

35. Applications of the Electron Probe Microanalyzer

By R. Castaing¹

There are many possible applications of the electron probe microanalyzer. We were mainly concerned with its metallurgical applications. Let us mention in this field the determination of curves to represent the diffusion of metals into one another, the study of local variations of the concentrations in alloys, and more especially the analysis of precipitates or of inclusions of an unknown or incompletely known nature.

Figure 35.1 is the micrograph of a copper-zinc diffusion sample that was obtained by heating a plating of the two metals at 400° C. for one hour. Two intermediate phases are visible. The whole diffusion area is about 0.1 mm wide. It is possible to perform a rapid quantitative analysis of the sample at any point, that is to determine the copper-zinc diffusion curve by simply moving the probe across the diffusion area.

Figure 35.2 shows the curve obtained by plotting the zinc-concentration across the sample, that is by adjusting the spectrometer on the radiation $\text{Zn } K\alpha_1$. The abrupt variations in concentrations that correspond to the change from one intermediate phase to the next, and the steady variation inside a given phase are very noticeable. The equilibrium diagram of the two metals is also given. Phase β does not show in this diffusion sample. Further experiments showed that phase β was actually present in the sample, but the layer was less than 1 micron thick. The intersection of the curve and the straight line $T=400^\circ$ should give the limit concentrations that correspond to the phase boundaries. The agreement is good, except at the limit of the phase γ , on the side of high copper concentrations. This disagreement could be explained by assuming a very steep decrease of the zinc concentration in phase γ , close to this limit.

The diffusion curve can also be drawn by analysing quantitatively the copper present in the sample, that is by adjusting the spectrometer on the radiation $\text{Cu } K\alpha_1$. Figure 35.3 shows the curve obtained. It is easy to check that the sum of the ordinates of the two curves is at any point equal to one within 1 percent. This is an excellent verification of the basic relations between concentrations and intensities of the characteristic radiation.

We will consider now an example of an analysis of precipitates. Figure 35.4 represents a micrograph of a copper-tin-antimony alloy which, in addition to big blocks of antimony about 0.1 mm wide, contains needles with a dark central area and a brighter rim. The problem was to determine the composition of these needles. A qualitative analysis shows immediately that they contain some copper; the absorption correction being taken into account, a quantitative analysis shows that the central part is constituted by the Cu_3Sn phase

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whereas the bright rim corresponds to the formula Cu_5Sn_4 . But the rim may contain some antimony. This will be easily checked as soon as the frequency band of our spectrometer is a little broadened so as to include the characteristic radiation of tin and antimony.

The next problem is to estimate the resolving power of this method, that is to determine the smallest diameter of the precipitates that can be quantitatively analysed. Figure 35.5 shows a copper-aluminum alloy that contains precipitates of Al_2Cu about 1 to 15 μ in diameter. If the probe is moved on precipitates of decreasing sizes, the intensity emitted of radiation $\text{Cu K}\alpha_1$ remains constant as long as the diameter of the precipitate is larger than 2 or 3 microns. For smaller sizes, there is a loss of intensity that is due to the diffusion of electrons outside the precipitate. We may derive from this experiment that for a very tiny probe the minimum diameter of the precipitates that are accessible to an accurate quantitative analysis would be about 1 μ . On the other hand, a qualitative analysis can often be performed on much more minute precipitates, close to the resolving power of a conventional light microscope.

I conclude with a few words about the possibilities of punctual crystallographic analysis with the same apparatus. When an electron beam hits a single crystal that acts as an anticathode, the emitted X-rays are diffracted in the anticathode itself, and what is known as Kossel pattern originates as in figure 35.6. The characteristic rays which propagate from the striking point S meet in the anticathode lattice the family of reticular planes P. All rays which have the Bragg angle with planes P are reflected according to the so-called selective reflection. Therefore, the reflected rays are located on cones of revolution, the axes of which are normal to planes P and the half-angle of which is equal to 90 degrees minus the corresponding Bragg angle. If a photographic film is placed above the anticathode, conic sections are printed on the negative. They are the intersections of the plane of the film with the peak intensity cones; consequently they are black on the negative. The operation can be performed by transmission through a thin anticathode; a film placed below it registers conic sections, which show in white. They are the intersections of the plane of the film with the cones of X-rays weakened by extinction. These conic sections are usually hyperboles and are known as Kossel lines. They characterize the crystallographic nature and orientation of the involved region of the anticathode. Thus the phenomenon can be used to perform a rapid crystallographic analysis of a sample by means of the Kossel lines it produces under the excitation of an electron probe. It could be feared that the low rate of the total intensity of the X-rays would entail very long exposure times if a 1- μ probe was used; it is not so, for the film can be placed very close to the anticathode without injuring the very good definition of the image because the lines on the negative are extremely thin. Figure 35.7 shows the Kossel pattern that has been obtained through a 0.1 mm thick aluminum leaf which had been covered by a 1- μ copper layer by vaporization in vacuum. The film lay 2 mm from the sample and the original picture is only 5 mm in diameter. Despite the large magnification, the hyperboles remain very thin and allow an accuracy of 2 min in the determinations of orientation.

Furthermore, after a method used by K. Lonsdale, the tiny curvilinear triangles formed by some of the Kossel lines can be used to determine the crystallographic parameters of the area which is studied,

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with a 10^{-3} accuracy. This result is very interesting since the method does not require any precision in the experimental setting. The fact that a 3 min exposure time was sufficient to obtain this pattern is very remarkable, too. The same exposure time is necessary to obtain a conventional Kossel pattern with an X-ray tube when the electron current intensity is 10^5 times higher.

Discussion

DR. L. MARTON, National Bureau of Standards, Washington, D. C.: I was very much interested in your experiments because at one time we had contemplated something somewhat similar, but the total energy required seemed to be excessive, and I see that, in fact, you need 60 kw/cm^2 . How far did you observe any modification of the samples?

DR. CASTAING: For an incident energy of 60 kw/cm^2 on a 1 micron probe, the calculated local rise in temperature is only 0.3° for a copper sample and less than 10° for other metallic samples. I think it would be possible to use fairly high intensities, as some experimenters have obtained with magnetic lenses, without being disturbed by thermal limitations. In fact, we have never observed any modification of the samples.

DR. D. GABOR, Imperial College, London, England: Is it carbonaceous contamination?

DR. CASTAING: I have seen layers of contamination, but the rate of contamination is not so fast; the layer is visible under the light microscope after irradiating the same spot for about 5 min; it is generally possible to perform the whole analysis before the production of any visible layer.

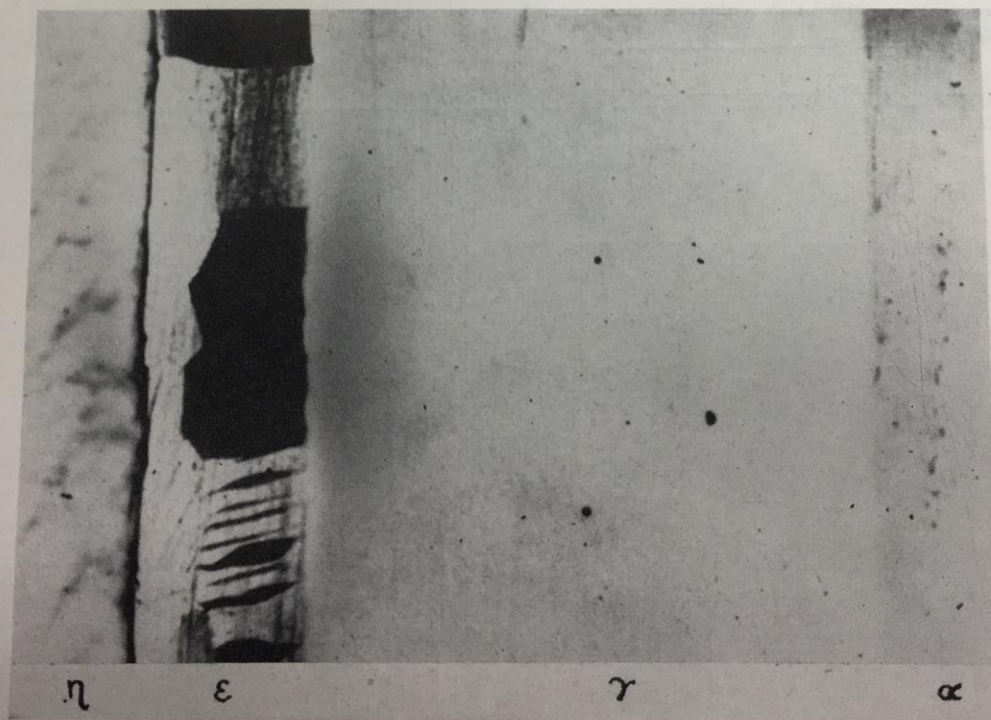


FIGURE 35.1.
Magnification $\approx X700$

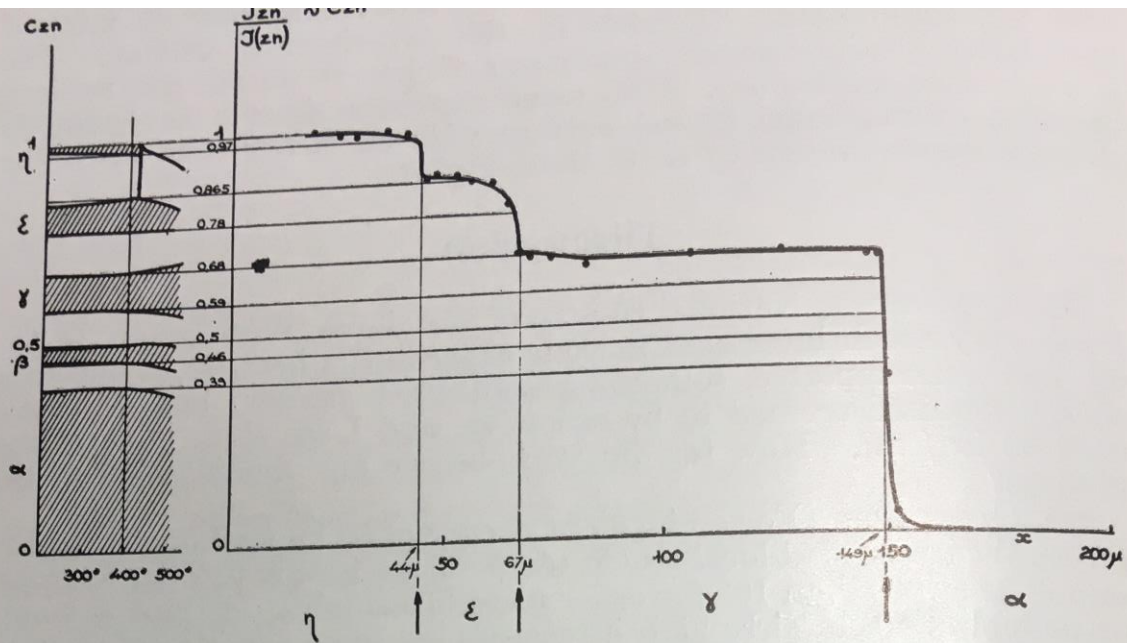


FIGURE 35.2.

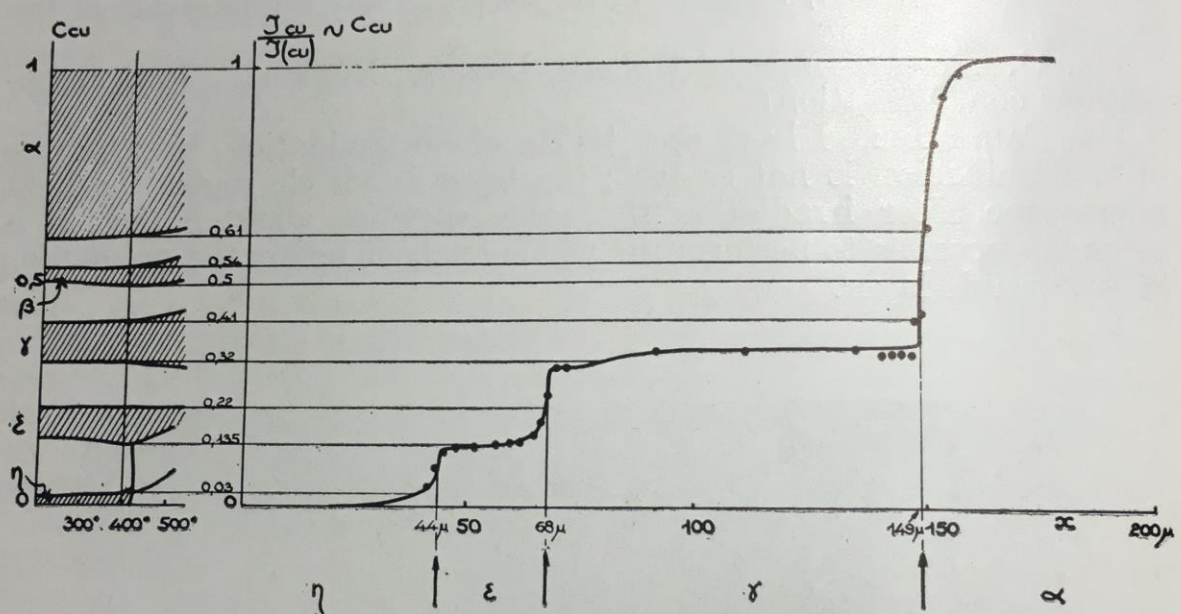


FIGURE 35.3.



FIGURE 35.4.
Magnification $\approx X250$

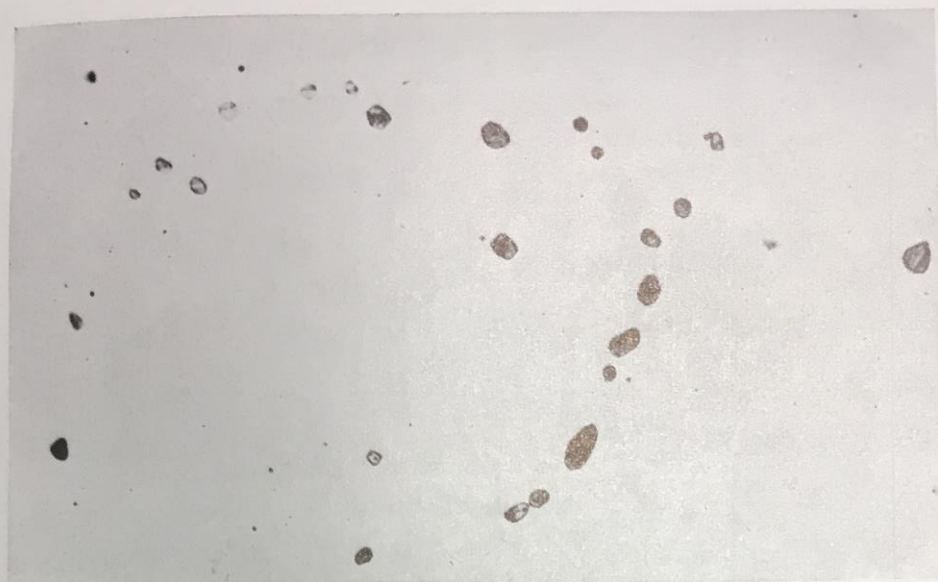


FIGURE 35.5.
Magnification $\approx X300$

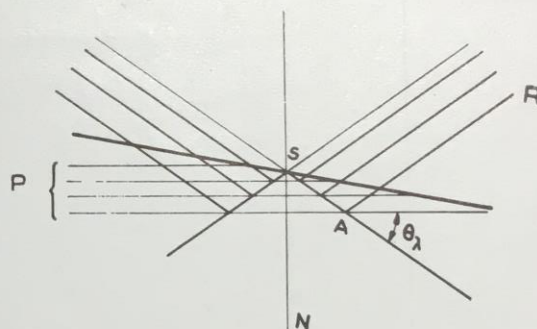


FIGURE 35.6.



FIGURE 35.7.