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SUBLIMATION PHENOMENA IN H451 GRAPHITE*

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ABSTRACT

H451 graphite was sublimed and impurity migration and sublimation behavior examined with a proton microprobe analyzer. Impurities migrate down thermal gradients during heating and are released at free surfaces. They are deposited on cooler surfaces and may form compounds. Sublimed graphite also deposits in cooler regions forming a hard graphitic mass.

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Introduction

This study was undertaken to evaluate the behavior of grade H451 graphite during a hypothetical loss of coolant scenario in which the core of a High Temperature Gas Cooled Reactor is assumed to reach the sublimation range (>3600°C). Particular attention was paid to the migration of impurities in the graphite since this would give a good indication of the behavior of fission product species which could be released from the core during heatup.

Experimental Procedures and Results

The H451 graphite specimen, which was the susceptor of a 30 KVA induction furnace, was in the form of a cylinder measuring 16.0 cm in height by 8.0 cm in diameter. Temperatures during the run were measured by an optical pyrometer focused on the base of a machined hole via a graphite sighttube. The specimen and the sighttube were surrounded by carbon black powder insulation and the upper part of the sighttube, which protruded from the furnace, was blanketed in argon to minimize oxidation.

During the runs the specimens were heated to the sublimation point (~3600°C) in about 1 hour and held in the 3600°-3800°C range for an additional 0.5-1.0 hour at which time the power was switched off and the furnace allowed to cool normally. The specimens were sectioned longitudinally into 2 equal pieces and each cut surface polished on silicon carbide papers to a smooth flat finish. The surfaces were cleaned to remove traces of silicon carbide and graphite dust originating from the polishing procedure.

Concentrations of impurities in the sectioned surface were measured with a proton microprobe by detecting proton induced X-ray emission. The proton beam is accelerated to 2.5 MeV in a Van de Graaff accelerator, collimated to a diameter of 25 μm, and strikes the specimen surface after traveling about 3 mm in air. Elements such as iron give detection sensitivities of under 1 ppm.

Figure 1 shows a sectioned specimen. The most severe sublimation occurred just below the midsection where the temperature was highest. Sublimation is also observed at the base of the internal hole. The sublimed regions are extremely powdery and material is readily removed by touching. Sublimed material from the central hole moves up the sighttube by convection and a series of colored deposition bands are formed. It is estimated that the top of the sighttube is at about 1000°C during a run and the base at about 2500°C. The deposition bands are, therefore, formed at approximately 1800°-2000°C.

As sublimation proceeds, observations through the optical pyrometer showed that heavy deposition occurs at the base of the sighttube. Filaments and nodules grow on the internal surface until the sighttube becomes completely sealed (Figure 1). During surface polishing it was clear that the

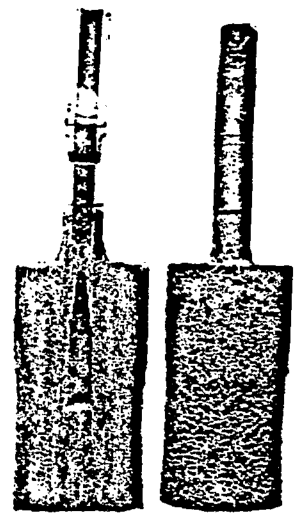

Figure 1. H451 graphite sublimed at 3600°-3800°C (Run 10); Mag. 0.3X.

plug of material formed was extremely hard compared to that in the specimen. X-ray diffraction experiments, however, confirmed that the material was still graphitic and the c/a ratio of 2.73 was similar to that for the specimen.

The concentrations of various trace impurities are shown in Figure 2. Values are given as

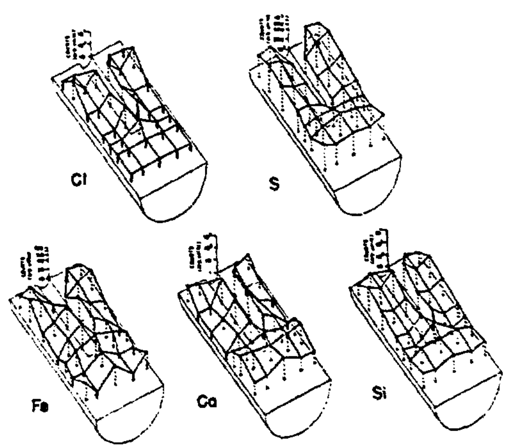

Figure 2. Impurity concentration gradients in H451 graphite after heating to approximately 3800°C (Run 10).

counts on a Si(Li) X-ray detector. The highest concentrations are usually adjacent to the inner hole which is cooler than the outer surface of the specimen, i.e. migration is proceeding from the hotter to the cooler locations, as expected. Sulfur appears to show anomalous behavior and displays a higher concentration at the outer specimen surface. The most plausible explanation is that sulfur is migrating into the specimen from the adjacent carbon black which contains about 12 times as much sulfur as the graphite. Heavy contamination will thus occur in these regions.

Proton microprobe scans were also made at 14 locations along the Run 12 sighttube (Figure 3). Elemental concentrations, given in Figure 4, show several distinct peaks with Si, Fe and Ca frequently in the same locations. This indicates that some form of interaction between these elements occurs during the deposition process. Because of this, an attempt was made to identify any compounds formed by carrying out X-ray diffraction experiments on powders scraped from the various deposition bands. It was found that β-SiO_2 is present in locations 1 through 7 and β-SiC in locations 2 through 12 (Figure 5). Small amounts of the SiC (moissanite) phase were also identified in locations 9 and 10. Possibly, the SiO_2 is formed in the upper regions because of the presence of small amounts of oxygen in the argon gas blanket over the specimen. The SiC may be formed by the reduction of this oxide by the graphite sighttube, or by the direct combination of the graphite with Si released from the specimen.

Figure 3. Deposition on sighttube of impurities released from H451 graphite heated to approximately 3800°C (Run 12). Mag. 0.5X.

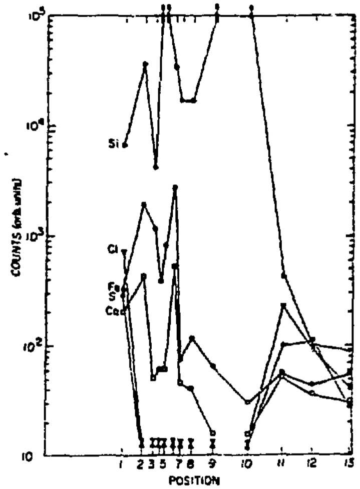

Figure 4. Concentrations of deposited elements released from sublimed H451 graphite at ~3800°C (Run 12).

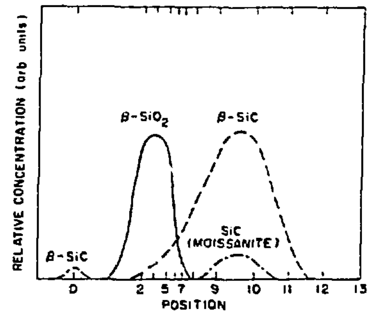

Figure 5. Relative concentrations of deposited compound formed from impurities released from H451 graphite during heating to ~3800°C (Run 12).

Conclusions

The following general conclusions may be made regarding the behavior of H451 graphite during heating to the sublimation range:

- Heating in the range 3600°-3800°C causes significant sublimation at free surfaces. There is both a general loss of material and more localized loss along what could be grain boundaries. For a hold time of 0.5-1.0 hour the depth of localized sublimation is about 5 mm.

- Sublimed material forms heavy deposits on cooler graphite surfaces at a temperature of about 2500°C. The material is graphitic but extremely hard.

- During the heating cycle impurities in graphite migrate from hotter to cooler regions.

- Impurities reaching free surfaces in the cooler regions escape and are redeposited in discrete bands on graphite surfaces at temperatures in the range 1800°-2000°C. Compounds formed in these locations include β-SiO_2, β-SiC and a small amount of the moissanite SiC phase.

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