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Microscopy AND Microanalysis

Keynote Address: The Time of Pioneers

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Abstract: This article, dedicated to the memory of the late professor Raimond Castaing, will evoke the birth and the first developments of electron probe microanalysis in France.

Key words: electron probe microanalysis, Castaing's microprobe, electron microscopy, X-ray spectroscopy, metallurgy, history

INTRODUCTION

This article is dedicated to the memory of Professor Raimond Castaing (1921–1998). I shall try to cover the history of the first steps of electron probe microanalysis in France. I was not personally concerned with the electron microprobe at its very beginning; it was only from 1955 that I have been fully involved in the field. That was close enough for me to get interesting information about the heroic times when, just after World War II, Raimond Castaing was preparing his doctor's degree.

EARLY DEVELOPMENT OF THE ELECTRON MICROPROBE BY R. CASTAING

As a graduate in Physics, Raimond Castaing entered the Institute for Aeronautical Research (ONERA), recently created by the French government, in January 1947. In the Materials Science Department, he was very lucky to be endowed with two electron microscopes, a very exceptional piece of equipment—a real luxury—in 1948. The first one, an American RCA instrument was devoted to metallurgical studies, especially to the precipitation in aluminium-copper alloys. This was a favorite field of Prof. André Guinier, who discovered, just on the eve of the Second World War, the origin of the hardening of these alloys which is due to small copper clusters that produce typical diffusion patterns in X-ray diffractograms, the now well-known GP (Guinier-Preston) zones. The hope of Guinier, and later the ambition of Castaing, was to observe these mysterious zones in real space, thanks to this new microscope.

It was during a conversation mostly devoted to the microstructure of Al-4%Cu alloys, with their various precipitates, θ, θ', and θ'', and the famous GP zones, that Guinier questioned Castaing about a possible local (point) analysis by bombarding an alloy specimen with electrons and detecting the characteristic X-rays, according to Moseley's law. Guinier was an expert in X-ray diffractometers with specially cut and ground quartz crystals, but he requested Castaing's opinion about the feasibility of such an experiment. Let us quote Castaing himself: "I replied straightaway that to my mind it was very easy to do and that it was surprising that no one had done it before." Due to poor communications during and just after the war, people were not aware of Hillier's suggestion to use characteristic electron energy losses in a transmission microscope. But Guinier's question was closely related to a classical metallographic approach, through the observation of the surface of bulk specimens. It avoided the need for preparing thin

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films—a difficult problem—that Castaing succeeded in solving a few years later, using ionic thinning in order to observe precipitates with his transmission microscope. Castaing was not very enthusiastic about Guinier's proposal. The idea seemed to him too simple, so simple—he mused—that it was quite surprising that nobody had done it before! Probably young scientists freshly educated would also think the same way, since such a type of analysis is nowadays so common in many places. I guess they would be surprised to learn about all the difficulties Castaing had to face. Let me just mention that liquid nitrogen was still a very rare product at that time.

I would like to emphasize that all these bright ideas, discussed by the two physicists, were not born in a laboratory of physics, but in a metallurgical environment, under the pressure of engineers, eager to improve the properties of light alloys for aircraft. Some preliminary experiments with a conventional X-ray tube, a curved crystal monochromator, and a Geiger counter, made Castaing change his opinion. A few pulses per minute would not suffice for any analysis, not even a qualitative one. This conclusion was too pessimistic, as a broad source of X-rays was not well matched to a focusing spectrometer. Results would be better with a point source. Therefore, the problem Castaing had to resolve was to obtain a fine beam of electrons. The second microscope he received, built by a French company, seemed to be a gift specially dedicated for this purpose. It was a machine working with electrostatic lenses, which he did not hesitate to cannibalize in order to produce the required fine electron beam, though not without a lot of practical difficulties. He had soon to face many physical problems, which made him understand why others had probably failed. Lens aberrations had to be corrected to produce an intense, fine beam of electrons. Surely there were excellent books describing the lens aberrations (Zworykin's especially), but these did not give any warning on dust particles, grease layers, and so on, that scatter the electron beam.

Again, let us quote Castaing: "By the beginning of 1949, I had succeeded in injecting into a probe of about one micrometer a current of a few thousandths of a microampere, and of this I was very proud. Certainly there were papers in which people claimed to have produced probes of two hundred Angströms, but I was not far from thinking they were out-and-out liars. . ." (Castaing, 1966).

Another problem soon arose with respect to X-ray detection. It was easier to detect the continuous background, but this was not very informative. Finally, Guinier lent to Castaing one of his precious quartz crystals (specially cut and ground, of the Johanson type). It was adjusted in a small spectrograph that fitted to the outside of the main column. In the first days of 1949, Castaing was able to measure the characteristic X-emission from a 1 μm, 4 nA, electron probe. Considering the poor conditions in France after a terrible war, the rapidity with which this result was obtained was quite remarkable.

This result was presented in July 1949 in Delft, the Netherlands, during the first European Conference on Electron Microscopy (Castaing and Guinier, 1950). According to the proceedings, a part of the discussion focused on the limited resolution due to the diffuse scattering of electrons in the specimen. A famous physicist, who later received a Nobel prize, explained to Castaing, in an after-session discussion, "It is a very nice method; it's a pity it won't be of any use!" At the same conference, Castaing gave a paper on an electron microscope study of the first stages of Al-Cu alloy age hardening, a typical testimony of Castaing's interests both in instrumental physics and in applications to metallurgy and materials science. Let us underline once more this metallurgical environment that surely was a powerful incentive for this research, in spite of the difficulties and of the expected "poor" performance. Castaing explained later how discouraged he was when he heard of the Thomson and Whiddington work (1912) about the penetration of the electrons that would drastically limit the resolving power of the analysis. That was a dramatic farewell to the study of GP zones.

In 1951, Castaing submitted his Doctor's Thesis at the University of Paris that was published in a series of ONERA reports (Castaing, 1951) and later translated into English by David Wittry. This publication remains a cornerstone in the field and is a must in the scientific literature. It has not aged, and reading Castaing's thesis should be recommended to everybody entering the field of microanalysis. All aspects were covered in depth: instrumentation, lens aberrations, optimal probe size, modeling of X-ray emission, the physical basis of the correction calculations, some applications to metallurgy, and even crystallography (Kossel diagrams). We are still speaking of $\varphi(\rho z)$ functions and $f(\chi)$ curves. We are still using $\operatorname{cosec}\theta$ although this notation is quite unusual for $1/\sin\theta$. Perhaps the more important idea was the determination of absolute concentrations, by the comparison of the intensities of the same characteristic line of a given element measured on the specimen with that on a target made of the same pure element. This approach was radically different to that used in other analytical methods, i.e., the empirical calibration curves. Castaing's approach was like a revolution, with a tremendous simplification since all instrumental effects disappear in the intensity ratio. But the other side of the coin was the necessity of a deep understanding of the physical processes involved in the diffuse penetration of the electrons and the emission and absorption of X-rays. Castaing proposed a very clear model of these processes that, in essence, have not aged after 50 years.

Prof. A. Guinier thought that things could not remain in this crude state and that the interest of these first results justified that an apparatus should be specially designed and constructed—a project that would have been impossible to realize in a university environment, but that should be a nice challenge for a large and young organization such as ONERA. Guinier, a really wise man, thought that the best solution would lie in the construction of two instruments, one for the inventor (his toy to play with and, of course, to progress in the study of light alloys and other aircraft materials) and the second for a metallurgical laboratory, that would use it regularly and demonstrate its usefulness and versatility. He easily convinced the French Institute for Steel Research (IRSID), created a few years before by the French steel companies, to take interest in the project and establish a financial agreement. The story looks a little like a fairy tale, as industry people were apparently so easily convinced to put money in a bright and promising, but risky, project. What did metallurgists really expect from such a future instrument in the absence of any precise specifications? A few lines from Prof. Guinier were sufficient to convince officials making their decisions. "Quantitative analysis is possible, with an accuracy of 1% or 2% on a mass of material as low as 10^{-11} g; the analysis is non-destructive. Presently the elements that can be analyzed have atomic number above titanium, but in spite of this limitation, the composition of carbides and oxides can be quantitatively determined in iron. Inclusions as small as a few microns can be analyzed. The applications of this method that we can muse about are very numerous" (A. Guinier, letter to G. Delbart, IRSID Director, June 4, 1951). I think the argument about inclusions was a strong one to persuade scientists to come to a positive decision, but that was not sufficient as they were not the ones who held the purse strings. Actually in these times, after the terrible war period, officials had confidence in long-term projects. I am afraid it would be quite different nowadays, and such a project surely would be rejected or, at best, submitted to a series of committees.

When, in 1953, I was hired at IRSID as a young researcher, I was told, in support of the excellence of this institute, that it would receive shortly a marvelous instrument, "une microsonde électronique." I was so impressed in front of my future employers that I dared not ask what kind of a "beast" or "beauty" a microsonde électronique could be. The "beauty" kept IRSID people waiting a longer time than expected. Castaing and his ONERA collaborators were surely working very hard, but designing an entirely new instrument, building it, testing the components, etc., was not a simple task. They had to face many delays, a lot of them not their own, such as finding a foundry for parts (for instance, the main column and the spectrometer envelopes were made of molded aluminium alloy, and had to retain a high vacuum). A fine body was also designed, but it was difficult to find a workshop able to make it; finally, a company that specialized in truck bodies was chosen, but not without some trouble and delays.

I remember my first visit to Castaing in his laboratory at ONERA (close to Paris). With my boss, Charles Crussard, we had prepared one or two specimens to get some more precise information about the real possibilities of the "marvel." As far I can recall, there were samples of steel containing some non-metallic inclusions, where we wanted to check the classical identification based on purely optical observations. I was deeply impressed. Castaing was very nervous—I dare say, as usual—and anxious to demonstrate the performance of his machine. Alas, there were a series of troubles: some current instabilities and gun flashovers. But Castaing refrained from kicking the machine as he used to do on bad days.

There were a lot of buttons that seemed very temperamental; the machine hardly recognized his master's voice, a very strong and convincing voice from my point of view. I was also impressed by the appearance of the machine, with its small spectrometer fitted outside the column in the air (Figs. 1, 2). Nobody seemed to worry about X-ray hazards! Happy times when the security regulations were not too severe. Nowadays, a lot of simple experiments could not be performed so easily. The small microscope allowed only poor observation of the specimen, which made it difficult to position the beam with the required accuracy on a chosen point. Finally, we got some pulses from Mn, a sign that we were looking at a manganese sulfide inclusion.

During the few weeks I spent later at ONERA in Castaing's laboratory, I realized how patient Jacques Descamps was, enduring all the day long a hurricane called Raimond Castaing. Castaing was thinking so fast that we could hardly follow him, and we had to ask him if he would please repeat for our slow minds. That made him still more nervous.

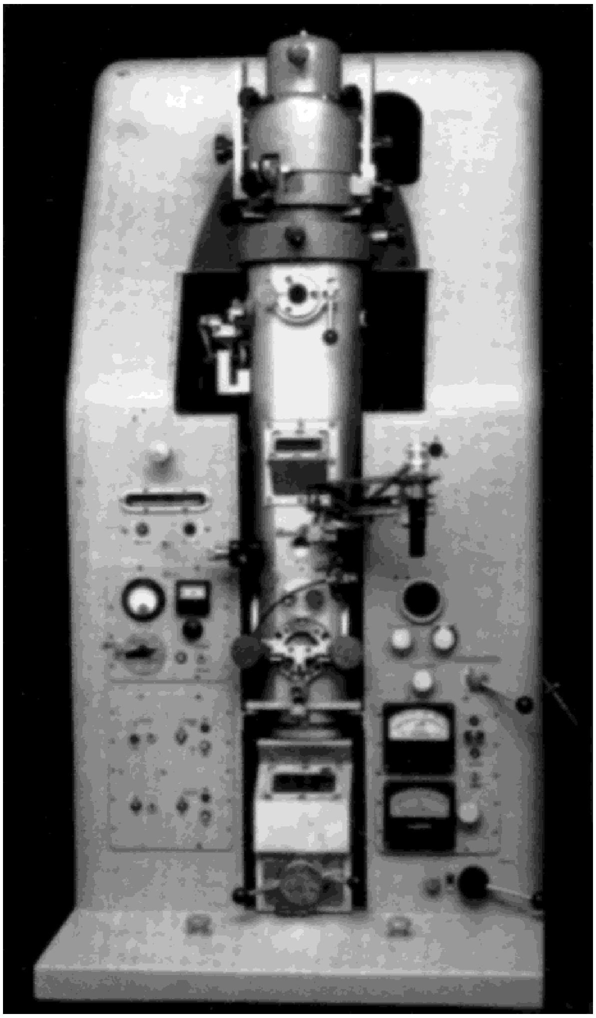

Figure 1. The first electron microprobe (from Castaing's thesis [reprinted with permission from Castaing, 1951]).

Descamps was his clever assistant who succeeded with the nice measurements of the so-useful φ(ρz) curves by the "tracer" technique (Castaing and Descamps, 1955)—so elegant but so difficult to realize—and other small marvels Castaing asked of him as simple services.

Finally, the first instrument was publicly presented in July 1955 at the Physics Exhibition, organized every year in Paris by the French Physical Society. The instrument was not only exhibited, but it was working in the corridors of the old Sorbonne, quite a challenge because of local difficulties in the electric power and the absence of a water supply. Its characteristics have been frequently described and will be mentioned in the paper by Peter Duncumb. The general appearance was that of a nice piece of furniture with the look of the electron microscopes of that time. Nevertheless, it was a prototype, without technical documents, guarantees, and maintenance contract, but with all the problems I should shortly have to grapple with.

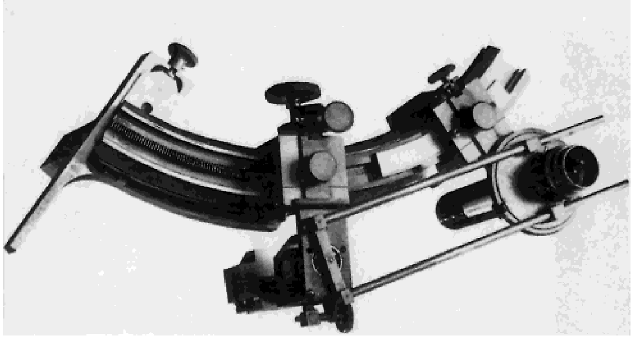

Figure 2. The curved crystal spectrometer fitted to the main column (from Castaing's thesis [reprinted with permission from Castaing, 1951]).

The new instrument was later delivered to IRSID and set up in the Physical Metallurgy Laboratory, where I was asked to take care of it, though my own doctoral thesis had not yet been submitted. Fortunately, I had been educated as a physicist and, in my last year at the university, I followed lectures on the physics of X-rays, so I was a little bit familiar with spectrometers, absorption coefficients, and so on. That was of great help for my beginning, making the study of the Compton and Allison book (1943), our "bible," easier. I tried to tune my mind on the Castaing deep approach of the physics involved in X-ray emission, but first of all, I had to keep the machine working every day, and to welcome the many colleagues who came to me with a lot of "very, very interesting" specimens.

The first years were, of course, filled with a lot of difficulties—the instrument did not obey the standards our young colleagues are now familiar with—and I had to fight against vacuum leaks, current instabilities, lens alignment, contaminated platinum apertures, and so on. On the other hand, this was a very rewarding period, as we had a crop of new results in all fields of metallurgy, from ores to corrosion, including dendritic segregation, non-metallic inclusions, carbide and other phase identification, grain boundary segregation, oxidation, diffusion, etc. Personally, I learned quite a lot of metallurgy at the "Microprobe School." The optical microscope, a specially designed mirror objective, was the cause of many troubles, but I was largely rewarded when I discovered the beauty of cathodoluminescence—the poor non-metallic inclusions were full of bright colors. I also found that a specimen of polished thoria was the best material to mark the impact of the beam, due to its bright luminescence. An inclusion in a steel speci-

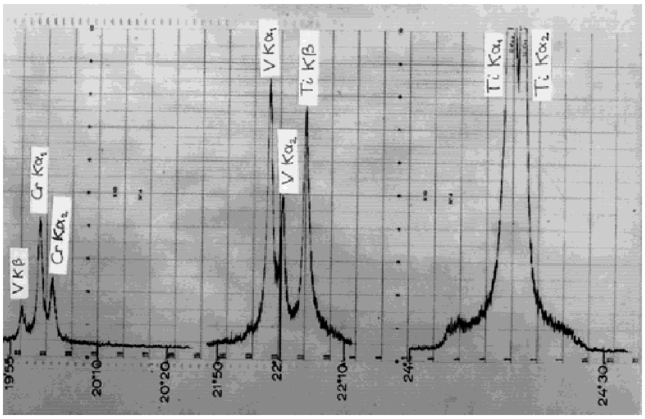

Figure 3. Testing the resolution of the spectrograph.

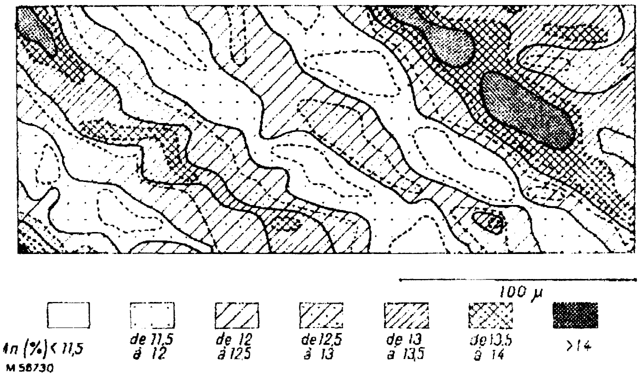

Figure 4. My first concentration map: high manganese steel and Mn isoconcentration curves.

men was especially nice, with the shape and the colors of a grouse, an unexpected bounty.

I also learned about the many traps I was ready to drop into, because of my lack of experience. Zinc was not a component of an inclusion, but a little bit of the fluorescent screen that was used to focus the beam. Finally, I was very fortunate not to make too many mistakes, as I realized later on; and I was happy when P. Duncumb and D. Melford confirmed my measurements on the evolution of the composition of chromium carbides in stainless steels. I was very proud of the high quality of the quartz spectrometer that I enjoyed demonstrating with some spectra (Fig. 3), but it also had its own drawbacks, as it made adjustments difficult and peak shifts or specimen surface preparation very critical.

I had the chance to present our results in several places, especially in this country (USA) in February 1957 at the American Institute of Mining and Metallurgical Engineers (AIME) meeting in New Orleans (Castaing et al., 1957). That was my first visit to the USA. The paper was coauthored by Castaing and Crussard. Shortly after that, I succeeded in producing my first segregation map, by computing the concentration "on-line," thanks to a long series of measurements on a few hundreds of points (there was no scanning facility on this instrument, because of the fully focusing spectrometer). I drew the curves of constant composition every 0.5%; the image revealed a nice band structure in a high manganese steel, inherited from dendritic segregation (Fig. 4). I cannot resist citing two other results of mine: the direct evidence of chromium-depleted zones close to chromium carbides in high chromium steels, a fact that was only indirectly known from the spreading of the Curie temperature and, not the least, the analysis of diffusion couples, mostly in collaboration with Yves Adda. The microprobe was indeed "the" tool for such studies. Actually this idea came from the first studies of Castaing, as one of his first specimens when he was checking his first set-up, was a Cu/Zn diffusion couple. He had been expecting to detect some concentration jumps when crossing the interfaces. (An optical microscope was not yet fitted to his machine at that time.)

I also had to understand the physics behind our analyses, a vital condition to produce reliable results. This included electron-diffuse penetration, X-ray emission and absorption, etc. Of course Castaing was a great help to us while the literature was still rather sparse. All the calculations were made by hand. To get high accuracy, I used a table of logarithms with eight digits, and for routine calculations, a nice slide rule 60 cm long (Fig. 5). I am still proud to keep this instrument in my desk, but I probably lost my nimbleness in playing with the rule—the fault of the electronic calculators.

The limited capacities of these tools were a powerful incentive to develop some improved method of performing correction calculations. The very few $f(\chi)$ curves published by Castaing and Descamps (1955) did not allow easy calculation of the needed corrections: quantitative analysis was a real challenge. On the basis of Castaing's model, I succeeded in deriving a handsome formula for the absorption correction that in a simplified form was easy to handle. It has been used for a long time by a lot of people and was a part of several computer software programs. This correction formula was presented at the Third International Symposium in Stanford (Philibert, 1963) by a French colleague, since, for some reason, I was unable to travel so far.

The crowning achievement of that period was the Fourth International Conference on X-ray Optics and Mi-

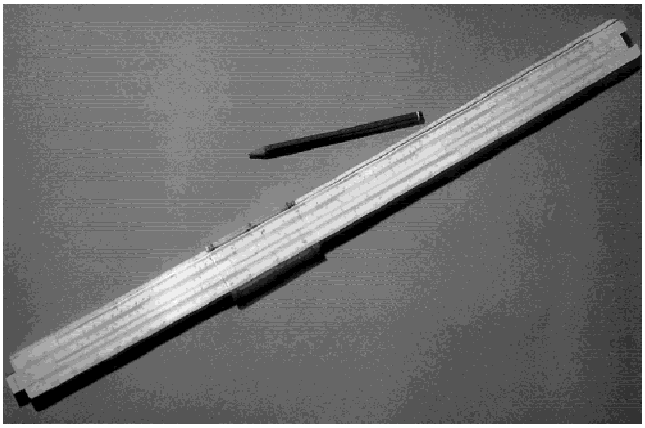

Figure 5. A marvelous instrument: the slide rule.

croanalysis (Castaing et al., 1966). I was one of the organizers with R. Castaing and my collaborator, P. Deschamps (not to be confused with Jacques Descamps). It was held in the Orsay campus of the Paris University where Castaing was a Professor of Physics. I would like to point out that Castaing was also an exceptional teacher. His lectures in Thermodynamics and Statistical Mechanics remain famous because of their originality and the deep understanding of the physical phenomena and theoretical models they demonstrate.

CONCLUSIONS

In conclusion, I would like to underline the interest in revisiting this period; success and failure remain a source of lessons for our present research activity:

- Postwar conditions opened the way to enthusiasm and free research facilities that permitted a blossoming of novelties. It was not too difficult to convince officials of the interest in long-term (and risky) projects. Why not in present times?
- Castaing opened a new approach to analytical procedures that remain a model for other analytical techniques.
- Today, more and more metallurgists, materials scientists, biologists, and biophysicists are using sophisticated instruments, without a sufficient understanding of the physics involved with their instruments. This situation can be dangerous, and mistakes or wrong interpretations are frequent. This problem is becoming worse with the automation of the instruments and procedures that deliver the final results. For most operators, software behaves like a black box. Workshops and summer (or "four seasons") schools are more essential than ever.
- Microprobe history is punctuated with a lot of unforeseen events; planned research is always an illusion.

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