# The Influence of Radiolytic and Thermal Oxidation on the Mechanical Properties of Nuclear Graphites

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## Introduction

It is well known that, for a given weight loss, thermal oxidation causes a greater reduction in mechanical properties than radiolytic oxidation. For example, Pickup[1] et al showed for a pitch-coke nuclear graphite that the decrement in dynamic modulus, E, due to thermal oxidation by $CO_2$/5%CO gas fitted an exponential relationship:-

$$E = E' \exp(-7.0\ x) \qquad (1)$$

where E' and x are the modulus of the unoxidised graphite and the fractional weight loss respectively. Similarly, Kelly[2] et al reported that the effects on the modulus of radiolytic oxidation of nuclear graphites in $CO_2$-cooled reactors could be described by,

$$E = E' \exp(-3.6\ x) \qquad (2)$$

Thus for a 5% weight loss the modulus would be reduced by approximately 30% for thermal oxidation but only by 16% for radiolytic oxidation. The influence of thermal and radiolytic oxidation on the strength of nuclear graphites can be fitted to similar equations which show that strength reductions are also more severe for thermal oxidation.

This paper presents, (i) evidence for the different microstructural effects of thermal and radiolytic oxidation, and (ii) an interpretation of the influence of these microstructural effects on elastic modulus using the analytical derivation of the Knudsen equation due to Buch[3].

## Experimental

Thermal oxidation[1] of a needle coke based nuclear graphite was carried out at 900°C in $CO_2$/5% CO gas at atmospheric pressure. [2]Radiolytically oxidised needle coke graphites were removed from Commercial Advanced Gas Cooled Reactors in the U.K. and examined at C.E.G.B., Berkeley Nuclear Laboratories, U.K.

Microstructural studies were made using inverted stage microscopes under polarised light or U.V. light. Good contrast between pores and graphite at high magnification was achieved by impregnating the graphite with fluorescent resin.

## Results

Fig.1. shows an unoxidised needle coke graphite and the same graphite oxidised thermally to 2.4% weight loss. The only significant changes in the microstructure are the development of fine filamentary pores, typically 1 to 5 μm in width, in the binder phase. Polarised light microscopy shows that these are Mrozowski cracks, i.e. cracks produced by differential contraction on cooling from graphitization temperatures.

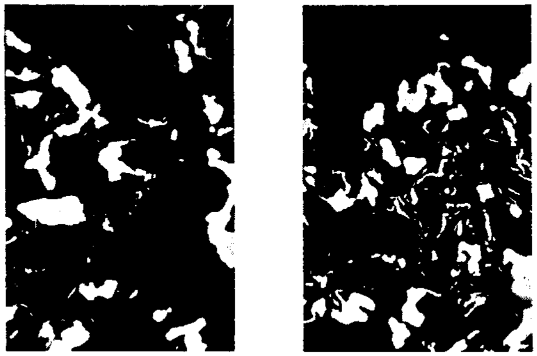


Fig. 1. Needle coke graphite (a) unoxidised (b) thermally oxidised to 2.4% wt.loss.

The effects of radiolytic oxidation on microstructure are illustrated in Fig.2, which shows an unoxidised needle coke graphite and the same graphite after oxidation to 4.2% weight loss. Radiolytic oxidation is much less selective than thermal oxidation producing pores, typically 0.1 mm in width, which have much lower aspect ratios than those developed by thermal oxidation.

## Discussion

The selective development of Mrozowski cracks on thermal oxidation (Fig.1.), may be associated with the thermal reaction anisotropy of graphites. Formation of Mrozowski cracks during anisotropic contraction from graphitization temperatures exposes graphitic basal planes. In thermally activated reactions with $CO_2$ and other oxidising gases basal planes are 2 to 3 orders of magnitude less reactive than prismatic planes, which, it may be supposed, are exposed at the ends of Mrozowski cracks. Thus the selective nature of thermal oxidation will preferentialy elongate this class of pores.

Ionising radiation in nuclear reactors greatly enhances the chemical activity of carbon dioxide, and consequently, it may be proposed that the oxidizing species is much less selective in its attack upon the microstructure of graphite than thermally activated $CO_2$, and hence,

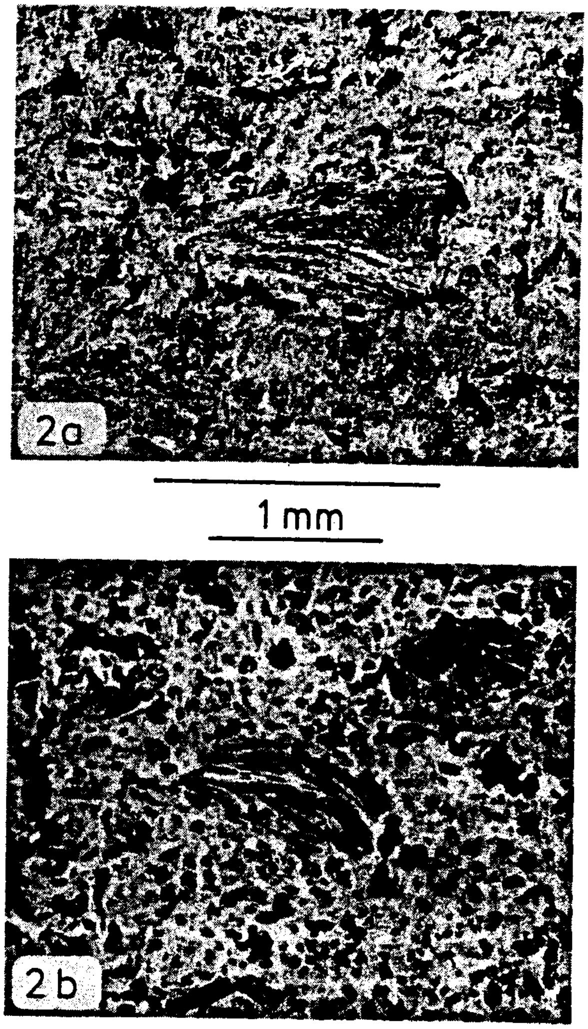


Fig. 2. Needle coke graphite (a) unoxidised (b) radiolytically oxidised to 4.2% wt.loss.

there is very little preferential pore development with radiolytic oxidation.

The empirical Knudsen relationship, between elastic modulus E and fractional porosity, P, is;

$$E = E_o \exp(-bP) \qquad (3)$$

where $E_o$ and b are constants, ($E_o$ is effectively the value of E at zero porosity). This equation has recently been derived theoretically by Buch[3]. By considering far field displacement effects, Buch showed that the modulus decrement was a function of pore aspect ratio, a/c, which is related to the constant b by,

$$b = 1 + 0.594\,(a/c) \qquad (4)$$

Pickup[1] et al used the Knudsen equation to relate experimentally observed modulus changes on thermal oxidation to porosity. For a needle coke graphite:-

$$E = E_o \exp(-7.5P) \qquad (5)$$

To derive an analogous equation for radiolytic oxidation it is necessary to transform equation (2). This can be done if it is assumed that radiolytic oxidation is entirely non-selective, and the external volume of the graphite remains unaltered on oxidation. These assumptions apply to a model for radiolytic oxidation which is analogous to drilling small holes in the graphite. There is some justification for this model, since Kelly[2] et al have shown experimentally that property decrements, similar to those found for radiolytic oxidation, can be obtained by drilling small holes in graphite.

If $P_i$ and $P_f$ are the initial porosity and the porosity after oxidation to fractional weight loss x, then it can easily be shown that

$$P_f = P_i + x\,(1-P_i)$$

for the above model for radiolytic oxidation.

Using this transform equation (2) becomes

$$E = E_o \exp(-4.5P) \qquad (6)$$

Substituting the exponential factors from equation (5), (thermal oxidation) and equation (6), (radiolytic oxidation) into equation (4) gives pore aspect ratios of a/c = 11 for thermal oxidation and a/c = 6 for radiolytic oxidation. This is in qualitative agreement with the microstructural evidence (Fig.1) for the development of higher aspect ratio pores on thermal oxidation. The more severe effects of thermal oxidation on the strength of graphites may be ascribed mainly to the effects upon modulus, since the strain to failure of graphites ($\sim 10^{-3}$) is roughly constant.

## Conclusion

The principal microstructural change on thermal oxidation of nuclear graphites is the development of fine pores of high aspect ratio which are identified as Mrozowski cracks. This selective attack is ascribed to the thermal reaction anisotropy of the graphite. The more energetic gaseous species participating in radiolytic oxidation are much less selective than thermally-activated $CO_2$, thus pores of lower aspect ratio are developed. Using a theoretical derivation of the Knudsen equation, the more severe effects of thermal oxidation on elastic modulus are related to the selective development of pores of high aspect ratio.

## Acknowledgements

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## References

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