7   Inhibiting impurities

7.1   Observed inhibition behaviour

One final aspect regarding the oxidation behaviour of the as-received RFL graphite remains to be characterised. There is a deviation from the expected behaviour based on active surface area development and catalytic activity, as described in the previous sections. To illustrate this discrepancy, two fundamental assumptions are needed, based on the previous two sections:

- The active surface area development of the RFL graphite is governed by some intrinsic characteristics of the flake geometry, the microstructure and pit formation. This behaviour is assumed to be temperature invariant.

- The only effect due to catalytic impurities, aside from possibly inducing the pit formation, is to increase the reaction rate and drop the activation energy. The catalysts do not affect the shape of the conversion function in any other way.

From this starting point the remaining variability is most easily visualised as follows:

- The isothermal, experimental behaviour at an arbitrarily chosen temperature is presumed to represent the inherent active surface area development. In this case the lowest experimental temperature, 600 ⁰C, is chosen.

- All experimental data are compensated for any gas switch effects.

- Each data set is used to calculate a conversion function at that temperature using the method discussed previously.

- By taking the ratio of these conversion functions from isothermal runs different to the reference run, any systematic deviation with conversion will be noticeable.

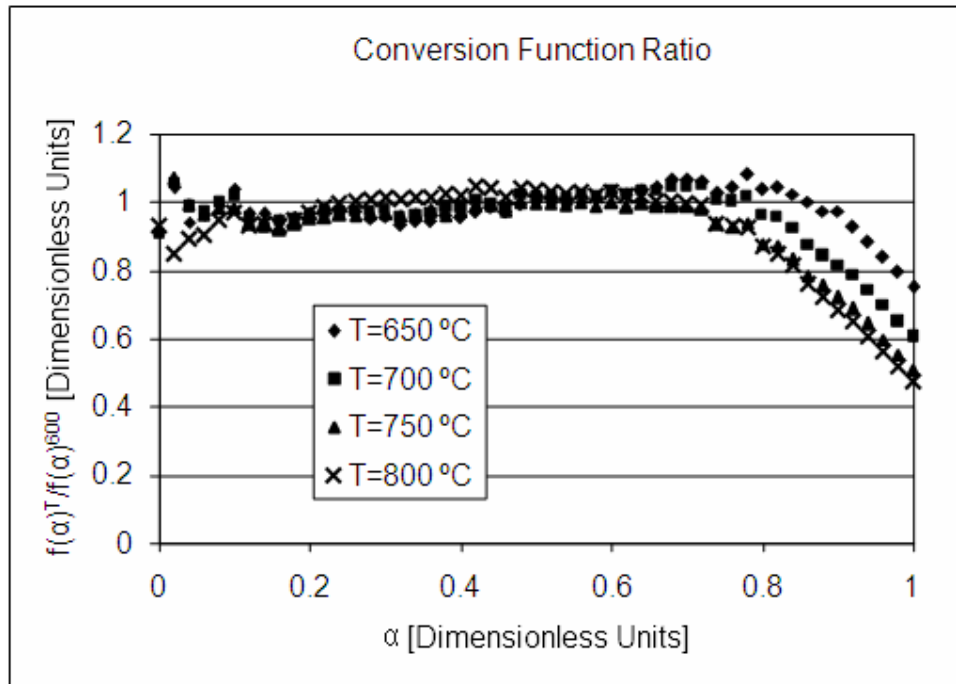The result of this procedure is shown in Figure 7-1.

Figure 7-1: Conversion function ratio for RFL graphite

As can be seen from Figure 7-1, the ratio is fairly constant at a value of one across a wide range of conversions, α = 0.1 - 0.8. Some minor variability still exists at low conversion due to the imprecision of the gas switch compensation, as well as the high degree of uncertainty during this period caused by the catalytic activity. This indicates that, in general, across a very wide range of isothermal temperatures, i.e. 200 ºC, the sample conversion function behaviour is very repeatable and consistent with the two fundamental assumptions made earlier. This reinforces the idea that the active surface area development is the dominant rate-controlling process.

However, a systematic drift is present in all samples at high conversions. This drift has three key aspects:

- The ratio of the conversion function at a specific temperature to the reference temperature shows a drop below one. This implies that the measured reaction rate was lower than expected from the behaviour at the reference temperature. Thus the oxidation is undergoing an inhibiting effect at high conversions.

- This effect increases with increasing temperature. Not only does the effect take place at progressively lower values of conversion, but also

the drop in the ratio is higher at higher temperatures. Thus the inhibition increases with increasing temperature.

- Finally, the behaviours at the two highest temperatures closely resemble each other. Thus the inhibiting effect appears be undergoing some kind of saturation effect at higher temperatures.

The graphite flakes were closely inspected in the SEM at varying levels of conversion at the highest isothermal temperature, 800 ºC. The presence of highly characteristic edge structures was observed. The first aspect that was clearly visible from a macro perspective was the jagged, saw-tooth nature of the graphite edge, as can be seen in Figure 7-2 and Figure 7-3.

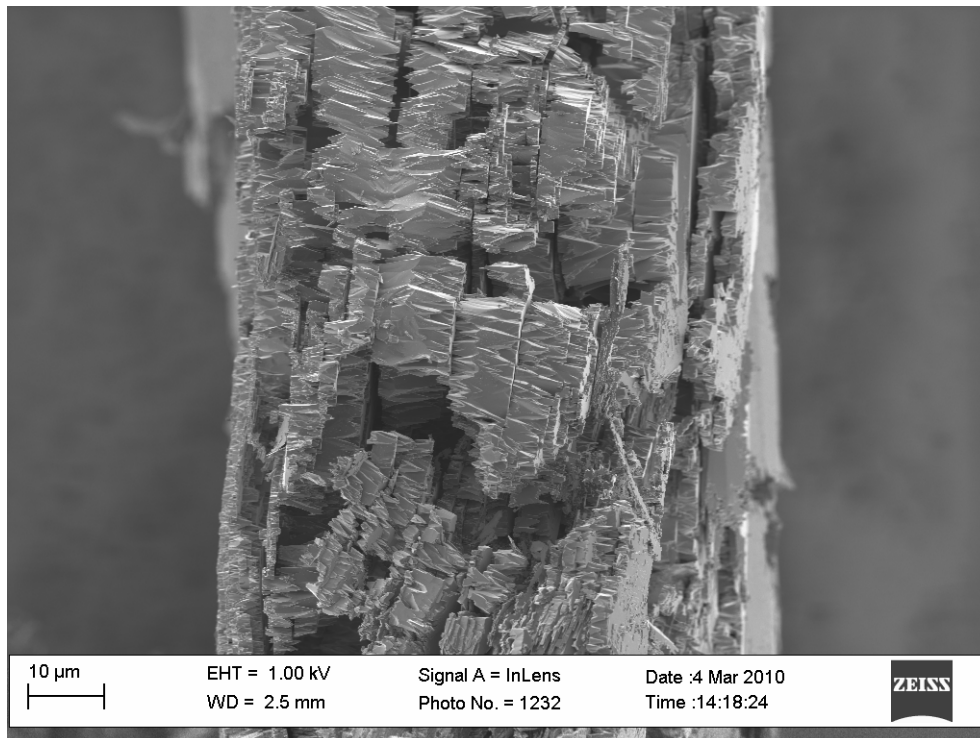| 10 µm | EHT = 1.00 kV | Signal A = InLens | Date :4 Mar 2010 | ZEISS |
| | WD = 2.5 mm | Photo No. = 1232 | Time :14:18:24 | |

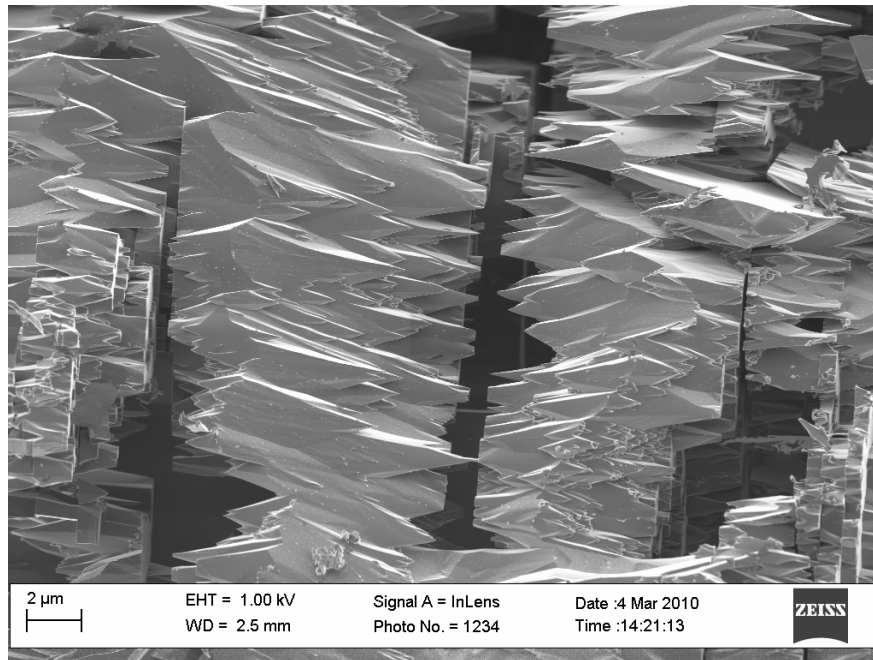Figure 7-2: Graphite saw-tooth edge structure 1 (2 000x magnification)

Figure 7-3: Graphite saw-tooth edge structure 2 (9 000x magnification)

Secondly, the accumulation of a fine dust on the graphite edge was discovered. This dust can be seen in Figure 7-4 and Figure 7-5. The particles are very small, having a diameter less than 100 nm.
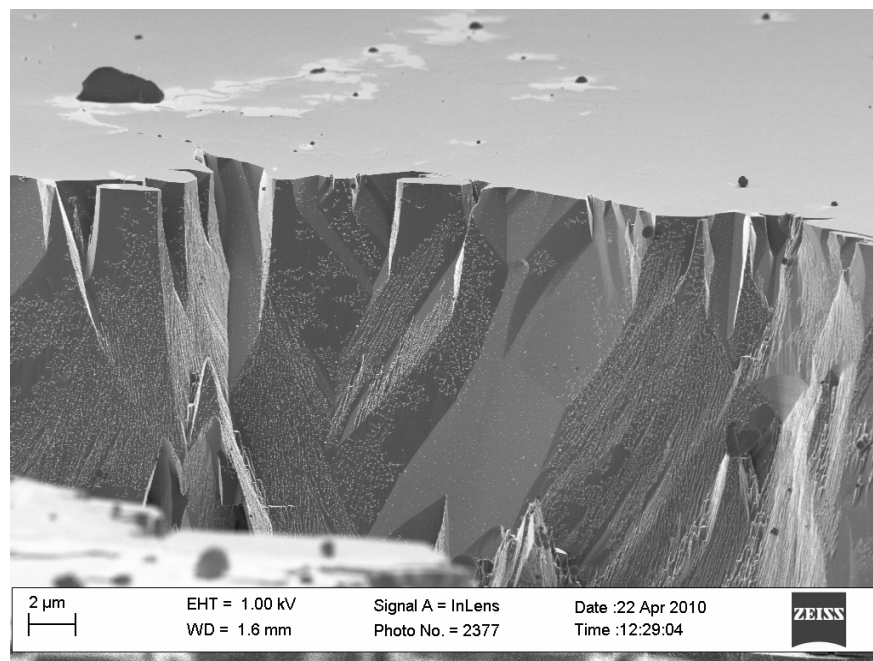

Figure 7-4: Dust accumulation at graphite edge 1 (8 000x magnification)

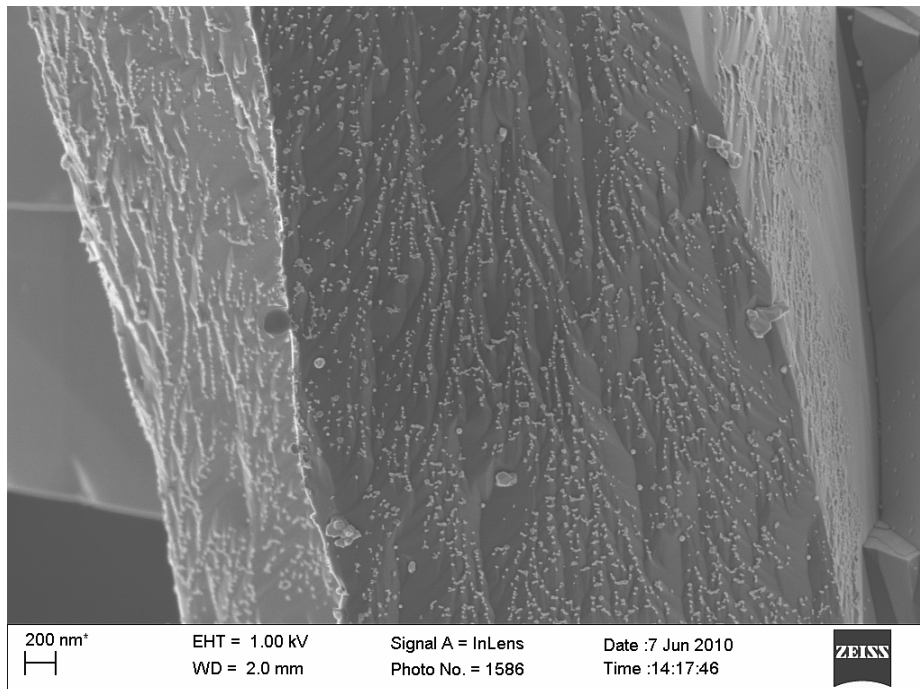| 200 nm* | EHT = 1.00 kV | Signal A = InLens | Date :7 Jun 2010 | ZEISS |
| | WD = 2.0 mm | Photo No. = 1586 | Time :14:17:46 | |

Figure 7-5: Dust accumulation at graphite edge 2 (50 000x magnification)

Upon closer inspection, a distinctive characteristic to the edge structures was observed. As can be seen in Figure 7-6, each of these particles may be found at the pinnacle of a tiny wedge shape on the graphite edge.

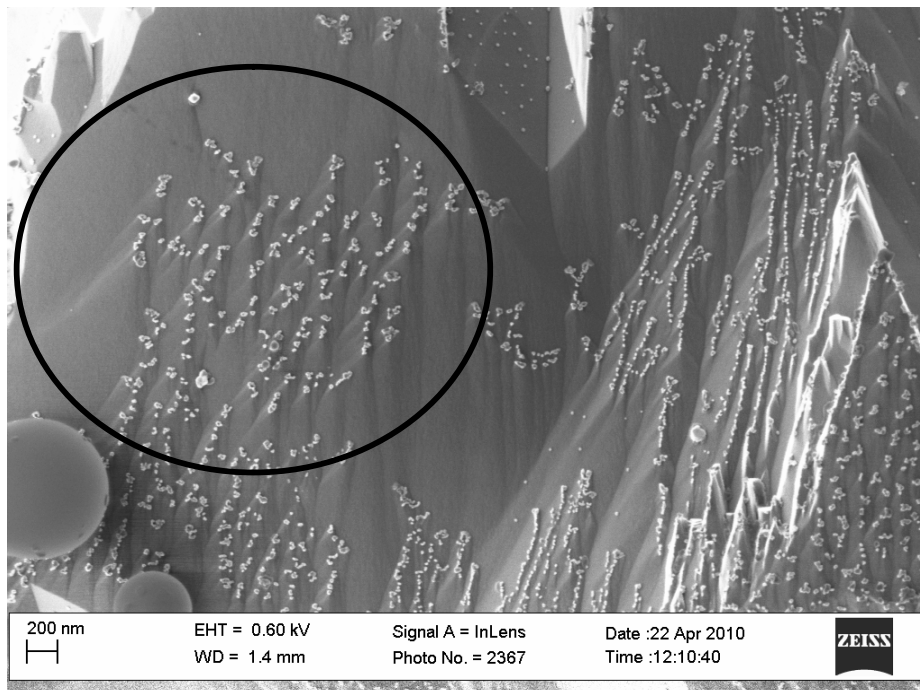| 200 nm | EHT = 0.60 kV | Signal A = InLens | Date :22 Apr 2010 | ZEISS |
| | WD = 1.4 mm | Photo No. = 2367 | Time :12:10:40 | |

Figure 7-6: Inhibitor particles (50 000x magnification)

Thus these particles block oxidation along a very small portion of the edge area, effectively creating a small basal area that cannot be attacked. This basal area shields subsequent layers below it, while the surrounding material is oxidised away. Over time this leads to the development of the characteristic, saw-tooth edge, as observed in Figure 7-7.
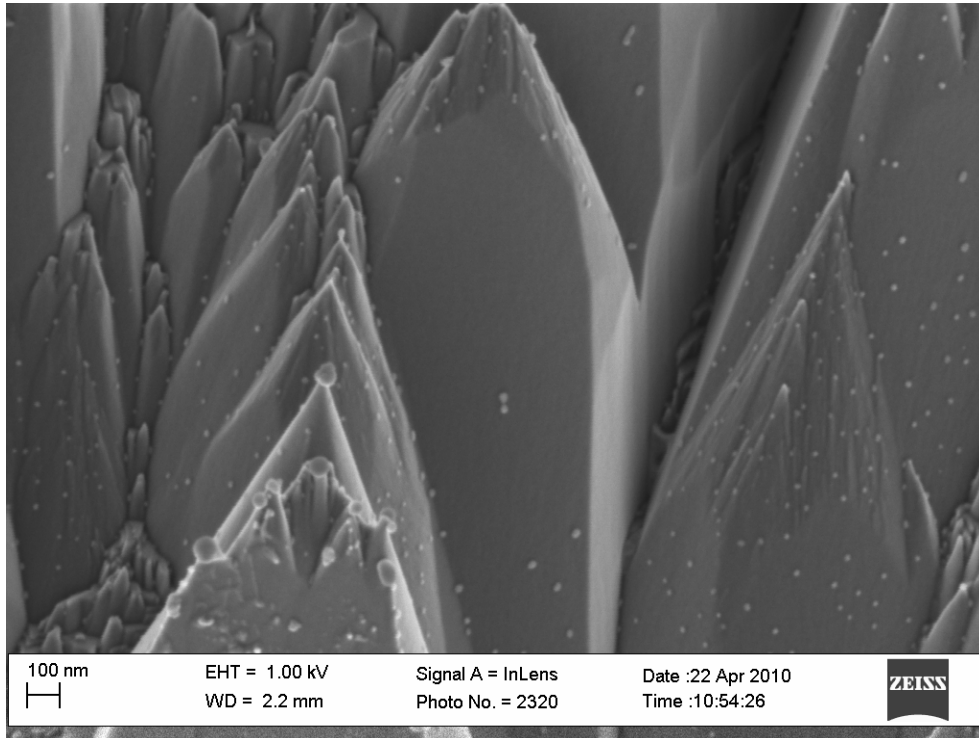

Figure 7-7: Inhibitor particle edge structures (100 000x magnification)

The pinnacle of this behaviour is exemplified by the nanodot in Figure 7-8 atop the summit of a minuscule graphite mountain.
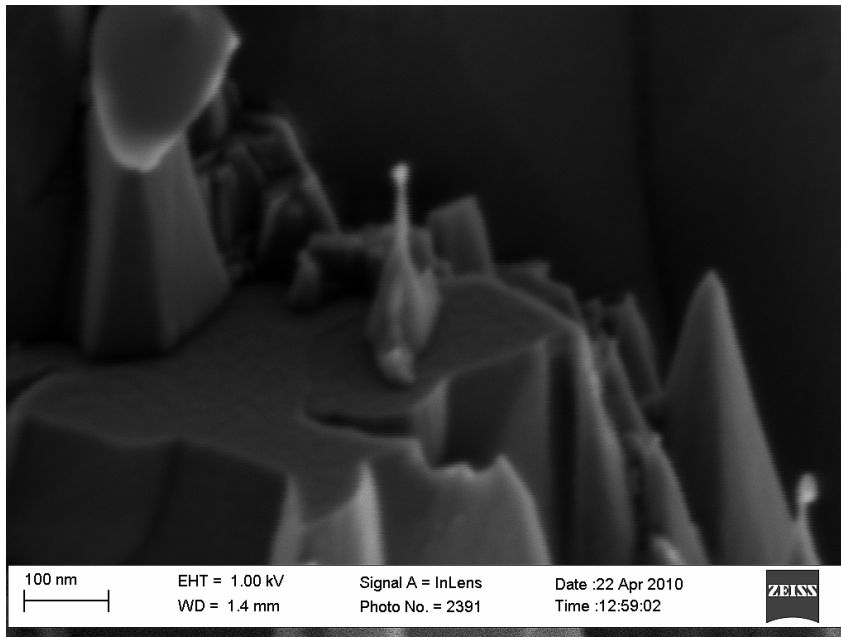
Figure 7-8: Nanodot on pinnacle of graphite (30 0000x magnification)

However, if samples oxidised at lower temperatures are examined, the saw-tooth edge structures are seen to have largely disappeared and the fine dust accumulation no longer takes place, as can be seen in Figure 7-9 and Figure 7-10.
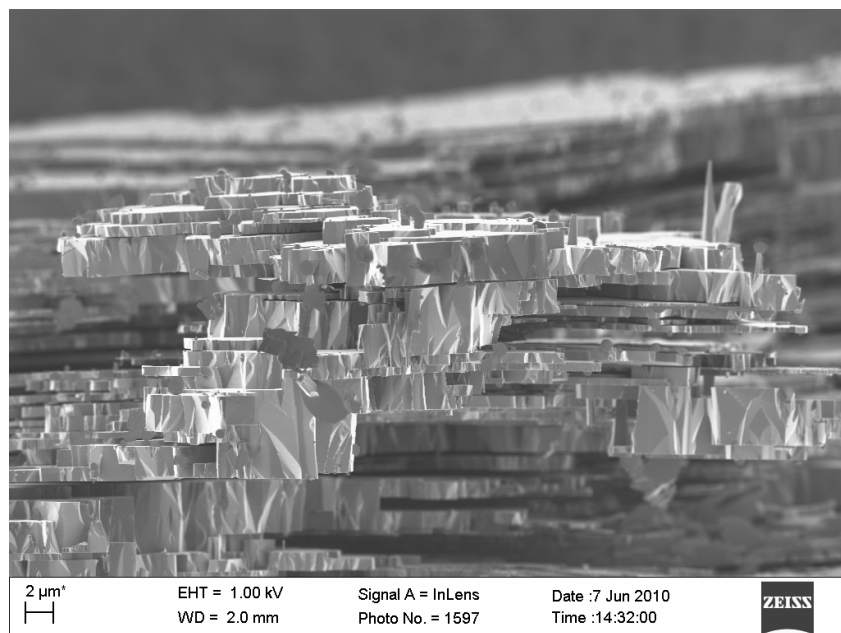

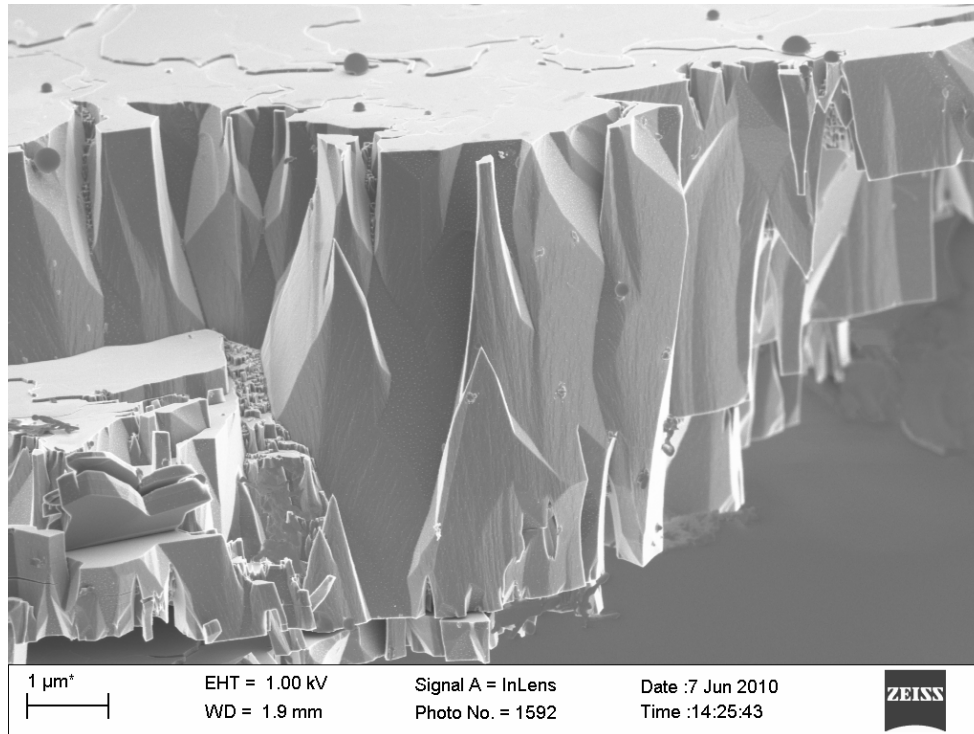Figure 7-9: Smooth graphite edge (5 000x magnification)

Figure 7-10: Absence of dust accumulation (25 000x magnification)

As oxidation proceeds, these impurities will accumulate at the edges of the graphite flakes, progressively reducing the reaction rate. Thus their influence will start at high conversion and become progressively worse as oxidation proceeds. This accounts for the gradual reduction in the ratio of Figure 7-1 at high conversions.

From the EDS spectra of these impurities given in Chapter 3, it may be deduced that these are silicates or perhaps carbo-silicates which are formed from silica reacting with metallic compounds, possibly carbonates, at higher temperatures. These reaction pathways are known to occur via carbothermic reduction at temperatures around and above 800 ºC. These silicates are known to be very stable and sodium silicate, for example, is used as a refractory and a fire retardant.

Thus at lower temperatures these compounds are no longer formed and oxidation follows the expected active surface area development. However, at progressively higher temperatures more of these silicates are converted.

Assuming an even distribution across the flakes, they will accumulate more rapidly at the edges, leading to the reactivity reduction effect emerging at lower conversion, as observed. The saturation effect may be caused by the fact that at a certain temperature all the available precursors have been converted to the inert, inhibiting material. At that point the only effect is accumulation at the edges, which is expected to be temperature independent as a function of conversion.

This type of inhibition is very different from the examples found in the literature. Despite the behaviour being similar in nature to an inert coating, the conversion-based behaviour is entirely different. Since this behaviour has not been observed before, it represents a new insight into the burn-off behaviour of graphite and carbon in general. A preliminary approach to modelling this behaviour is presented in the next section.

7.2   Inhibitor model

From a visual inspection it is seen that the inhibitor particles accumulate at the edges as the graphite particle shrinks, progressively blocking an increasing number of active sites via the pyramid formations that give rise to the saw-tooth edge. However, at some point these structures start to overlap and interfere with each other. At this point the catalyst particles appear to start accumulating along discrete ridges, as can be seen in Figure 7-5. Thus the orientations of the pyramid-like structures rotate slightly as they are eroded away from adjacent sides. Successive pyramids eventually line up to produce a continuous ridge. The sides of the ridge slope downward towards the graphite particle, as opposed to during the initial stages when the slope of the pyramids from the pinnacle is actually directed slightly outwards from the particle; this can be seen in the right-hand side of Figure 7-6.

Since the individual particles now accumulate along discrete ridges, as opposed to forming individual pyramids, their combined inhibiting effect is reduced. Furthermore, at high conversions, channels, fissures and any structural anomalies in the particle will start to coalesce as the particles become smaller and smaller, which leads to oxidation from multiple angles at edges, as opposed to the smooth gradual shrinkage of the ideal disc model. This will further add to

the diminished inhibiting activity caused by the site-blocking particles since the particles will no longer have the fairly regular edges present during steady oxidation, but attack will now be possible from regions that were previously protected by bulk graphite material.

Thus it is expected that the particles will gradually accumulate at the edges until some critical mass is achieved, at which point inhibition will become noticeable. However, as higher conversions are approached, the inhibiting effect will be diminished as the site-blocking capability of the particles is compromised by ridge accumulation and flake irregularities. This behaviour can be empirically quantified in terms of the fraction of active sites that are blocked as a function of conversion. By multiplying two exponential expressions together, one representing inhibitor accumulation and one representing the diminished return on site blocking, the function shown in Figure 7-11 can be obtained. Quantitatively, this function denotes the fraction of active surface area that is no longer available for oxidation.
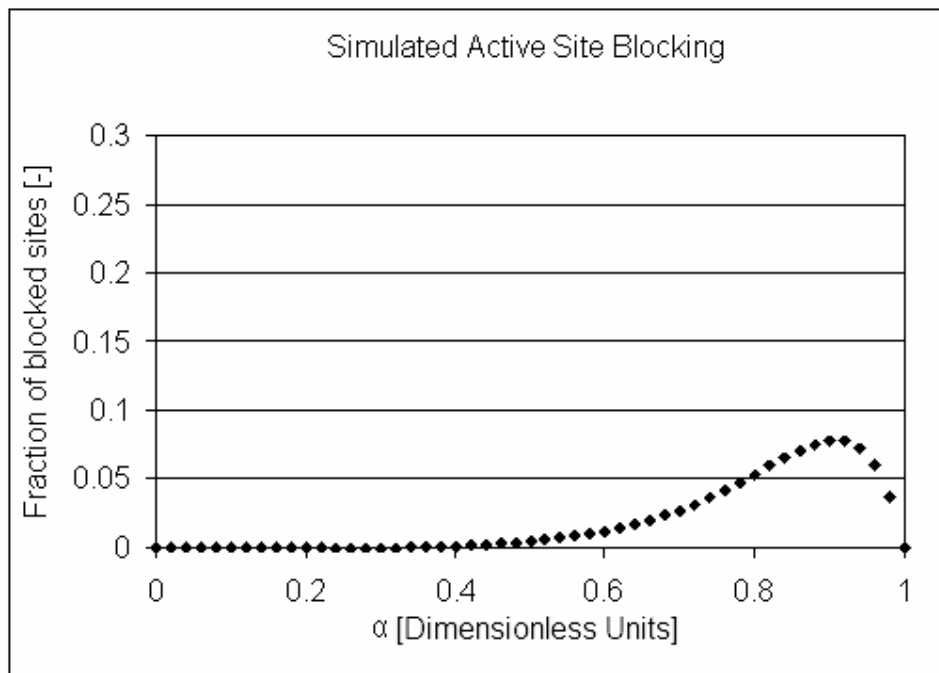

Figure 7-11: Fraction of inhibited active sites

This function may be directly subtracted from the original conversion function, which represents the total available active sites if no inhibition was

present. By taking the ratio of this new function to the original conversion function, a plot similar to that shown in Figure 7-1 can be constructed for the simulated inhibitor effect, as shown in Figure 7-12.
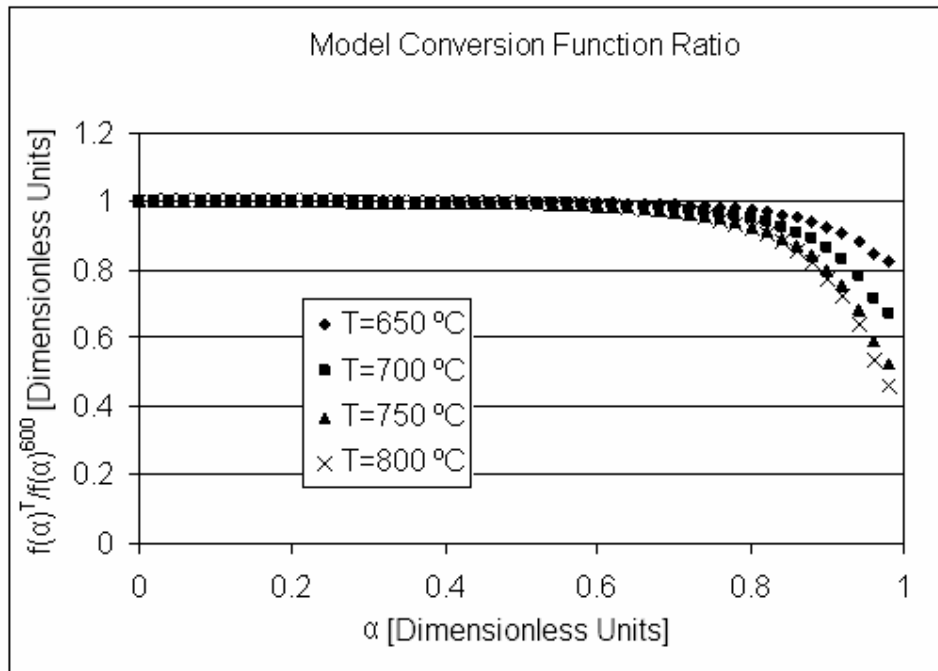

Figure 7-12: Modelled conversion function ratio

Qualitatively, the behaviour is similar to that observed for the experimentally determined inhibitor effect. The temperature dependence was recreated by adjusting the parameters of the exponential functions. While this provides an empirical model that is loosely based on the observed and expected behaviour, it cannot be extrapolated to other types of inhibitor particle. This model qualitatively describes the observed effects of this new inhibitor action. However, more work is needed to gain a fundamental understanding of the mechanism whereby the inhibiting particles are formed and subsequently accumulate at the graphite edges. This, in turn, will allow a better understanding of the driving force behind the temperature-based behaviour.