DEGRADATION OF GRAPHITE IN GAS COOLED REACTORS DUE TO RADIOLYTIC OXIDATION

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ABSTRACT

Magnox reactors employ pile grade A (PGA) graphite as a moderator. Reactor cores are constructed typically of twelve to thirteen layers of graphite bricks. Fuel channels (FC) are in the centre of all bricks and interstitial channels (IC) at the centre of the corners of every second set of four bricks. The reactor core is cooled by carbon dioxide, the temperature of graphite core increases from 250°C at the bottom to 360°C at the top of the core. The neutron dose increases progressively with the operating time of the reactor. The graphite core loses mass as a result of radiolytic oxidation. The process is dependent on both total energy deposition and temperature which correlates with core height. Fast neutron dose accumulates at the same rate as the total energy deposited and is readily available. The reduction of density of moderator graphite increases the porosity and in turn changes both the physical and mechanical properties of graphite. The mechanical properties and density of graphite are measured either on samples installed in the reactor prior to service or trepanned from graphite bricks. The data obtained on these samples are interrogated using probability modeling to establish trends with increasing service life. Results of the analyses are illustrated in the paper.

PGA graphite is an aggregate of coarse needle coke filler particles within a matrix of fine coke flour particles mixed with pitch binder. The bricks are fabricated in the green condition by extrusion of dry calcinated coke impregnated with liquid pitch binder and then graphitized at 2800°C. This produces a polygranular aggregate with orthotropic properties. The strength properties of graphite are measured using different types of tests. The most commonly used tests involve bending, uniaxial and diametral compression. The initiation and propagation of cracks was investigated to improve understanding of strength behaviour. Cracking was examined on macro-scale using optical microscopy and on micro-scale using focused ion beam, FIB. In addition, digital image correlation was used to investigate the initiation of cracking. It was shown that highly localized strain regions are formed on the tensile surface of beams loaded in bending. One of the strained regions develops into a process zone which initiates cracking when reaching a length of 2 to 3mm. Crack propagation then occurs rapidly along an irregular path.

INTRODUCTION

The oldest generation of gas cooled nuclear reactors in the United Kingdom uses Pile Grade A, PGA, graphite as neutron moderator and the core of the reactor. The reactor core is constructed from twelve to thirteen layers of graphite bricks. These were manufactured from a mixture of dry calcinated coke and liquid pitch binder. The raw materials were extruded, baked at a temperature of approximately 800°C to remove volatile substances, pitch impregnated and finally graphitised at a temperature of approximately 2800°C [1]. The microstructure of graphite consists of relatively large graphitised filler particles (i.e. 100 to 1000 µm scale) dispersed in a matrix of finer (below ~10µm) graphite crystallites from “flour” (fine calcined filler particles) and graphitised pitch binder. The virgin graphite has approximately 20% porosity, caused by gas evolution and shrinkage, resulting from both baking and graphitisation [1]. The porosity is a mixture of interconnected pores open to gas ingress from outside and closed pores, mainly in the filler, which are not accessible to gas from outside. The extrusion process causes the needle-like coke particles to align with the extrusion axis, thus producing aggregate material with orthotropic properties.

The bricks in the reactor core are arranged into units of eight as shown in Figure 1. There is an equal number of octagonal and square bricks with a fuel channel in the centre of each brick. In addition, there are interstitial channels at the corners of every second set of four bricks.

Fig.1: Arrangement of a unit of eight bricks in a Magnox reactor core.

Fast neutron irradiation induced dimensional changes and temperature transients give rise to elastic strain and in turn stresses. If the stresses and the self-weight of the reactor core exceed the strength of graphite then structural integrity of the core may become a concern. Parallel dimensional change generates axial shrinkage at a faster rate at the fuel channel wall than the outside of the brick resulting in tensile stresses at the wall balanced by axial compressive stresses at the outside of the brick creating bending stresses. Two different processes change the properties of graphite during service: irradiation hardening and radiolytic oxidation. The former increases the strength of graphite by introducing defects in crystal lattice. The latter results in a loss of mass thus increasing the porosity of graphite and in turn decreasing the strength. Overall, the irradiation strengthening dominates at low doses giving rise to an initial increase of strength. As the extent of weight loss increases, its effect on strength becomes dominant, strength peaks and thereafter strength decreases. The overall balance between these two contributions is influenced by dose rate.

This paper reviews the changes of some mechanical and physical properties of graphite during service and cracking behaviour of graphite investigated using laboratory experiments.

DENSITY

The density of reactor core graphite decreases progressively by radiolytic oxidation during the service due to energy deposition which correlates with the adjacent fuel dose. The density is measured on samples trepanned throughout the service from reactor core bricks in both interstitial and fuel channels. The trepanned cylinders are 12mm in diameter and 20mm long. They are subdivided into three slices which are used to measure the weight and volume to obtain density. The measured density varies with the adjacent fuel dose and reactor core height. The form of the relationship depends on the type of the channel. For the interstitial channels, the density of radiolytically oxidized graphite is independent of the distance from the channel wall. The relationship obtained from data for all three slices has the form:

$$\hat{\rho}_{ijl} = \hat{A}_0 + \hat{b}_{0l} + (\hat{A}_1 + \hat{b}_{1j})d_i + \hat{A}_2 h_i d_i + \hat{\sigma} \varepsilon_{ijl} \quad (1)$$

where ρ is the density, d is the adjacent fuel dose, h is the reactor core height and 'A's, 'b's and ' σ ' are constants estimated by regression analysis and are denoted by $\hat{}$. The intercept, $\hat{A}_0$, varies randomly between the reactor core layers and this variation is characterized by a probability distribution with standard deviation of b_{0l} . The slope of the density dependence on dose, A_1 , varies systematically with reactor core height as given by term $\hat{A}_2 h_i d_i$. Furthermore, A_1 , varies randomly between the channels and this variation is characterized by a probability distribution with standard deviation of b_{1j} . The standard deviation for random scatter within the brick is given by σ . Observations, reactor core layers and channels are indexed by i , l and j , respectively. ε_{ijl} denotes the standard normal deviate for the i th observation, l th layer and j th channel. For the fuel channels, the relationship for density depends on the distance from the fuel channel wall and for a specific slice number, the relationship has the form:

$$\hat{\rho}_{ijl} = \hat{A}_0 + \hat{b}_{0l} + (\hat{A}_1 + \hat{b}_{1j})d_i^2 + \hat{A}_2 h_i d_i^2 + \hat{A}_3 h_i^2 d_i^2 + \hat{\sigma} \varepsilon_{ijl} \quad (2)$$

Comparisons of the measured and predicted values of density are illustrated as a function of adjacent fuel dose in Fig. 2.

Fig 2: Comparisons of measured and predicted densities for a Magnox reactor a) fuel channels slice 1, b) fuel channels slice 2, c) interstitial channel slices 1-3 and d) layer 4 specific predictions for interstitial channel slices 1-3.

Random variability in the coefficients between reactor core layers and channels and systematic variability with reactor core height give rise to scatter in the predicted mean values in Figures 2a-c. The same variables except layer to layer variability give rise to waviness of the quantiles in Figure 2d.

MECHANICAL PROPERTIES

Flexural strength is measured in four point bending [2] on beams, approximately 9×9×50mm in size, machined from cylinders that have been installed in reactors prior to service. Depending on the length of a cylinder, either one or two specimens can be extracted from the same cylinder. The strength of graphite is dependent on the orientation of the long axis of the cylinder/specimen in relation to the extrusion axis of the brick. Both, the weight loss and density of the cylinders can be obtained. Dependence of flexural strength on weight loss is illustrated in Fig. 3. It can be seen that the flexural strength is higher in the parallel than in the perpendicular orientation. With increasing weight loss, the strength of graphite in the parallel orientation increases initially up to a peak value and then continues to decrease. This behaviour is due to the joint effect of irradiation hardening and radiolytic oxidation on strength. The effect of the first process saturates early in the service whereas the second process occurs continually during service resulting in an overall decrease of strength. Flexural strength is displayed against fractional weight loss in Fig. 3. The weight loss in Fig. 3 can be related to density in Fig. 2 using a relationship between weight loss and density which, without taking account of shrinkage, is given by $x = (1.73 - \rho_{ir})/1.73$, where 1.73 and ρ_{ir} are the densities of virgin and radiolytically oxidized graphite, respectively.

Fig. 3: Variation of flexural strength with fractional weight loss.

Size Effects on Flexural Strength

The size effect addresses the problem of scaling which is required because of a large difference between the reactor core bricks and specimens tested in a laboratory. Flexural strength of specimens of different sizes can be evaluated on specimens that are geometrically similar for which the ratio between the height, width and length of the specimen remains the same for each specimen size. Alternatively, a change of specimen size can be achieved by varying each of the three dimensions independently of the other two. Measurements of strength on geometrically similar specimens which conform to the ASTM standard requirements indicate a small decrease of strength as a function of size of specimen's stressed area under tensile loading. However, when the three dimensions are varied independently of each other, then the flexural strength decreases with increasing length but the strength increases with increasing width and height of the specimens. Examination of flexural strength data for virgin graphite of different specimen sizes showed that dependence of strength of graphite on stressed area is given by $area^{-0.055}$. Similar statistical analysis of strength data for virgin graphite performed as a function of specimen's load span length and width of the area under tensile loading gives strength to be dependent on the product of $length^{-0.316} \times width^{0.344}$ indicating that the strength decreases with length and increases with width. One of the main hurdles in evaluating the separate effects of length and width is ensuring that specimens remain loaded under bending as the width to load span ratio increases. Indeed to ensure this requirement, the standard requires this ratio to be greater than one. Whether the most appropriate description of the size effect is in terms of stressed area or of separate effects of load span and width on strength depends on whether graphite behaves as a linear elastic brittle or a quasi-brittle material. In the former, the strength is dependent on the weakest link and failure occurs when the energy released from cracking is greater than the energy required to form new surfaces. If the material contains a distribution of flaws of different sizes then the largest flaws that are potential crack initiation nuclei will be in the tails of the probability distribution of flaws. The probability of finding the largest flaw increases with increasing stressed area and hence the specimen size regardless whether the increase was achieved by increasing the width or length of the specimen. In order to understand the cracking behaviour of graphite it is necessary to examine how the cracks are formed in graphite.

FRACTURE OF GRAPHITE

Failure is induced by crack initiation and propagation. The driving force is the release of elastic (potential) strain energy as the crack extends. If this is greater than the energy required to create new surfaces and absorbed by energy dissipating processes, then unstable failure occurs usually under linear elastic conditions. Graphite does not exhibit plastic deformation. The main energy dissipation process involves formation of the fracture process zone.

Fig. 4: Load vs displacement curves obtained for radiolytically oxidized graphite specimen loaded under bending.

Cracking has been generated in graphite by loading samples in several different ways and observing the cracks either on macro-scale using optical microscopy or micro-scale using a focused ion beam microscope, FIB.

In the first instance, load vs displacement traces can be examined. The appearance of load vs displacement traces of graphite depends on mode of loading and porosity of the material. Four point bend test, uniaxial and diametral compression, also known as Brazilian disc test, are most frequently used mechanical tests for graphite. Examples of load vs displacement curves obtained from flexural tests are illustrated in Fig. 4. The black curve shows engineering elastic brittle failure at the peak load. The curve also indicates a small amount of cracking prior to instability. The green curve also shows elastic behavior up to the maximum load, followed by a small load drop and a further displacement prior to instability. The displacement prior to instability is greater than for the black curve and is consistent with a greater amount of cracking than for the black curve. The difference in the maximum load between the two curves is due to different amount of weight loss caused by radiolytic oxidation.

To study the initiation of cracking, digital image correlation was used to obtain surface displacement and strain [3]. Along the tensile surface of the specimen it was found that strain accumulation is more rapid in localized regions of the specimen. As the load increases, one or two highly strained regions are created forming a process zone approximately 2-3mm long. The process zone formed approximately 20% below the peak load is shown in Fig. 5.

Fig. 5: Strain fields formed in a tensile stressed region of a plain specimen approximately about 20% below the peak load applied in bending.

This process zone becomes the initiation site for cracking. Subsequent crack growth occurs very rapidly. The resulting crack extends approximately 80% through the width of a plane sided specimen. The cracked specimen and the associated strain distribution are shown in Fig. 6.

Fig. 6: Showing crack path and high strain intensity regions in a bend specimens.

The path of cracks in beams of virgin graphite subjected to bend loading and discs subjected to diametral compression was examined by optical microscopy. The route of the crack across the tensile face of the bend specimen and the adjacent side faces is shown in Fig. 7. The crack across all three faces is zig zagging between filler particles through the matrix tracing a tortuous path associated with some dissipation of energy. The energy absorption is expected to be greater than for elastically brittle materials such as glass or ferritic steels at low temperatures.

On microscopic scale, cracking behaviour has been studied by FIB, and scanning electron microscope. This involved milling two trenches, separated by an approximately $8\mu\text{m}$ thick wall, placing a fixed sharp metal probe behind between two trenches, and then mowing the specimen progressively against the probe. This provided a means of applying a small progressive localized force whilst observing crack growth in the FIB microscope. Local deformation and cracking could be studied at high resolution within several chosen regions of specimens.

Fig. 7: Cracking of a beam loaded in bending.

Formation of cracks in radiolytically oxidized graphite observed in a FIB microscope [4] is illustrated in Fig. 8. Cracking of the wall between the trenches is shown in Fig. 8a and b. Furthermore, Fig. 8b shows formation of twins which disappear when the load is removed.

Cracking behaviour under diametral compression was investigated [4] by partially loading specimens whilst being observed by an optical microscope. After observation of cracking, a loaded specimen was transferred to FIB and further loaded. The load vs displacement trace exhibited nonlinearity and small drops and rises of load. The observed shape is consistent with significant amount of subcritical cracking, culminating in a formation of a crack that caused failure of the disc.

Fig. 8: Cracks observed in graphite after loading by a probe in FIB. a) Cracking of a wall between trenches. b) Cracking and formation of elastic twins.

DISCUSSION

Review of radiolytic oxidation, and strength of graphite shows that that radiolytic oxidation brings about a progressive increase of porosity and associated weight loss in reactor core moderator graphite. After an initial rise in strength, the strength decreases with increasing weight loss. Comparison of strength of geometrically similar specimens of different sizes, conforming to ASTM test standard [2], shows a small decrease of strength with increasing specimen size. However, comparison of strength values obtained for different aspect ratios between specimen width and length shows that strength increases with width and decreases with length. This can be rationalized by observations of cracking using DIC and optical and FIB microscopes. DIC shows that a process zone forms and grows in size on tensile surface of bend specimens. When the process zone is approximately 2-3mm in size then cracking is initiated. Under bending, the crack grows across the specimen rapidly across approximately 80% of specimen depth. The crack path and the crack surface appearance are irregular. This is consistent with quasi-brittle behaviour. If graphite behaved as a linear elastically brittle material then the fracture surface would be flat and the initiation of cracking would be expected to occur by cracking of filler particles or large pores.

CONCLUSION

Review of radiolytic oxidation, some mechanical properties and cracking of graphite indicates that it behaves as a quasi-brittle material. Cracking behaviour depends on how the loading is applied. Load vs displacement records display linear and non-linear parts. The latter represents formation of the process zone, subcritical cracking and irregular crack path during failure. The trench probe method was used to apply a small localized force to the specimen mounted in the focused ion beam microscope to observe cracking as it occurred.

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