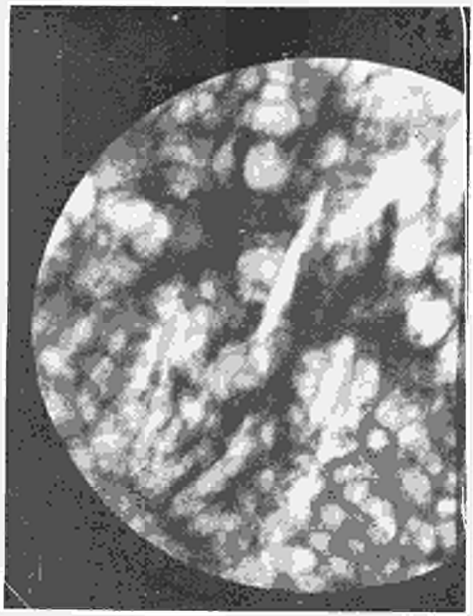

Figure 4. X-ray projection micrography of U Ni Al diffusion layer; U Ni Al = dark zone; Ni_2Al_3 = bright grey dentrites. X250

In U-Ni-Al nuclear fuel elements, treated at 450°C, the formation of a ternary diffusion layer of approximate composition U Ni_7Al_{13} has been identified by microprobe analysis [15].

At heat treatments above 650°C this layer decomposes into two different phases. The composition of these phases were determined by microprobe analysis.

$$U\ Ni_7Al_{13} \rightarrow U\ Ni\ Al_4 + 3\ Ni_2Al_3\ .$$

A film 1 μ thick of Cu was chosen as X-ray source. The selective absorption of Cu radiation by a 15 μ thick sample produces the X-ray micrograph shown in Figure 4.

Furthermore, the special sample holder may be used for studies on electron transmission and backscattering by thin films as well as for electron diffraction purposes.

CONCLUSIONS

High resolution and precision microanalysis may be achieved by the proposed use of the thin film technique.

General use of this method is limited by the delicate and time consuming preparation of samples and standards.

Application includes microanalysis of small inclusions and setting up of calibration curves for complex alloys. Furthermore, projection X-ray metallography combined with electron probe microanalysis may lead to valuable information in physical metallurgy.

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