

Quantitative Electron Probe Microanalysis of Carbon in Binary Carbides

I—Principles and Procedures

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Introductory investigations performed in order to make quantitative electron-probe microanalysis of very light elements such as boron, carbon, nitrogen or oxygen possible are described. The practical problems encountered in this kind of work are discussed in detail and, where possible, solutions are proposed. It is shown that with very light elements such as carbon it is no longer permitted to measure x-ray intensities at the position of the maximum of the emission peak as the shape of the carbon $K\alpha$ peak is subject to strong alterations, depending on the type of chemical bond involved. As a consequence, integral measurements have to be performed and it is shown that errors of 30–50% can easily be made if this is neglected. The lengthy procedures, connected with integral intensity measurements, can be shortened considerably by the introduction of area/peak factors, which, by definition, represent the ratio between the correct area (integral) and the peak intensity ratio. The accurate determination of such factors for 13 binary carbides is described. This set of factors will permit future measurements simply on the peak; multiplication of the peak intensity ratio by the appropriate area/peak factors will then yield the correct integral intensity ratios.

INTRODUCTION

Since the development in the early 1960s of pseudocrystals with sufficiently large interplanar spacings to make the detection of very light elements ($Z < 10$) possible, a number of papers (e.g. Refs 1–12) have appeared on the subject of quantitative electron probe microanalysis of these elements. With a few exceptions,^{4,8} these publications dealt only with isolated cases or discussed the practical problems typical of this particular kind of work. Only in one case¹ did they lead to the introduction of a new matrix correction procedure.

Owing to the limited range of experimental conditions and specimens investigated, however, it is still an open question which of the existing correction procedures, if any, is capable of dealing with, e.g., the enormous absorption correction (up to a factor of 18–20 in unfavourable cases) which sometimes has to be applied in order to convert the measured intensity ratio into concentration units. Recently, our own correction program^{13–15} has been added to the list of existing programs and it has been indicated¹⁴ that this particular program, based on the use of Gaussian $\phi(\rho z)$ (ionization vs mass depth) curves, might be well suited to application to light element analysis.

Frankly, it must be stated that the reasons for the uncertainty about the performance of any correction program are two-fold: firstly, there is a general lack of reliable data over a substantial range of experimental conditions and on a sufficiently large number of specimens, and secondly, there is a considerable uncertainty about the mass absorption coefficients (MAC) for light element radiation; reported values^{1,6,9,10,16,17} differ by as much as 50–100%.

If it is realized that, on average, a 1% change in the MAC for carbon can produce a 1% change in the calculated concentration, it becomes immediately obvious that the performance of any correction program can only be judged in conjunction with the particular set of MACs used. Anyway, a large file of reliable data is necessary for a comparison of programs.

One of the main objectives of this work, therefore, was to supply a sufficiently large data file of accurate measurements on carbon, on which a number of existing correction programs (as well as future, possibly improved, programs) can be compared in conjunction with the various sets of MACs currently available.

A second motive for the present work was the fact that a long-term investigation is in progress in our laboratory into the diffusion of carbon in the ternary systems Ti–Fe–C and Ti–Co–C, for which it was necessary to develop microanalytical techniques capable of measuring carbon with a relative accuracy of better than 2–3%. For this reason, special emphasis has sometimes been laid on measurements in various TiC specimens. Some preliminary results of this work have been published,¹⁵ and full details, including all numerical data, have been presented in an internal report.¹⁸

Part I here is devoted to a discussion of the practical problems connected with light element analysis and to the procedures along which the correct intensity measurements should be carried out. Part II deals with the conversion of measured intensity ratios into concentration units, using four of the currently available matrix correction programs and three different sets of MACs.

PROBLEMS IN LIGHT ELEMENT ANALYSIS

Anyone who attempts to measure very light elements, such as B, C, N or O, is confronted with a number of problems. Some of these are of a technical nature or are concerned with measuring procedures, and others are related to the physical backgrounds of the technique.

Firstly we usually have a low count rate, coupled with a relatively inefficient detection system. The answer to a low count rate would be simply to increase the beam current. One has to bear in mind, however, that this produces an increased risk of running into dead-time problems for the metal lines if the metal partners have to be measured simultaneously. Recourse to higher orders of reflection can, in this case, provide a solution.

Next we have a group of problems that are connected with the way in which the background should be measured. Interference of higher order metal lines is a well known nuisance; notorious examples in this respect are the metals Cr, Mn, Zr and Nb. In order to remove unwanted interferences one would be inclined to apply sharper discriminator settings in the pulse-height analyser (PHA), with the inherent risk of becoming more vulnerable to pulse shifts which may result from the often large differences in count rates (up to two orders of magnitude) between the standard and the specimen, especially if elemental standards are used. Recently, in the detection of B $K\alpha$, we observed that an increase of a factor of 3 in the count rate produced a pulse shift of -0.1 V in the PHA; hence this could really present a problem if narrow settings in the PHA are used. Solutions to this problem would be either to move the window along with the shift in pulse or to perform all measurements at the same count rate, i.e. to adjust the beam current. Clearly, neither of these solutions is very practical. One should, however, at least be aware of this effect.

Carbon contamination is a major problem in the detection of light elements, especially, of course, in carbon measurements. Contamination is the result of a carbonaceous deposit which is built up continuously at the point of impact of the electron beam. The sources for carbon lie in the presence of hydrocarbons (diffusion pump oil), polishing agents, cleaning fluids, etc. Several solutions have been proposed to these problems, including a liquid nitrogen cooling trap and/or the use of an air-jet. We conducted a detailed investigation¹⁸ into the effects of these devices on contamination, and also of the various experimental conditions (potential, beam current, type of specimen, specimen preparation, etc.) on this effect and as a result we found that nothing could match the performance of an air-jet, certainly not in the long term (up to several hours). The presence of oxygen in the gas seems to be vital and tests for up to 16 h on the same spot (on ZrC) showed a perfectly stable and minimum carbon count rate. The general conclusions of this investigation can be summarized as follows:

1. It is advisable to wait for some time after positioning the beam to allow the carbon count

rate to attain a stable and minimum value. The initial count rate, and also the absorbed current, are always higher than after 30–60 s.

2. The time necessary to attain this minimum depends on the accelerating voltage: the lower the kV, the more time is required.
3. Likewise, the more the beam is defocused (or scanned over larger areas), the longer it takes to attain the equilibrium count rate.
4. The contamination rate can differ appreciably from element to element; it is almost zero for elements such as B or Si and is highest on the transition metals. This observation suggests that contamination is somehow connected with the heat conductivity of the specimen: elements with a low thermal conductivity, such as B and Si, might cause a better 'burn-off' of contaminating carbon.
5. In spite of all efforts, it is impossible to prevent contamination completely. A small but persistent amount of carbon remains present and this has to be taken into account, especially when low ($<1\%$) levels of carbon have to be measured.

Some of the effects discussed so far, are shown in Fig. 1, where several points should be noted. Firstly, there is a more or less pronounced carbon peak at ca 124 nm (44.4 Å), which is the result of contamination, in spite of the use of the air-jet. Secondly, there is strong interference of the second order Cr $L\alpha_{1,2}$ line, in spite of the sharp discrimination applied. Similarly, a multitude of interferences are possible (not necessarily present under the actual PHA conditions)

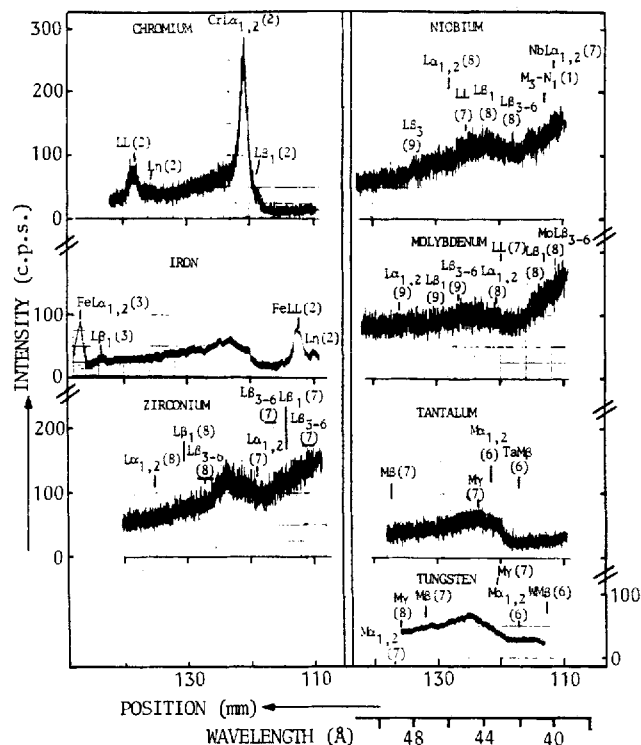


Figure 1. Backgrounds recorded in the spectral region of the carbon $K\alpha$ peak on various metals. Experimental conditions: 10 kV; 300 nA; stearate crystal; counter HT 1700 V; gain 64×5 ; lower level 1.0 V; window 2.0 V; JEOL Superprobe 733; take-off angle 40° . Note that, for technical reasons, the horizontal scale is in a different direction compared with Figs 2 and 3.

for the heavier metals. Thirdly, there is a continuous background, which can have an unpredictable shape.

Summarizing the background-related problems, we can state that the background is obviously composed of three parts: a continuous background, remnants of interfering higher order metal lines, and residual contamination. Hence, it would seem that it is no longer permitted to measure the background at the left- and right-hand sides of the carbon peak, followed by interpolation, as is usually done. A better procedure would probably be to measure the background at the position of the carbon peak on the constituent elements, a procedure similar to that proposed by Ruste¹. We shall return to this point later. The next problem in carbon analysis is the choice of a carbon standard. There are a number of allotropic forms of carbon, e.g. synthetic and natural diamond, various types of graphite and glassy carbon, which makes it difficult to arrive at a well founded decision in favour of one of them. Weisweiler, in a series of papers,⁴⁻⁶ preferred glassy carbon, mainly because of its good electrical conductivity (in contrast to diamond) and its isotropic behaviour (in contrast to the strongly anisotropic graphites). In many respects Weisweiler found that diamond was an exception in the series of allotropic carbons.

In this investigation we preferred cementite (Fe_3C) as a standard, mainly because the expected count rate for carbon is more or less comparable to that in most binary carbides, which would rule out problems of pulse shifts in cases of strong discrimination. Moreover, cementite can easily be prepared and has a fixed composition. A last advantage is that many practical cases require the analysis of carbon in ferrous materials; hence, the physical conditions of the standard are already close to those in the specimen.

The next two problems are the choice of a suitable matrix correction program and the adoption of a reliable set of MACs. These problems will be treated in Part II.

Perhaps the most vital problem in light element analysis is related to the apparently trivial question of how the intensity should be measured. Usually in wavelength-dispersive analysis we tune at the peak in the standard and specimen and determine the peak-intensity ratio. We often do not realize that we do this with the tacit assumption that the peak intensity is a good measure of the integral emitted intensity, in other words that the peak intensity is proportional to the integral intensity. Fortunately, this is true for most medium to heavy element K and L lines, so in most cases there is no problem. However, this is not true in light element analysis. The excitation of a K line in a light element means that we are exciting the electrons involved in the chemical bond and this manifests itself in two ways:

1. In peak shifts: this is not a serious problem because we can simply retune the spectrometer.
2. In peak shape alterations: this effect gives rise to very serious problems because the peak intensity will no longer be a reliable measure of the integral intensity. This is demonstrated in Fig. 2, where the C K α emission profiles from glassy carbon and TiC

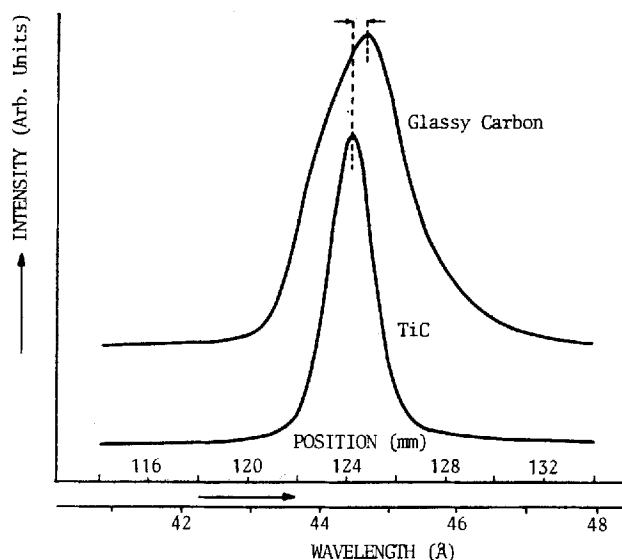


Figure 2. Carbon K α emission profiles recorded in glassy carbon and TiC. Both profiles have been scaled to the same peak intensity. Arrows indicate the peak shift. Experimental conditions as in Fig. 1, except lower level 0.5 V and window 5.0 V.

are represented. To facilitate comparison, both profiles have been scaled to the same peak count rate. It is immediately obvious that, although the peak count rates are the same, the integral intensity from TiC is only half that of glassy carbon. Hence it would be incorrect to compare only peak intensities, in which case TiC would be strongly overrated. Visually estimated, one would have to apply a correction factor of 0.5 in the case of TiC if one would measure at the peak only. Figure 3 shows three more peak shapes, for Fe_3C ,

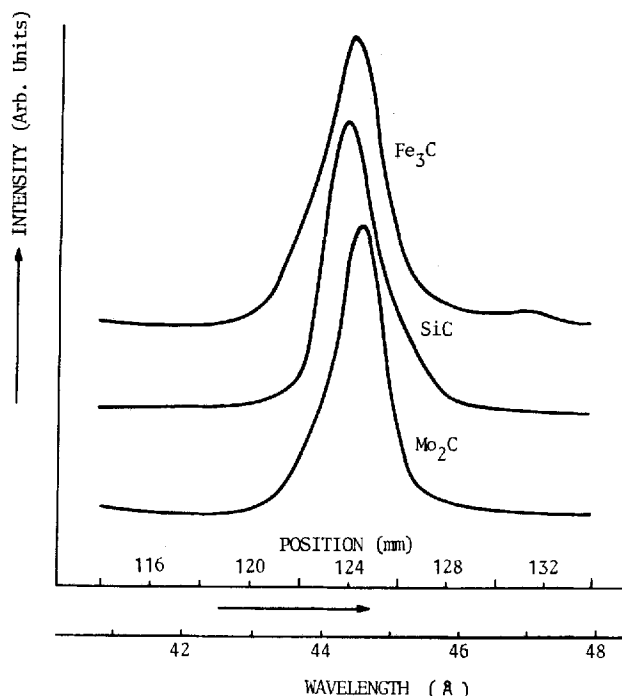


Figure 3. Carbon K α emission profiles recorded in Fe_3C , $\alpha\text{-SiC}$ (0001) and Mo_2C . All profiles have been scaled to the same peak intensity. Experimental conditions as in Fig. 1.

SiC and Mo₂C. Note the development of shoulders in the profiles (left-hand side for Fe₃C and Mo₂C; right-hand side for SiC), which seems to be typical of most emission profiles from non-cubic compounds. Obviously such shoulders contribute further to a deviation between peak and integral measurements because a lot of intensity is no longer concentrated around the peak maximum.

Together, Figs 2 and 3 clearly indicate that the peak intensity is no longer a good measure of the integral intensity and that integral (area) measurements are required. With few exceptions,^{5,8} this has probably been ignored up to now.

It is realized, of course, that for many non-automated microanalysers it is not easy to perform integral measurements, because it requires a tedious process of graphical integration of strip-chart recordings. Also, a lot of time is required to perform a single analysis; therefore, in order to improve the statistics, this process would have to be repeated many times.

A considerable reduction in effort can now be obtained by the introduction of so-called area/peak factors (APFs). The APF is defined as the ratio between the area (integral) *k*-ratio and the peak *k*-ratio for a given binary carbide with respect to a given standard and for a given spectrometer. The underlying idea is that once the APF has been determined, future measurements can simply be carried out on the peak again. Multiplication with the appropriate APF will then yield the correct integral *k* ratio. In fact, a substantial part of this work has been devoted to the accurate measurements of APFs for 13 different binary carbides under widely varying experimental conditions, both for the metal lines as well as for the carbon K α line.

EXPERIMENTAL

The requirements for accurate microprobe analysis demand the availability of 100% dense (over sufficiently large areas), homogeneous samples of binary carbides of known composition. As such specimens are difficult to obtain commercially, it was decided to prepare them in our laboratory. The only exception concerned a single crystal of α -SiC, which was kindly supplied by Mr G. Verspui of Philips Research Laboratories, Eindhoven, The Netherlands.

Preparation and characterization of carbides

Most of the carbides were prepared by repeated argon-arc melting of mixtures of elemental powders (purity better than 99.9%), pressed before into pellets. The monocarbides of Ta and W could not be prepared in this way; evaporation of carbon resulted in the partial production of subcarbides. Instead, layers of WC and TaC were grown up to 20 μ m thickness on the metal substrates in an RF furnace using a graphite + purified hydrogen environment at a temperature of 2000 °C for 70 h. Massive specimens of W₂C with thicknesses up to 150 μ m could easily be

Table 1. Survey of binary carbides used and their carbon contents

Carbide	C (wt-%)	Carbide	C (wt-%)
B ₄ C	20.19	ZrC	8.55
α -SiC	29.95 ^a	NbC	8.55
TiC	18.40	Mo ₂ C	5.58
VC	16.00	HfC	N.a. ^b
Cr ₂₃ C ₆	5.78 ^a	TaC	6.00 ^c
Cr ₇ C ₃	9.10	WC	6.13 ^a
Cr ₃ C ₂	13.30 ^a	W ₂ C	3.16 ^a

^a These carbides were assumed to have the stoichiometric composition; in those cases with narrow homogeneity regions (e.g. chromium carbides) microscopic evidence, e.g. the presence of second phases, was used to fix the final composition.

^b Not analysed because of gross inhomogeneities.

^c The x-ray diffraction pattern, together with the characteristic golden colour, typical of near-stoichiometric TaC¹⁹ was used to fix the composition.

prepared in the same way. Any dissolved hydrogen was removed afterwards by vacuum annealing.

Table 1 gives a complete survey of the carbides, together with their compositions. The latter were determined in most cases by conventional combustion techniques. Thanks are due to Dr P. Karduck of Aachen University of Technology for providing the carbon analyses. The measured compositions were further corroborated by the analysis of the metal lines ('carbon by difference'). Also, in a number of cases, e.g. with ZrC and NbC, whose compositions are virtually at the substoichiometric edge of the homogeneity region,¹⁹ microscopic evidence such as small Zr or Nb₂C precipitates was found to substantiate the reported analyses.

Cementite, which was used as the carbon standard, was prepared by argon-arc melting of an Fe-4 wt.% carbon alloy, followed by homogenization for 1 week at 1000 °C in an evacuated silica capsule. This procedure usually yielded large platelets of cementite. In many cases cementite in the shape of needles, about 20 μ m in diameter, was also used; this was supplied by Mr A. P. von Rosenstiel of TNO, Apeldoorn, The Netherlands. Microanalysis showed that the carbon contents of both types of specimens were identical.

In the final stages of the investigation a number of measurements were made with respect to glassy carbon as a standard. This specimen was kindly supplied by Dr P. v.d. Straten of Philips Research Labs., Eindhoven, The Netherlands.

Further details on mounting, polishing and cleaning of the specimens can be found in Ref. 18.

Check on the operating conditions of the microprobe

All measurements were performed on a fully automated JEOL Superprobe 733, equipped with three crystal spectrometers and an energy-dispersive system (Tracor Northern TN2000). The first spectrometer was equipped with a lead stearate crystal, on which all carbon measurements were performed, and

a TAP crystal. The counter was of the gas-flow type; the counter gas was argon–10% methane. The other two spectrometers each contained a PET and an LiF crystal, and the counters were of the sealed Xe type.

The correctness of the acceleration voltage was checked using the short-wavelength cut-off, measured on the screen of the CRT of the multi-channel analyser in the EDX system. Deviations from the nominal voltage could not be detected and must, therefore, be assumed to be less than 20 eV, even for the lowest voltage used (4 kV).

The stability of the beam current was found to be excellent; variations of less than 1% over 16 h were not uncommon. In addition, the instrument was equipped with an automated beam current detector which automatically corrected for small variations in beam current. The long-term stability of the beam with respect to position was found to be more than satisfactory. Any wandering of the beam would have manifested itself in a sudden increase in the carbon count rate because of the beam moving into the brown halo which, in spite of the air-jet, was still observed to surround the (bright) point of impact of the electron beam.

Measurements of Area/Peak Factors

The APFs for carbon were measured by recording the integral C K α emission profile for Fe₃C (standard) and the specimen. The spectrometer was therefore scanned stepwise (0.03–0.05 mm or 0.011–0.018 Å) over the spectral range of interest. At each successive point a large number of counts were accumulated and stored in successive channels of the multi-channel analyser. After completion the data were stored on floppy disk. Typical counting times per step were 5–10 s and the time required for a full spectrum was about 1.5 h. The stored spectra were then processed to obtain the net integral and peak intensities from the standard and specimen.

In some cases, notably with the chromium carbides (see Fig. 1), it was considered necessary to exercise more care in background subtraction because of strong interference. In such cases the profile, recorded on pure chromium under identical conditions, was also recorded. All values were then multiplied by the calculated *k* ratio for Cr L α radiation in the carbide in question (using Henke *et al.*'s¹⁷ MACs) and stripped from the appropriate carbon spectrum, after which the usual procedure was continued.

For a number of carbides (SiC, TiC and ZrC) the APFs were measured between 4 and 30 kV, both for carbon and for the metal lines. As the APFs turned out to be essentially independent of potential contrary to earlier expectations,^{5,6} all other measurements were concentrated between 4 and 12 keV, where the peak-to-background ratio for carbon has its maximum, with the emphasis on values around 10 kV. The accuracy of each individual measurement was estimated to be better than 2%, which was corroborated by the observation that the APFs for the metal lines, in spite of the relatively coarse step size for the narrow metal peaks, was usually between 0.98

and 1.02. As an effect of chemical bond is not to be expected here, one would expect a value of 1.00, which was indeed obtained when the step size was reduced. Hence, for carbon, with its much broader peaks, the step size used is more than adequate and this justifies the estimated accuracy of $\pm 2\%$. All together about 600 spectra were recorded and the final average, APFs have an estimated accuracy of 1%.

RESULTS

The results of the APF measurements can be summarized as follows: the APFs for both metals and carbon were independent of potential, and the APFs for the metal lines were equal to 1, with the exception of boron.

The results of the APF measurements for carbon with respect to cementite as a standard are summarized in Table 2, together with the observed peak position and some crystallographic information. It is immediately obvious that errors of up to 30% (with ZrC and TiC) can easily be made if peak-shape alterations are not taken into account. This would further deteriorate to even 50% if the measurements were made relative to glassy carbon, because the APF of Fe₃C relative to glassy carbon was 0.725. This is an immediate result of the fact that glassy carbon exhibits a much broader carbon peak than Fe₃C.

A further conspicuous feature in Table 2 is the extreme shift in the peak position between WC and W₂C, which actually represents the widest shift observed so far. In this particular case the location of the peak makes the identification of the carbide absolutely certain. Perhaps the most interesting feature in Table 2 is the sawtooth-like appearance of the APF with the atomic number of the metal partner. This behaviour is completely synchronous with the beginning of a new period in the Periodic system. The

Table 2. Area/peak factors (APFs) for carbon K α radiation in binary carbides with respect to Fe₃C as a standard

Carbide	APF	Peak position (nm)	Wavelength (Å)	Structure
B ₄ C	1.048	124.25	44.477	Rhombohedral
α -SiC (0001)	0.861	124.03	44.398	Hexagonal
Fe ₃ C	1.000	124.25	44.477	Orthorhombic
TiC	0.723	124.06	44.409	Cubic
VC	0.773	124.22	44.466	Cubic
Cr ₂₃ C ₆	0.801	124.21	44.462	Cubic
Cr ₇ C ₃	0.803	124.19	44.455	Hexagonal
Cr ₃ C ₂	0.825	124.12	44.430	Orthorhombic
ZrC	0.715	123.88	44.344	Cubic
NbC	0.787	124.17	44.448	Cubic
Mo ₂ C	0.822	124.39	44.527	Orthorhombic
HfC ^a	0.831	124.03	44.398	Cubic
TaC	0.968	124.37	44.520	Cubic
WC	0.974	123.87	44.341	Hexagonal
W ₂ C	1.021	124.57	44.591	Hexagonal

^a Although the APF was measured, this carbide was excluded from further measurements because of gross inhomogeneities.

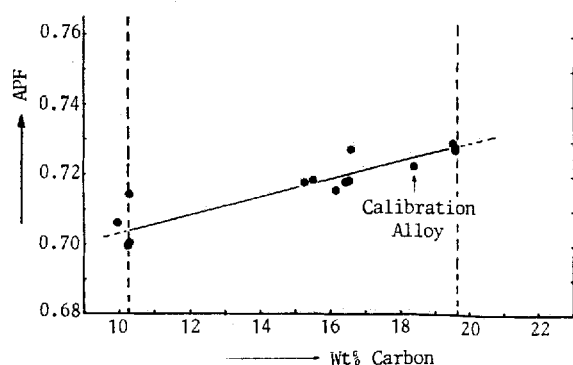


Figure 4. Variation of area/peak factors, relative to Fe_3C , with composition of TiC. Dashed lines indicate the limits of the homogeneity region. Experimental conditions as in Fig. 2.

minimum values are held by notoriously strong carbide-forming elements such as Ti and Zr.

Clearly, at this stage, a number of important questions about APFs are still open.

The first question concerns the problem that many binary carbides can have wide homogeneity regions. TiC, for example, can contain between 10 and 20 wt-% of carbon. Does the APF have a constant value over this range or does it change? The answer can be found in Fig. 4. The APFs for the extreme compositions were measured in two-phase alloys: the Ti-TiC eutectic and the TiC-graphite eutectic. The other compositions were prepared in the same way as the calibration alloy and their compositions were measured using our own correction program (see Part II). As Fig. 4 indicates, the APF varies only slightly with composition and for most practical purposes it can be assumed to be constant.

The second question is what happens to the APF in the case of a mixed (ternary) carbide. In practice, of course, many problems are not restricted to binary carbides. Now, if the APF is discussed in terms of the typical metal-carbon bonds involved, then one would expect that the APF in a mixed carbide (A, B)-C can perhaps be composed on the basis of the atomic fractions of the metals, as these can be considered to be directly related to the number of A-C vs B-C bonds. This hypothesis was verified on two examples of W/Ti carbides, for which case the constituent metal carbides fortunately represent the largest possible difference in APFs (see Table 2).

As Fig. 5 shows, the calculated APFs agree within 2-3% with the measured values, which must be considered satisfactory. Similar observations were made on some quaternary (Ti, Fe, Cr) carbides. These specimens were, in fact, TiC layers, produced by CVD techniques, and contaminated by Fe and Cr. The directly measured APF agreed within 2% with the calculated value, taking Cr_3C_2 , Fe_3C and TiC as the constituent carbides.

The third vital question is: whether the APFs are typical only of the specific microprobe with its specific crystal, spectrometer and Rowland circle, or whether they have a more universal value. At first sight one would perhaps be inclined to assume that the APFs apply only to the particular instrument and conditions on which they were measured. This would be in accordance with the reasoning that in a bad

spectrometer more and more intensity is concentrated in a small region around the maximum. In a very good spectrometer, on the other hand, more and more fine structure in the profile would be resolved, leading to an increasing discrepancy between integral and peak intensity measurements. One has to realize, however, that all measurements are performed with respect to a standard and that in taking the ratio perhaps many spectrometer characteristics are divided out. There is some evidence²⁰ in favour of the last opinion. Some measurements have been repeated on the same specimens but with a completely different microprobe (ARL) and the preliminary results were fairly close to our values. It is clear, however, that final conclusions in this respect cannot be drawn until similar measurements have been repeated on a number of different instruments.

There is still one more vital problem, concerned with the question of whether the peak shape and the total (integral) emission of C $K\alpha$ radiation is dependent on the crystallographic orientation of the specimen. For symmetry reasons such an effect is not to be expected for the many cubic carbides (Table 2). It could be perfectly conceivable, however, for any of the non-cubic specimens.

As there was a sufficiently large supply of SiC crystals available, it was decided to perform a number of experiments with these crystals. To this end a number of α -SiC crystals (hexagonal platelets, colourless) were mounted in all kinds of orientations and their APFs were measured, both as a function of crystallographic orientation of the polished face exposed and of the rotational position with respect to the electron beam. The main result was that all orientations yielded exactly the same APF as the value reported in Table 2, i.e. the peak shape is not dependent on orientation. The same observations were made on a batch of (supposedly) β -SiC crystals (yellow, presumably cubic).

The only peculiar observation was that the α -SiC (0001) face, which was used in the APF measurements in Table 2 and in all subsequent peak intensity measurements (see Part II), proved to be an exceptional orientation: the absolute integral intensity

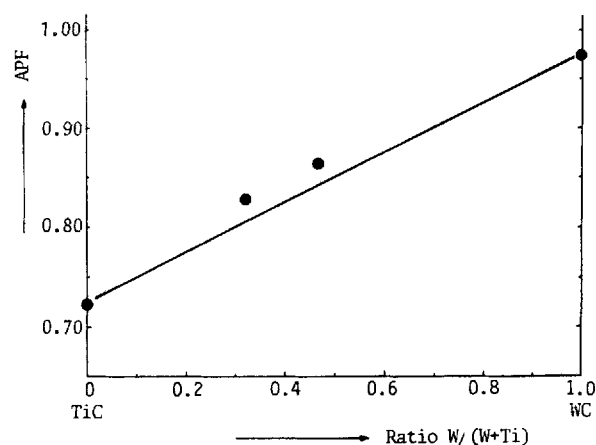


Figure 5. Variation of area/peak factors, relative to Fe_3C , with composition in ternary (W, Ti) carbides. Experimental conditions as in Fig. 1.

emitted from this face was *ca* 5% higher than from any other crystallographic plane. At the same time the absorbed current was found to have the lowest value, *ca* 2% smaller than in planes parallel to the hexagonal axis. Probably this can be explained on the basis of the typical pronounced layer structure of α -SiC. Apparently, electrons penetrating in directions parallel to the hexagonal axis (i.e. perpendicular to the layers) produce a shallower and broader excitation volume, which is accompanied by a more pronounced backscatter process (lower absorbed current). Owing to the lower average penetration depth, more x-ray photons are able to escape from this heavily absorbing matrix. For all other directions it is probable that the average depth of x-ray production is higher and that more electrons are captured (higher absorbed current); however, fewer photons are released. Anyway, this anomaly must certainly be kept in mind when measuring polycrystalline SiC, in which case it is advisable to account for this effect by adopting a correction factor of 1.05 for measurements made

relative to an (0001) α -SiC plane.

Such an effect has never been found in Fe_3C , which has been measured as a standard numerous times. In all other cases the effect has gone unnoticed; the small crystal sizes, usually available, precluded a more detailed investigation. If such an effect were present in Mo_2C , W_2C or WC , it must be assumed to be smaller than the measuring error and consequently it may have been lost in averaging.

Summarizing the results, we can say that we are now in a position to perform large numbers of peak intensity measurements for the binary carbides. This is necessary in order to overcome the small problems with slight inhomogeneities, inevitably present in most specimens, and to improve statistics. Multiplication of the measured peak intensity ratios by the APFs will yield accurate integral intensity ratios. The resulting data file will enable us to compare the performance of the various correction programs in conjunction with some recent sets of mass absorption coefficients. This is the subject of Part II.

REFERENCES

1. J. Ruste, *J. Microsc. Spectrosc. Electron.* **4**, 123 (1979).
2. J. Ruste and M. Gantois, *J. Phys. D*, **8**, 872 (1975).
3. J. Ruste and C. Zeller, *C.R. Acad. Sci., Ser. B* **284**, 507 (1977).
4. W. Weisweiler, *Mikrochim. Acta* **2**, 145 (1982).
5. W. Weisweiler, *Mikrochim. Acta* **1**, 611 (1975).
6. W. Weisweiler, *Mikrochim. Acta* **11**, 179 (1975).
7. W. Weisweiler, *Arch. Eisenhüttenwes.* **49**, 555 (1978).
8. G. Love, M. G. C. Cox and V. D. Scott, *J. Phys. D* **7**, 2131 (1974).
9. E. Kohlhaas and F. Scheiding, *Arch. Eisenhüttenwes.* **41**, 97 (1970).
10. D. Fornwalt and A. Manzione, *Norelco Rep.* **13**, 39 (1966).
11. T. Shiraiwa, N. Fumino and J. Murayama, in *Proceedings of the 6th International Conference on X-Ray Optics and Microanalysis*, edited by G. Shinoda, K. Kohra and T. Ichinokawa, p. 213. University of Tokyo Press, Tokyo (1972).
12. P. Duncumb and D. A. Melford, in *4th International Conference on X-Ray Optics and Microanalysis*, edited by R. Castaing, p. 240. Hermann, Paris (1966).
13. G. F. Bastin, F. J. J. van Loo and H. J. M. Heijligers, *X-Ray Spectrom.* **13**, 91 (1984).
14. G. F. Bastin, H. J. M. Heijligers and F. J. J. van Loo, *Scanning*, **6**, 58 (1984).
15. G. F. Bastin and H. J. M. Heijligers, in *Microbeam Analysis*, edited by A. D. Romig, Jr. and J. I. Goldstein, p. 291. San Francisco Press, San Francisco (1984).
16. B. L. Henke and E. S. Ebsu, *Adv. X-Ray Anal.* **17**, 150 (1974).
17. B. L. Henke, P. Lee, T. J. Tanaka, R. L. Shimabukuro and B. K. Fujikawa, *At. Data Nucl. Data Tables* **27**, 1, (1982).
18. G. F. Bastin and H. J. M. Heijligers, *Quantitative Electron Probe Microanalysis of Carbon in Binary Carbides*, Internal Report, University of Technology, Eindhoven (1984).
19. E. K. Storms, in *The Refractory Carbides*, edited by J. L. Hargrave. Academic Press, New York (1967).
20. A. P. von Rosenstiel, Metaalinstituut TNO, Apeldoorn, The Netherlands, personal communication (1984).