8   Conclusions and recommendations

8.1   Conclusions

An attempt was made to determine the fundamental factors that govern the oxidation of graphite under atmospheric pressure in pure oxygen under the kinetically controlled reaction regime. Based on an extensive literature survey, several possible influencing factors were determined, including:

- Graphite morphology, ranging from the crystalline structure to the nature of any amorphous carbon structures present
- Factors that influence the reaction of carbonaceous materials in general with oxygen, including surface coverage, product gas composition and the influence of the product gases on the kinetics
- The possibility of mass transport limitations and pore structure-related influences, even at low temperatures
- The concepts of active surface area and surface complexes
- Possible kinetic mechanisms for the oxidation, ranging from simple power law models to very complex, multistep reaction schemes that account for surface heterogeneity
- The graphite microstructure
- The influence of catalytic impurities
- The influence of inhibiting impurities

It became clear that an understanding of the micro and atomic structures of graphite was essential in developing a model that would represent the oxidation. An extensive microstructural investigation of eight graphite samples was conducted, including both oxidised and as-received materials, using ultrahigh-resolution SEM imaging. From the manufacturing process it was evident that there would be a difference between natural and synthetic materials. However, analytical techniques such as XRD and Raman proved incapable of providing tangible evidence of the gross differences between these materials noticed during the microstructural investigation of the oxidised materials.

A variety of other characterisation techniques were attempted, such as XPS, DRIFT and TPD, without success. This is due mainly to the extremely low

active surface areas of highly crystalline, high-purity graphite samples. This is an area of particular interest given the complexity of the influence that surface complexes are thought to have on the graphite oxidation kinetics. With recent advancements in *in situ* sample analysis during exploratory SEM investigation, as well as the possibility of determining atomic composition using EELS technology, this area may soon yield useful information regarding the nature of graphite surface complexes.

Furthermore, several factors were found that influence the microstructure of certain graphite samples. The graphite was found to be particularly sensitive to damage through handling. In particular, the jet milling of certain natural graphite samples was found to induce extensive microstructural damage, leading to very complex, irregular shapes. The presence of a particle distribution was found to be significant since the graphite flakes tend to agglomerate and adhere strongly to one another. Thus the practice of wet sieving in ethanol was developed to consistently produce single flakes of a narrow particle size range without any smaller attached flakes.

Synthetically produced graphites clearly showed an inhomogeneous blend of particles. Visual investigation revealed a clear distinction between pitch-derived particles, with an exceedingly complex microstructure as a result of the mosaic texture caused by flow, and needle coke-derived particles, with a high aspect ratio and visibly layered texture. Despite this apparent regularity, the needle coke flakes still showed significant inhomogeneity when viewed edge-on, showing the development of a folded texture with long, thin slit-shaped pores.

Ultimately, one particular sample of high-purity naturally mined graphite (sample RFL) was identified as the best archetypal sample for fundamental modelling based on a variety of reasons:

- This sample consisted of large, flat, thin flakes
- It appeared to be highly crystalline and homogeneous since the basal plane remained intact during oxidation
- No inherent porosity was visible

To elucidate different aspects of the as-received material behaviour, a portion of RFL material was fully purified by an extensive heat treatment. Some of this impurity-free material was then re-contaminated with an oxidation catalyst.

Based on the solid state kinetic approach, the activation energy and specific active surface area of each sample were identified using non-isothermal data. The investigation revealed significant levels of uncertainty in the activation energy estimate during both low (<10%) and high (>90%) levels of conversion. There are several possible explanations for this uncertainty. Specifically, the presence of impurities during the initial part of the reaction is thought to influence the rate-controlling mechanism during low conversions, whereas at high conversions the coalescence of channels and fissures, combined with structural irregularities in the particle, results in erratic fluctuations in the reaction rate.

The conversion functions for each of the samples were also identified. Broadly, these were found to fall into two categories, i.e. decreasing over the whole range of conversion, or initially increasing, then decreasing. The investigation also demonstrated the dangers and large errors that are possible when a solid state kinetic analysis is done on a sample where the incorrect conversion function is used as a basis, despite apparently excellent Arrhenius plots.

For some samples the estimated specific active surface area was in accordance with expectations. However, the clear presence of a kinetic compensation effect brings the validity of these values into question. Samples with higher activation energies always have correspondingly higher specific ASA values. This is most problematic for the different RFL graphite samples since the heat treatment is not expected to have influenced the ASA to any extent. Yet these samples show a clear increase in specific ASA and activation energy moving from as-received to purified, and a similar reduction moving from purified to re-contaminated.

However, extensive isothermal testing was also conducted. Once these experimental results had been compensated for gas atmosphere, buoyancy and TGA drift effects, they showed excellent agreement with the non-isothermal data. This bestows a large degree of certainty on the derived conversion functions since isothermal data are not subject to the skewing effects that plague non-isothermal data (e.g. based on the use of an incorrect activation energy).

Since a relatively large temperature range (200 ºC) was covered during the isothermal study, this is especially true.

A probability-based, Monte Carlo-type finite element simulation was developed in an effort to easily simulate the complex microstructures found in the graphite flakes. Using this program a variety of directly observed microstructures, which arise during the oxidation of RFL graphite, were simulated. To a lesser or greater extent, each of these structures was shown to have an active surface area development and hence conversion function that agrees with the experimentally determined conversion function for RFL graphite. This provides a tangible link between the active site concept, the visual development of the active surface area and the measured reaction rate.

The model also performed well in simulating a variety of complex surface structures, as well as providing a satisfactory explanation for the observed conversion function of the purified RFL graphite (PRFL). In the last case it was, however, necessary to introduce a particle size distribution effect, presumably caused by the heat-treatment step. In addition, it was possible to recover, to a certain degree, the RFL conversion function from the PRFL function by simply inducing pit growth within the PRFL macrostructure, indicating consistent behaviour as expected from the removal of pitting impurities (or possibly lattice defects) during the heat-treatment step.

A myriad of complex catalytic channelling behaviours were observed in the oxidised, as-received RFL material. These included movement along preferred crystallographic directions, as well as completely random erratic movement. This made it impossible to deduce the mechanism that was active at the graphite-metal interface. Furthermore, modelling each of these widely differing behaviours would be very difficult. Instead, the purified RFL material was re-contaminated with one specific catalyst in a known concentration. Sodium carbonate is known to be catalytically active during oxidation and is specifically responsible for inducing random, erratically shaped channelling in graphite. The sample was therefore subjected to one specific type of catalytic activity.

Based on this single catalytic mechanism, an extension to the probability-based simulation was developed to recreate the erratic channelling effect. Using this model, certain conclusions were reached which are consistent with both the as-received and re-contaminated RFL samples:

- Due to the activity of channelling catalysts, an initial roughening period is expected. However, due to the very high reaction rates observed for graphite catalysts, this effect occurs very quickly and is not generally noticeable on experimentally determined conversion functions.

- After this initial roughening period, the inherent microstructure of the particle, i.e. the active surface area development, governs the shape of the conversion function.

- The temperature-based behaviour of the composite system undergoing both catalysed and uncatalysed oxidation can be described by a single activation energy, attributable to the catalysed oxidation only.

- Thus the addition of channelling catalysts to graphite retains the original conversion function but increases the reaction rate via active surface area creation and drops the activation energy to that of the catalysed reaction.

Finally, a temperature-dependent decline in the reaction rate for the RFL graphite was noticed at high conversions. This was attributed to the accumulation of an inert material at the graphite edge, as indicated by SEM imaging. The material acts as a site blocker, protecting subsequent layers of graphite from oxidation and leading to the formation of a characteristic saw-tooth edge structure. This is a new mechanism for oxidation inhibition which has not yet been extensively investigated. Furthermore, the inhibitor exhibited a temperature-dependent presence, possibly indicating that it is formed only by carbothermic reduction at higher temperatures. Based on these observations, a simple empirical model was developed to reproduce the observed effect.

8.2   Recommendations

From these conclusions a few recommendations concerning future work and key focus areas may be stated:

- The square elements of the probability-based model should be modelled to reflect the hexagonal nature of the graphite crystal structure. This may allow direct visual verification of the edge

structures observed in the purified RFL graphite (PRFL), as well as the reaction anisotropy between zig-zag and armchair edges.

- The current probability-based model should be modified to account for the remaining observed conversion functions and extended to new samples, including more synthetic varieties.

- The most complex behaviour, in natural graphite (NNG), is most likely due to a combination of the small particle size and catalytic activity. Due to these factors, catalytic particles coalesce, leading to a rapid drop in activation. The model should be extended to account for this effect.

- The cause of, and ways to mitigate, the kinetic compensation effect should be explored. If this effect is removed, the solid state kinetic approach will allow easy comparison of graphite samples based on active surface area as derived from kinetic data. Preferably, this should be validated by direct ASA measurement.

- The influence and nature of surface complexes should be explored. The use of isotope labelling to identify the surface reaction pathways would be extremely helpful in this regard, and purified RFL graphite (PRFL) provides the ideal starting material for such an investigation.

- Future developments in *in situ* analytical techniques for electron microscopy should be monitored closely. These could provide unique insights into the surface complexes present on graphite, due to the ability of these techniques to overcome the extremely low concentration of these complexes found in graphite.

- The influence of different types of catalyst should be investigated. Using purified material, the influences of specific catalytic behaviours on the observed kinetics and conversion functions can be determined and categorised.

- The probability-based model should be extended to simulate the effect of inhibiting impurities. This work could be extended beyond the site-blocking impurity discovered in this investigation to include the numerous other types of oxidation inhibition.

- The possibility of extending the simulation to materials with active surface areas, but more complex microstructures, should be explored. Such materials may allow the measurement of the active surface area of the sample as a function of conversion, allowing outright validation of the ASA progression as the origin of the conversion function.