It is fairly well known that the irreversible expansion during the final heat treatment to graphitization temperatures is related to the sulfur content in filler cokes. While this expansion, commonly called puffing, is well known and carefully monitored in industry, very little has been published concerning the reaction. The major concern has been in eliminating or inhibiting the reaction with stable sulfide-forming additives. Rarely is the sulfur reaction related to fabrication or physical properties. It is the purpose of this investigation to isolate the effects of sulfur as a single variable and to describe those properties dependent upon the sulfur content in the filler coke.

The filler cokes in this study were all derived from A-240 petroleum pitch using a small 4 kg laboratory coker. The sulfur content of the A-240 pitch varied from 0.3 to 3.25 wt %, yielding green cokes with 0.25 to 2.70% sulfur. Iron oxide was studied as an inhibitor by additions to a 3% sulfur A-240 pitch before coking. The filler cokes were made by two procedures, one to produce the typical acicular coke yielding a highly anisotropic graphite; the second, using a modified process to randomize the coke structure to yield more isotropic graphites. The latter procedure accomplished the isotropy while retaining the inherently high crystallinity of the cokes made from the A-240 petroleum pitch. The filler cokes were all coked to 500°C, ground and screened such that 100% <88 μm.

The graphites were all made using an ORNL process to plasticize the outer surfaces of the green filler coke. This was done to achieve highly efficient binding and uniform packing of moldings with the different fillers. Coal tar pitch 30M was used as the plasticizer and A-240 pitch as the final binder. The green as-molded bulk density was a constant 1.31 to 1.33 g/cm³ in all cases. Several moldings of each mix were made and baked under restraint. In each case, one molding was graphitized without impregnation, a second molding was given a single A-240 pitch impregnation, and in most cases a third molding was rebaked and given a second pitch impregnation. The final graphites were evaluated by obtaining the 1000°C mean coefficient of thermal expansion (CTE), electrical resistivity, sonic velocities, and bend test properties.

The generally accepted concept of the irreversible expansion or puffing reaction is related to the sudden release of sulfur. This release creates adequate internal strains to cause a significant increase in micropores less than 0.1 μm in diameter. This increase in volume by the microporosity results in lower final bulk densities and alterations in both the thermal and mechanical properties of the graphite. The decrease in final bulk density with increased sulfur content is shown in Fig. 1. It is also clearly demonstrated that the volume expansion is independent of impregnation. Obviously, this would be expected if the porosity generated occurs after the impregnation and not before.

The always less-than-theoretical coefficient of thermal expansion is a result of the material expanding into the defect structure. To be effective, the defects must be preferentially aligned normal to the c axis. The volumetric CTE (2x with-grain CTE + against-grain CTE) used to cancel anisotropy differences is shown in Fig. 2 to be significantly reduced by increased sulfur content. This suggests a preferential alignment of porosity which may well result from the internal pressure splitting the lower strength interlayer bonds. The effect of Fe₂O₃ to

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*This work was funded by the Naval Surface Weapons Center under Contract No. N-60921.

†Operated by Union Carbide Corporation for the Energy Research and Development Administration.
inhibit the reaction increases the CTE, as shown in Fig. 3, suggesting an elimination of the microporosity.

Fig. 3. Fe$_3$O$_4$ Additions Decrease the Thermal Stress Resistance of Graphite.

The ability of graphite to significantly microfracture without rapid crack propagation to failure distinguishes brittle graphites from those with significant toughness. The microcracking is actually a stress relief system to homogenize the stress, reducing the potential for crack propagation. It was observed that while the actual fracture strength-total porosity relationships are essentially independent of the sulfur content, the fracture strain is significantly improved by increased sulfur content. The effect of Fe$_3$O$_4$ inhibitors is again to reduce the fracture strain with little effect on fracture strength. The elastic properties, evaluated by sonic velocity measurements, demonstrated the singular dependence of the bulk compressibility to total porosity. However, Poisson’s ratio decreased, as shown in Fig. 4, with increased sulfur content. The implication is that, with higher sulfur content and higher microporosity, a significant portion of the strain is a result of void opening or closure. The fineness of the structure allows for greater fracture strains without a decrease in strength.

In summary, the effect of increased sulfur content in a soft coke, as derived from Ashland A-240 petroleum pitch, is to first reduce the potential bulk density of the final graphite by an irreversible volume expansion. The microporosity produced by the sulfur-gas evolution effectively reduces the CTE and increases the strain to fracture without a loss in strength. The implication of these results, with the reduced Poisson’s ratio, is that the porosity is very fine, evenly distributed, and oriented normal to the c axis. In effect, increased sulfur content offers a fine solution to obtaining graphites with extraordinary thermal stress resistance and toughness.

References