MICROSTRUCTURAL FEATURES THAT CONTROL THE COEFFICIENT OF THERMAL EXPANSION OF NUCLEAR GRAPHITES.

P. J. Hacker, G. B. Neighbour and B. McEnaney
Nuclear Materials Group, Department of Materials Science and Engineering, University of Bath, Bath, BA2 7AY, UK.

Introduction

During the life of a graphite-moderated fission reactor, the graphite core experiences property changes due to neutron irradiation and radiolytic oxidation. The Coefficient of Thermal Expansion (CTE) plays an important role in the generation of internal stresses due to the temperature and flux gradients that exist within the core. Surprisingly, the CTE of nuclear graphites remains constant after radiolytic oxidation to at least ~20% weight loss, although other properties, such as Young's Modulus and thermal conductivity, are known to decrease exponentially with weight loss. The reasons for the insensitivity of CTE to oxidation are not known. This paper presents measurements of the CTE of two nuclear graphites thermally oxidised to weight losses up to 60%. As CTE is believed to be influenced by small-scale features, Transmission Electron Microscopy, TEM, was used to study the nanometric structure of these materials. A model based on the existence of a continuous network is proposed to explain the CTE behaviour.

Experimental

The first grade of graphite studied was a near isotropic, Gilsocarbon graphite, grade GCMB which is used in Advanced Gas Cooled Reactors in the UK. The second was an anisotropic needle-coke graphite, grade PGA, which is used in Magnox reactors. Specimens from each grade were thermally oxidised and their thermal expansions measured between 20-600 °C as described elsewhere [1]. As PGA graphite is anisotropic, the thermal expansion was measured both parallel and perpendicular to the extrusion direction.

Samples of as received and oxidised PGA and GCMB graphite were prepared for TEM by fine polishing and subsequent ion milling of 3 mm discs of material to perforation.

Results and Discussion

The average CTE values in the temperature range 20-600 °C are shown for GCMB graphite and PGA graphite in the parallel and perpendicular directions in Figures 1 and 2. Although the CTE values of GCMB graphite and PGA graphite in the parallel direction are clearly insensitive to oxidation, the CTE of PGA graphite in the perpendicular direction shows a slight increase. Initial investigations have attributed this to compression of the sample during measurement, although further investigations are required.

Mrozowski cracks, 20-30 nm in width are believed to control CTE behaviour by offering accommodation to expanding crystallites [2]. These cracks are thought to remain unaffected by oxidation [3]. However, at high weight losses Mrozowski cracks must be being removed as much of the material has been gasified. Jenkins [4] showed that a constant strain approximation could continue to be applied to polygranular graphites, even if individual crystals were removed, until the material disintegrated. If a continuous path across the material exists and if the Mrozowski cracks within these paths remain unchanged by oxidation, the thermal strains generated remain unchanged and the CTE remains constant.

Example TEM micrographs of the nanometric structure of unoxidised GCMB and PGA graphite are shown in Figures 3 and 4 respectively. The structures of both materials are similar with both exhibiting an extended network of ribbons consisting of graphitic stacks separated by fine lenticular cracks. Circular features are also seen in both materials that may be relics of disclinations [5]. These TEM investigations are in broad agreement with the findings of Sutton and Howard [6] who found cracks ~30 nm in width with a periodicity of 500 nm. However, the present work shows that Mrozowski cracks exist in a large size distribution with some being less than 5 nm in width. The TEM images of GCMB graphite thermally oxidised to ~30% show similar shape and crack size distributions to those in Figure 3. For PGA graphite the effects of oxidation on the density of Mrozowski cracks are less clear.

Conclusions

The average values of CTE for GCMB and PGA graphite measured in the parallel direction are unaffected by thermal oxidation to 60% weight loss in both the 20-120°C (not shown) and 20-600°C measurement temperature ranges. The existence of a continuous network able to transmit thermal strains and the insensitivity of Mrozowski cracks to thermal oxidation are proposed as the two factors responsible for this invariance. The average CTE of PGA samples measured in the perpendicular direction shows a steady increase in CTE but this is believed to result from an experimental artefact. TEM has shown that Mrozowski-type cracks exist in a range of shapes and sizes which seem to be unaffected by oxidation in GCMB graphite. The effects of oxidation on Mrozowski cracks in PGA graphite are less clear.

References

1. Neighbour GB, Hacker PJ, McEnaney B. The Effects of Oxidation on Thermal Expansion in a Polygranular Graphite. Extended Abstracts, Eurocarbon '98. Strasbourg, France, 1998;717-718.

2. Mrozowski, S. Mechanical strength, thermal expansion and structure of cokes and carbons. Proc. Of the 1st and 2nd Conference on Carbon, 1956;31-45.

3. Martin DG and Caisley, J. Some studies on the effect of thermal and radiolytic oxidation on the neutron small angle scattering from graphite. Carbon. 1978;15:251-255

4. Jenkins, GM. The thermal expansion of polygranular graphite. J. Nuc. Mater. 1964;13(1):33-39.

5. White, JL. The formation of microstructure in graphitizable materials. Prog. Solid State Chem., 1975;9:59-104

6. Sutton, AL. and Howard, V. C. The role of porosity in the accommodation of thermal expansion in graphite. J. Nuc. Mater. 1962;7(1):58-71.

Acknowledgements

We thank the UK Health and Safety Executive for providing financial support for this work.

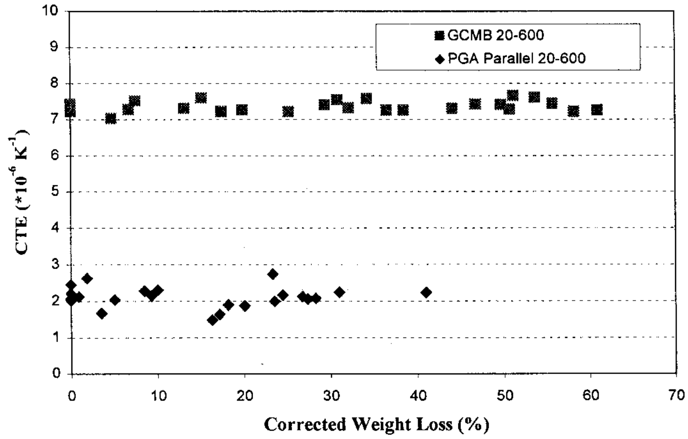

Figure 1. The Coefficient of Thermal Expansion for GCMB graphite and PGA measured parallel to the extrusion direction with increasing thermal oxidation.

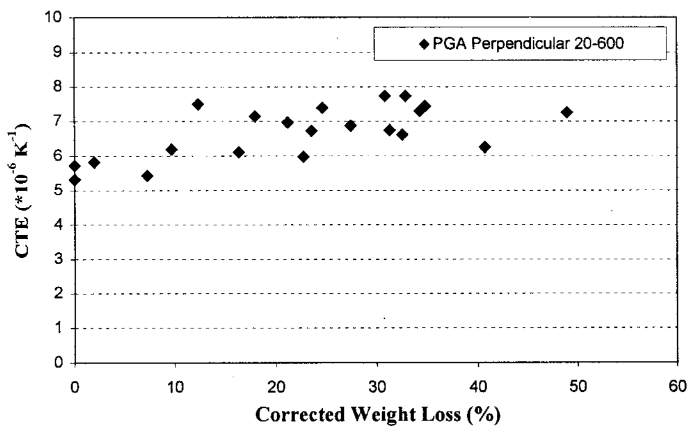

Figure 2. The Coefficient of Thermal Expansion for PGA graphite measured perpendicular to the extrusion direction with increasing oxidation.

Figure 3. TEM micrograph of unoxidised GCMB graphite.

Figure 4. TEM micograph of unoxidised PGA graphite.