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Micro-area Auger analysis of a SiC/Ti fibre composite

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The reaction zone of an annealed W–SiC/Ti fibre composite was studied by means of micro-area Auger spectroscopy. The Auger peaks and the respective concentrations of the reaction products across the fibre–matrix reaction zone were analysed using small-spot line scans. In spite of surface topographical limitations it was possible to semi-quantitatively determine elemental concentrations with spatial resolutions much higher than are possible using X-ray micro-analysis and to speculate on the formation of different compounds as reaction products.

1. Introduction

The reaction zone formed upon annealing reinforced SiC fibres in a Ti-matrix determines the fracture strain of these materials, reducing the failure strain of the composite to that of the reaction products [1]. The zone has a very distinctive multi-layered structure. The available information about the nature of the reaction products in the SiC/Ti system concludes that a TiC phase [2] is present in the reaction zone and suggests that some titanium silicides should be included. The formation of these silicides seems to be dependent on the annealing times and temperatures. At temperatures below 1000 K only the formation of the TiC phase is observed [3] and, if there is a silicide region formed, its thickness is below the experimental resolution; at higher temperatures both the $TiSi_2$ and Ti_5Si_3 phases are definitely present [2, 4].

These conclusions were drawn from the results of experiments using X-ray microprobe analysis and X-ray diffraction pattern analysis. The spatial resolution of this method is limited to a few micrometres, however, and so this work reports the study of the concentration of elements across the reaction zone of a W-reinforeced SiC-fibre in a titanium matrix using the technique of micro-area Auger electron spectroscopy (AES) with a spatial resolution less than 50 nm.

2. Experimental procedure

The SiC/Ti specimen† was annealed at 1150° C for 8 h and then cut and polished. The details of this preparation were reported previously [5]. The measurements were carried out in an ultra-high vacuum environment at pressure less than 1×10^{-10} torr. Auger spectra were obtained with a scanning Auger system [6] consisting of a small-beam oxygen-processed thermal field emission (FE) integral-electron gun used in conjunction with a variable-resolution cylindrical mirror analyser (CMA). The specimen was electrically isolated from the sample holder so that induced specimen current could be recorded. The incident electron beam struck the sample at an angle of about 30° from the sample normal. Prior to the AES measurements, the specimen was cleaned by argon ion bombardment, with 3 keV ion energy, until the O KLL Auger peak on the W-core of the SiC fibre was below the system noise level. This corresponds to an oxygen contamination of less than 0.1 monolayers.

The distribution of chemicals in the reaction zone was obtained by measuring the peak-to-peak height of the energy-differentiated Auger peaks as a function of electron beam displacement across the sample surface (line scan). The small-area Auger electron spectra and the line scans were obtained with the CMA set to an energy resolution,

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†The sample was prepared and kindly supplied by Dr H. Dudek, DFVLR (Cologne/Wahn), W. Germany.

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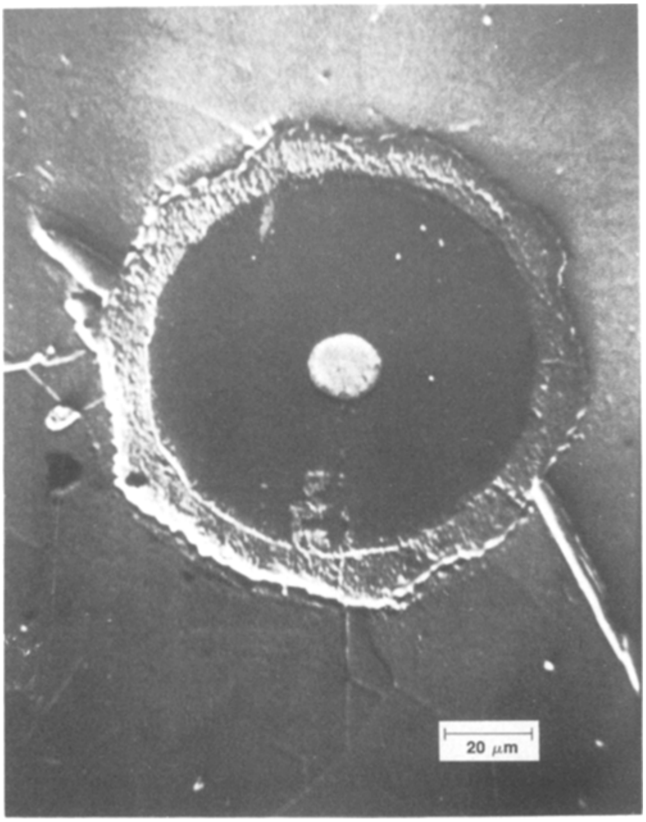

Figure 1 Secondary electron micrograph of the W-reinforced SiC fibre / Ti composite. The bright zone at the centre is the tungsten core surrounded by the SiC filament which, in turn, is surrounded by the reaction zone and the Ti-matrix.

$\Delta E/E$, of 0.5% and 1%, respectively. The primary beam energy was 5 keV. The electron beam spot-size at the sample was less than 50 nm [6], which is approximately the spatial resolution when recording spectra. The Auger spectra were recorded in the $E\,\mathrm{d}N(E)/\mathrm{d}E$ mode, where N is the number of Auger electrons of energy E, by standard lock-in techniques and with normalization of the Auger signal to the incident beam current. This normalization was accomplished by analog division of the CMA output signal by a voltage proportional to the beam current (measured directly in the FE gun). This division reduced the effect of slow drifts in the incident beam current during the aquisition time for spectra or line scans.

The secondary electron images were obtained using a channeltron electron multiplier coupled to a standard visual display unit.

3. Results and discussion

Fig. 1 shows a secondary electron image of a SiC fibre in the Ti-matrix fibre. The bright centre is the tungsten core of the SiC fibre which is about 15 μm in diameter. Surrounding this core is the reaction zone between the SiC and the Ti which, in turn, is surrounded by the titanium matrix. The overall diameter of the reacted fibre is about 100 μm. It is obvious that the thickness of the reaction zone is not uniform but varies between 7 μm and 12 μm.

Line scans across the entire fibre for the Si (LMM, 92 eV), C (KLL, 272 eV), Ti (LMM, 418 eV), W (NOO, 169 eV) and O (KLL, 503 eV) Auger transitions [7] are shown in Fig. 2. Fig. 2b depicts the Si, Ti and W profiles (the small W Auger peak at 413 eV overlapping the Ti transition has been subtracted). In Fig. 2c the carbon and oxygen line-scans are shown. Fig. 2a delineates the sample geometry, the shaded region indicating the reaction zone. The line-scan signals in the reaction zone vary in a complicated way, and it will be shown subsequently that this is due to both local changes in elemental concentration and to specimen morphology effects.

Some information on the mechanism of the formation of the reaction zone can be attained considering the line shapes of the Auger peaks in the different regions of the composite. Fig. 3 shows general features of the Auger spectra. It can be seen that the tungsten core contains an appreciable

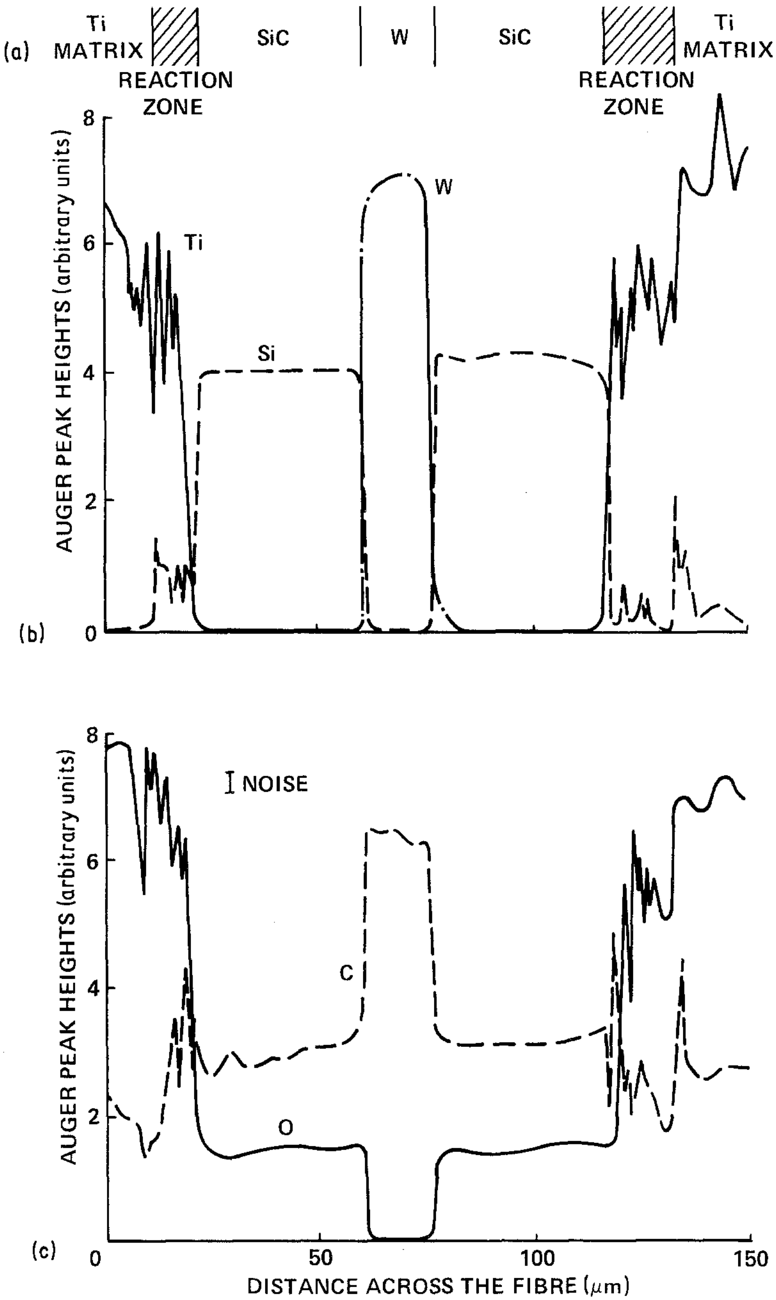

Figure 2 Over-view line scans of the composite sample. (a) A schematic diagram of the sample, the shaded regions represent the reaction zone; (b) Ti, Si and W line-scan profiles; (c) C and O line-scan profiles. The maximum FE noise is indicated with an error bar.

amount of P that has not been removed by the sputter cleaning and which probably arises from bulk contamination of P in the W core (Fig. 3a). The silicon peak in the silicon carbide fibre agrees in shape and energy position with that reported by Van Bommel *et al.* [8] for hexagonal SiC crystals (Fig. 3b). On the other hand, the silicon peak that appears in the outer part of the reaction zone (see Fig. 3c) is shaped like that of elemental silicon [9], except for a higher positive deflection, a more pronounced energy loss structure on the low-energy side and a shift of + 3 eV. The fine structure of the low-energy side of the carbon peak in the core region (Fig. 3a) shows a WC structure [10] and, in the fibre area (Fig. 3b), shows a structure typical of SiC [10]. The titanium peaks in the matrix have the shape of oxidized titanium [11].

The definite TiC structure in the reaction zone and the low concentration of carbon in the Ti-matrix support the assumption that there is carbon transport into the matrix during the reaction of SiC/Ti [4]. Furthermore, the homogeneous WC

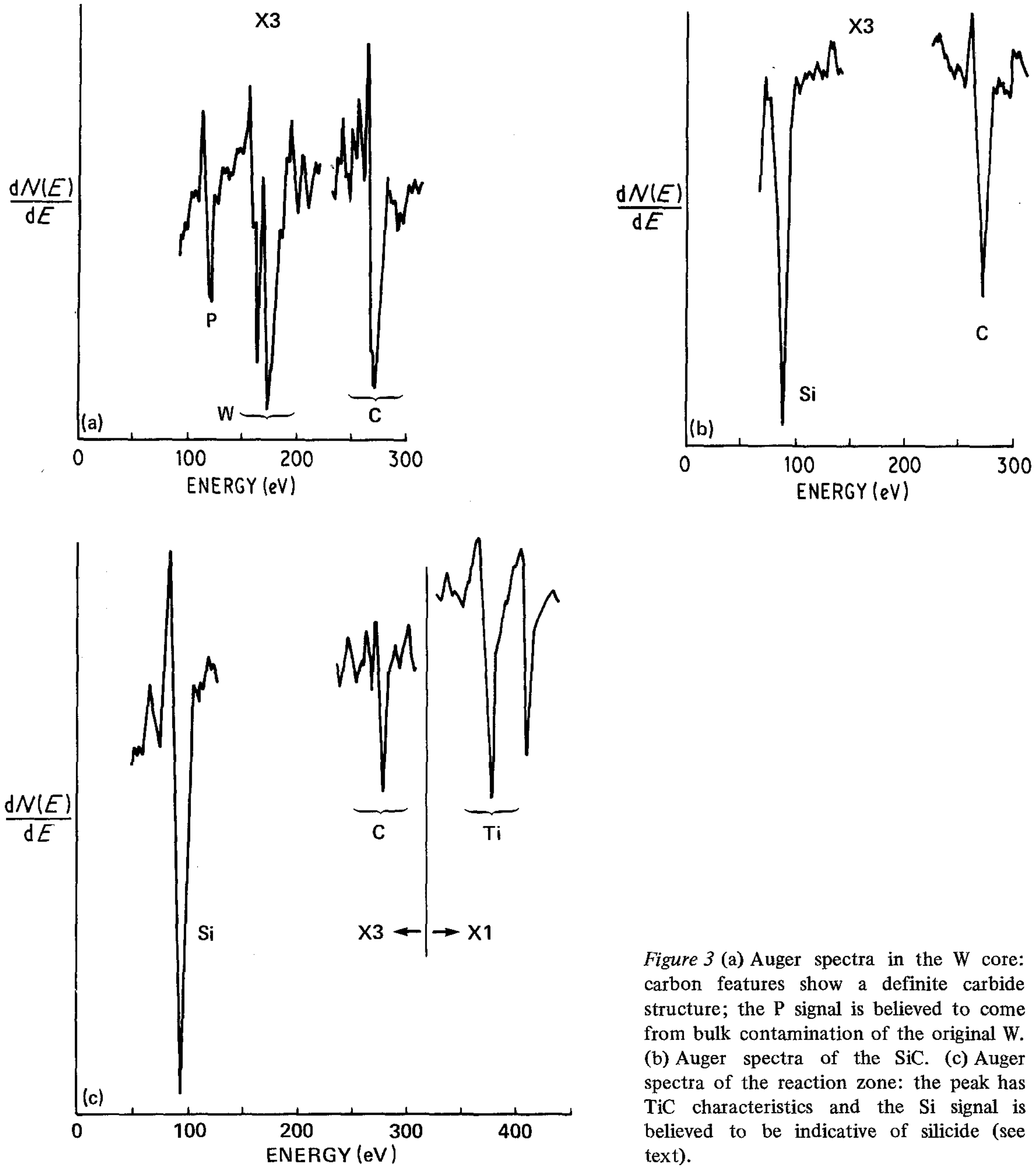

Figure 3 (a) Auger spectra in the W core: carbon features show a definite carbide structure; the P signal is believed to come from bulk contamination of the original W. (b) Auger spectra of the SiC. (c) Auger spectra of the reaction zone: the peak has TiC characteristics and the Si signal is believed to be indicative of silicide (see text).

structure in the tungsten core suggests that there has been a uniform solid-state reaction with the core, although no W/SiC reaction zone has been observed with the present spatial resolution.

Due to the small size of the primary electron beam, a more detailed analysis of the reaction zone was possible. A micrograph of the reaction zone at higher magnification is shown in Fig. 4a where the various characteristic topographical features developed can be quite clearly distinguished. However, it is also evident that topography is still severe and complicates quantitative measurements. In order to identify possible chemical changes and calculate concentrations, peak scans of Si, C, Ti and O were recorded while stepping the electron beam across the reaction zone. The peak-to-peak heights of the four elements were then used to calculate the approximate atomic concentrations, C_i, using the relation [10]

$$C_i = \frac{\alpha_i I_i}{\sum_k \alpha_k I_k}, \qquad (1)$$

where the α_k are the inverse sensitivity factors,

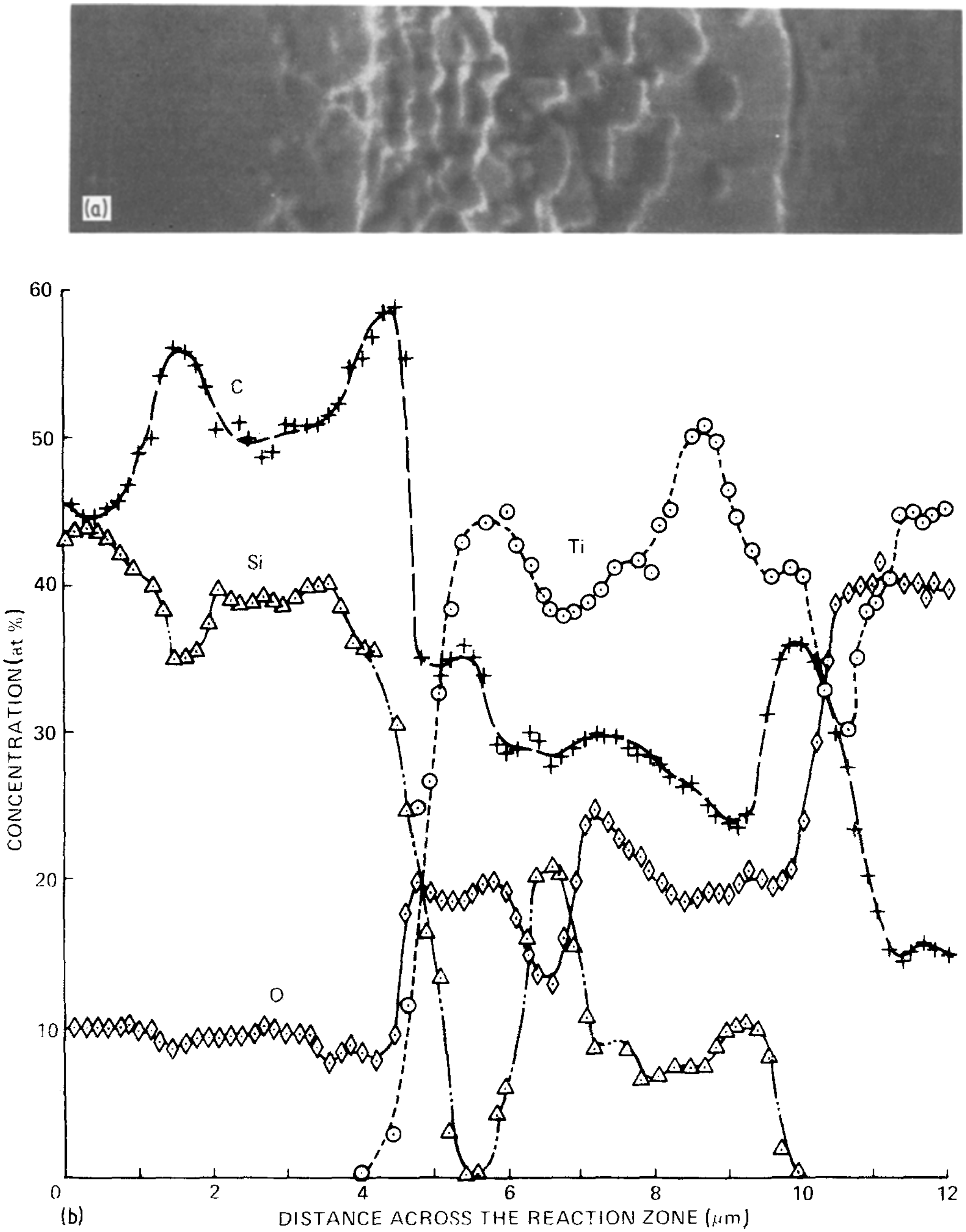

Figure 4 Detailed analysis of the reaction zone. (a) Micrograph of the reaction zone; (b) calculated concentrations obtained from peak-to-peak line scans across the reaction zone: + carbon, △ silicon, ○ titanium and ◇ oxygen.

and I_k are the peak-to-peak heights of the differentiated Auger spectra. These calculated concentration values are plotted in Fig. 4b. The line scans show 45% concentrations of Si and C at the fibre with a small (10%) level of O. The Si and C signals decrease, and the Ti signal starts increasing when crossing the boundary between the fibre and the inner part of the reaction zone, where the line scans show a total depletion of Si and a locally elevated Ti signal. At the outer part of the reaction zone (towards the matrix) the Ti signal maintains an average value with fluctuations that are thought to be strongly topography-induced, and the Si signal increases again but to an average level corresponding to a smaller concentration than that measured in the fibre; toward the outside of the reaction zone the Si signal decreases again. For the Ti matrix, comparable concentrations of Ti and O and a smaller concentration of C are observed. The shape of the line scans for different signals should be correlated if the variations all arise from topographical effects. Inspection of the line scans shows correlation only for the smallest features, as seen in Fig. 4, and there is no correlation for the large variations. This suggests that the larger variations are due to actual changes in concentrations.

In the mechanism proposed by Ratliff [2] for the formation of the reaction zone, the Ti/SiC reaction is initiated by the reduction of the silicon carbide by the titanium. This releases free silicon, which is the most mobile species, and forms the Ti_5Si_3-phase adjacent to the Ti-matrix. The carbon participates in the process by diffusing through the Ti_5Si_3 region and forming the TiC-phase in the outer reaction zone.

However, the results obtained in the present work do not completely support this view. Fig. 4 shows the silicide region (silicide zone, as discussed above) existing nearer to the matrix, whereas the TiC-phase is spread with local variations all through the reaction zone, exhibiting a region of increased concentration close to the fibre. The two carbon pile-ups at the inner and outer interfaces of the reaction zone can be identified by peak-shape analysis as SiC at the fibre side of the inner interface and as a mixture of TiC and graphite at the matrix side of the outer interface. This particular effect is probably due to the non-uniform ion-bombardment cleaning of this poorly polished interfacial region of the sample.

The X-ray microprobe line-scans of Ziegler and Dudek [5] show an appreciable sulphur $K\alpha$ signal throughout the reaction zone with a maximum at the fibre–reaction zone interface. Since Auger spectroscopy is quite sensitive to sulphur (less than 0.1 monolayers can be detected), and sulphur easily segregates to the surface [12], its absence in our line scans suggest that the Argon ion cleaning bombardment probably removed most of the surface sulphur. If any sulphur remained in the bulk, its concentration was below the AES detection limit.

The rest of the X-ray scan results of Ziegler and Dudek [5] are very similar to those obtained in this work, considering the much poorer spatial resolution of the X-ray microprobe technique which averages over a larger sample volume. One major effect of this decreased spatial resolution is that the X-ray silicon line-scan completely misses the Si-depletion in the reaction zone near the SiC fibre (the depletion zone has a full-width-at-half-maximum of the order of the spatial resolution of the X-ray technique). Also, the small Si pile-up at the matrix side of the silicide region of the reaction zone is broadened considerably in their observations.

4. Summary

The relative concentrations of the elements of a SiC/Ti composite sample as a function of location in the fibre–matrix reaction zone have been determined by means of Auger micro-area analysis. Although the elemental concentrations so obtained are affected by the morphology of the surface of the reaction zone more than for the X-ray microprobe analysis technique [5] they have the advantage of a much higher spatial resolution and avoid the problems of bulk averaging that characterize the X-ray technique. The overall changes in concentrations, particularly the increase of the Si signal at the matrix side of the reaction zone, are in good agreement in both techniques. However, depletion of silicon at the fibre interface, and the accumulation of carbon at both interfaces of the reaction zone are missed by the X-ray microprobe analysis.

The shape of the Auger peaks allows us to improve the determination of the spatial distribution of the chemical compounds across the sample surface: however, the chemical and metallurgical consequences of these new results will have to be studied in more detail. Also, major experimental efforts are needed to assess more quantitatively the influence of the surface topography upon the Auger signals produced with this advanced analytical technique.

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