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CONF-781113--18
BNL-25191

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at High Temperatures Using a Proton Microprobe

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Presented at

Fifth Conference on Application of Small Accelerators

November 6, 7, and 8, 1978

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Denton, Texas 76203

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MEASUREMENTS OF IMPURITY MIGRATION IN GRAPHITE
AT HIGH TEMPERATURES USING A PROTON MICROPROBE

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Abstract

The migration of fission products and other impurities through the graphite core of a High Temperature Gas Cooled Reactor is of prime importance in studies of reactor safety. Work in this area is being carried out in which graphite specimens are heated to temperatures up to $\sim 3800^{\circ}\text{C}$ to induce migration of trace elements whose local concentrations are then measured with a proton microprobe. This instrument is a powerful device for such work because of its ability to determine concentrations at a part per million (ppm) level in a circular area as small as $10\ \mu\text{m}$ while operating in an air environment. Studies show that Si, Ca, Cl, and Fe impurities in graphite migrate from hotter to cooler regions. Also Si, S, Cl, Ca, Fe, Mn, and Cr are observed to escape from the graphite and be deposited on cooler surfaces.

Introduction

In considering a hypothetical loss of coolant event in a High Temperature Gas Cooled Reactor, in which the graphite core may be subjected to a high temperature excursion, the migration of fuel, fission products, and graphite impurities through graphite is of great importance. At the present time there is an urgent need to experimentally measure the concentrations of these materials in core graphite in a fast, accurate, and reproducible manner. In order to meet this need for information, experiments are being performed in which reactor-grade graphite is heated to high temperatures, and the resultant migration of trace impurities is determined with a proton microprobe.

The proton microprobe was used to map trace element concentrations in the graphite samples for several reasons. The capability of performing the measurements in air for nonhygroscopic samples is a significant advantage because it allows convenient handling and changing of the rather large samples (the possibility of large migration distances at high temperatures requires the use of 15 cm-long specimens). The proton microbeam's good spatial resolution in the large samples allows easy target preparation; the graphite need only be sectioned, polished and cleaned of loose particles. This is much easier, for example, than carefully cutting the sample into thin sections and measuring elemental compositions of the slices by chemical techniques. The resolution of the proton microprobe is sufficient to be sensitive to structures as small as individual graphite crystals; thus, it may be feasible to examine impurity segregation in grain boundaries. There is no other readily available technique for measuring ppm impurity concentrations with spatial resolutions of this size.

Sample Preparation

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 optical pyrometer at the base of a machined hole via a graphite sight tube. A schematic of the specimen and induction furnace is given in Figure 1. Owing to the exposure of the inner hole to an external argon environment the regions adjacent to the hole are cooler than the outer specimen surface.

During the run the specimen was heated to the sublimation point ($\sim 3600^{\circ}\text{C}$) in about 1 hour and held in the 3600°C - 3800°C range for an additional 0.5 hour at which time the power was switched off and the furnace allowed to cool. The specimen was removed from the furnace, sectioned longitudinally into 2 equal pieces and each cut surface was polished on silicon carbide papers to give a smooth flat finish. The surface was carefully cleaned to remove traces of silicon carbide and graphite dust from the polishing procedure.

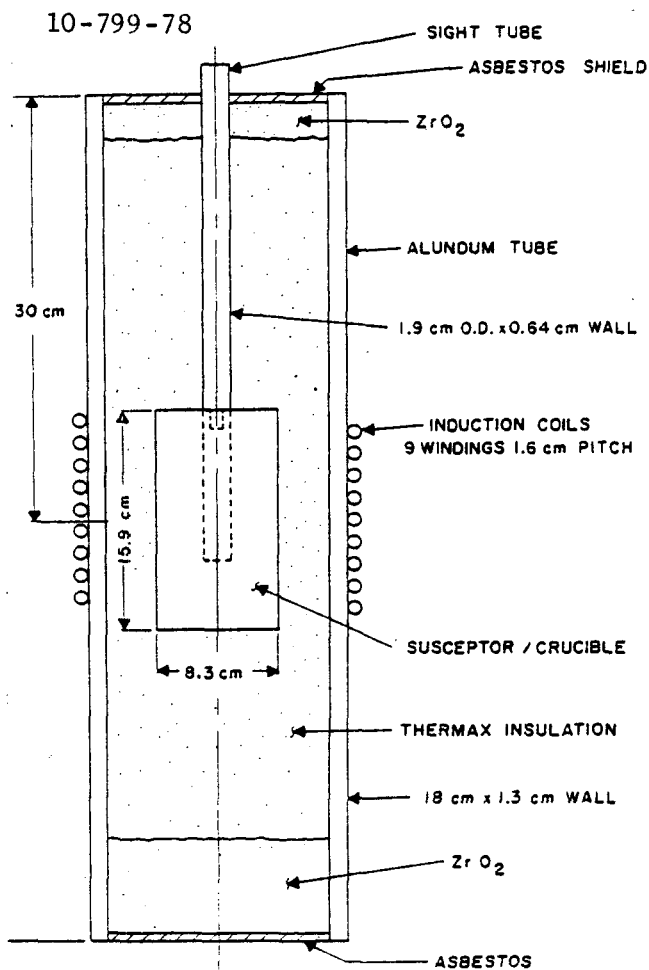


Fig. 1. Schematic of the induction furnace with graphite susceptor.

Analytical Techniques

The concentrations of trace impurities in the samples were measured with a proton microprobe by detecting proton-induced x-ray emission. The microprobe is illustrated in Figure 2 and has been described previously.¹ The proton beam, accelerated to 2.5 MeV by a Van de Graaff accelerator, passes through a pair of pinhole collimators² that determine the beam size and angular divergence. The first collimator, which has a diameter of $356\ \mu\text{m}$, is 7.0 cm from the final pinhole collimator, which usually has a diameter of $25\ \mu\text{m}$, although smaller sizes are available. Since readily available commercial collimators are either not thick enough to stop the beam or are constructed from

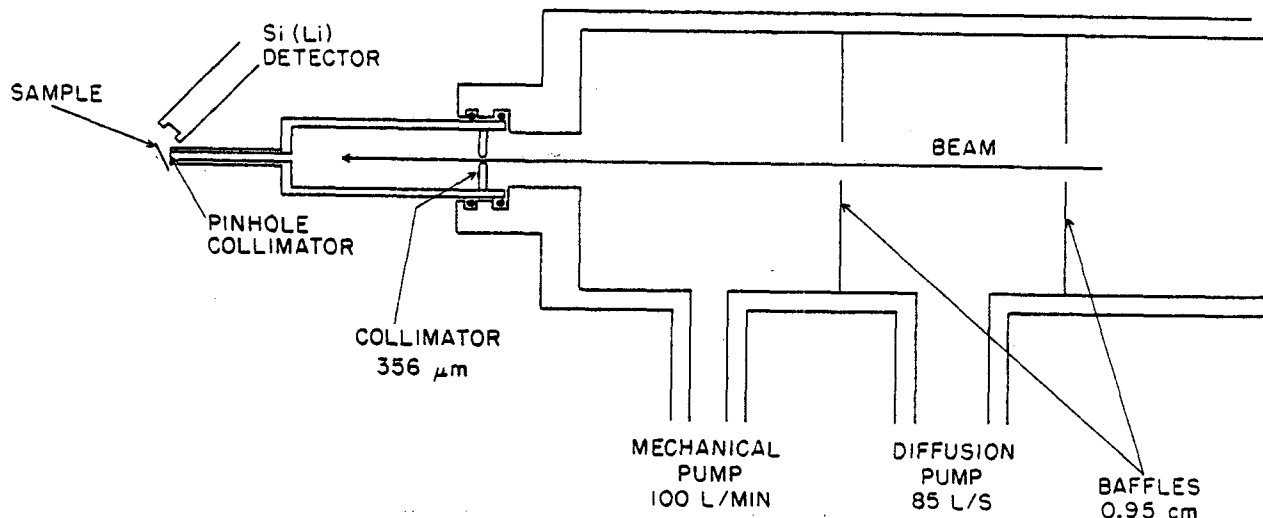


Fig. 2. A schematic diagram of the proton microprobe used to measure trace impurity concentration in the graphite.

materials that produce an intense x-ray background, a pinhole was produced by punching a 25- μm hole in a 100- μm thick sheet of high purity Al.

After collimation, the beam emerges into the air and travels 3 mm before striking the sample. In this distance the proton beam increases in diameter by $\sim 15 \mu\text{m}$ due to its angular divergence. Both the beam spreading due to multiple scattering and the beam energy loss ($\sim 25 \text{ keV}$) are much smaller than the beam size and energy, respectively. In order to separate the accelerator vacuum system from the air, the differential pumping system shown in Figure 2 was constructed. This differential pumping system was found to function well for pinholes up to 50 μm in diameter; larger pinholes could be used with smaller diameter baffles, which are currently large to allow easy alignment. Instead of a differential pumping system, a foil over the exit port could be used to separate the accelerator vacuum from air, but an exit foil was found undesirable because: 1) organic foils that do not produce a background of characteristic x rays suffer beam damage at the required current densities, 2) scattering in the foil increases beam divergence, 3) there is a beam energy loss in the foil, and 4) secondary electron bremsstrahlung backgrounds are produced when the beam strikes the foil.

In order to automatically scan the samples, they are mounted on X-Y micrometer drives that are driven by stepping motors. X rays induced by the proton beam are detected with a Si(Li) detector covered with a 400 μm layer of polyethylene that stops backscattered protons. To allow the detector to easily be shielded from x rays produced in the collimator, the pinhole is at the end of a long, thin tube so that the x-ray detector can be placed at back angles. To keep the collimator assembly from blocking the x-ray detector, the target is positioned at a 15° angle with respect to the beam. A surface barrier detector is mounted above the Si(Li) detector to determine the amount of proton beam striking the sample.

The size and shape of the proton beam were measured by scanning a straight edge across the beam. In this method, a razor blade was stepped between the collimator and a ZnS(Ag) scintillator. Transmitted

beam intensity was determined from the scintillation intensity, which was measured with a photo-transistor.¹ Diameters of $\leq 15 \mu\text{m}$ have been measured for a beam 1 mm from a 12.5 μm collimator.

Minimum detectable amounts were determined for this proton microprobe by measuring graphite samples with known impurity concentrations and by measuring a commercially available standard of filter paper containing known amounts of dried salts. Sensitivity to elements not in a standard can be determined by interpolating with the use of well-known x-ray cross sections. In these measurements, the minimum detectable amount was taken to be three times the square root of the background. It was found that in a two-minute run, sensitivity to $\leq 5 \text{ ppm}$ could be obtained for elements with $Z > 13$; in many cases, such as Fe, sensitivities to under 1 ppm are obtained. In comparison with an electron microprobe from an SEM, which is the only other readily available means of measuring elemental concentrations with good spatial resolution, it was found that the proton microprobe has much greater sensitivity. This improved sensitivity is due to the much lower bremsstrahlung backgrounds for protons, a consequence of their larger mass.

Results and Conclusions

Trace element measurements on the heated susceptor show that Si, Ca, Cl, and Fe generally have higher concentrations near the center of the sample. This is expected since migration normally proceeds down a thermal gradient, i.e. from the hotter to the cooler zones. Sulfur appears to be anomalous in this respect since a higher concentration was noted for the outer regions of the susceptor. It is believed that this behavior is a result of contamination from the carbon black insulation (Thermax) during the run. Since the Thermax contains about 12 times as much S as the graphite sample, high concentrations of this element would be expected near the outer surface of the sample. There is an indication in Figure 3 that Si is also being transferred from the Thermax to the sample in a similar fashion to the S. For Si the impurity level in the Thermax is about 25 times that in the graphite.

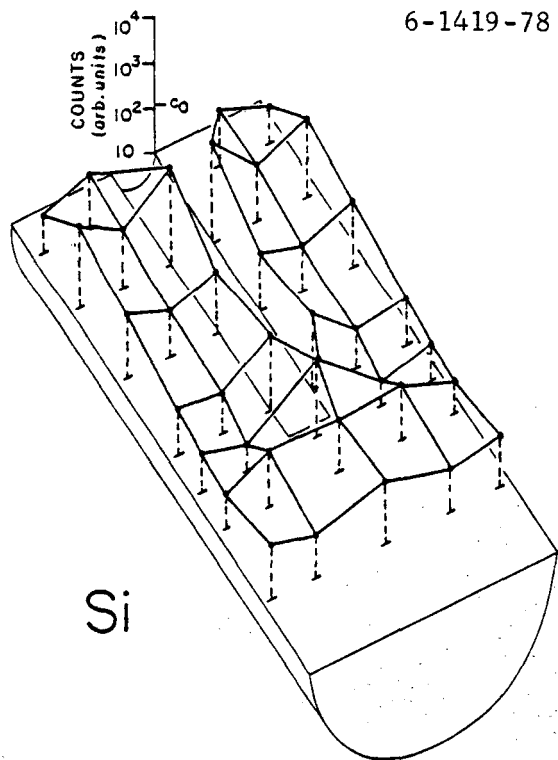
At some stage during the heating cycle the

impurities at the inner hole of the susceptor vaporize and move upwards by convection until they deposit on the inner wall of the somewhat cooler graphite sight tube (approximate average temperature of 2000°C). Figure 4 gives results of the proton microprobe scans that were conducted to determine the nature of these impurities along an axial slice of the sight tube which displayed colored bands indicating specific depositions. The positions of the scans in Figure 4 range from the hotter position 1 to the cooler position 7. Position 1 is approximately 12.7 cm above the top of the susceptor, and position 7 is 5 cm above that; intermediate positions are spaced as shown. From this figure it is seen that impurities mainly segregate in a narrow band, suggesting that perhaps some form of chemical interaction occurs between them during deposition.

Preliminary x-ray diffraction work on powdered samples taken from various positions on the sight tube walls show the presence of SiO₂ in the cooler regions, whereas SiC is located in a slightly hotter adjacent region.

Summary

Elemental determinations of trace concentrations have been carried out on graphite samples subjected to very high temperature excursions. It was found that impurities migrate generally from hotter to cooler regions within the graphite samples and that some vaporization occurs at surfaces with subsequent discrete condensations at cooler regions. The present study of the migration of Si, S, Ca, Cl, Mn and Fe is being extended to include other elements such as Mo and La which are



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Fig. 3. The experimentally determined concentration gradient of impurity Si in a heated graphite sample.

fission products. It has been shown that a proton microprobe with an external beam available in the laboratory is a powerful tool for measurements of trace impurities in large, awkward samples with little sample preparation.

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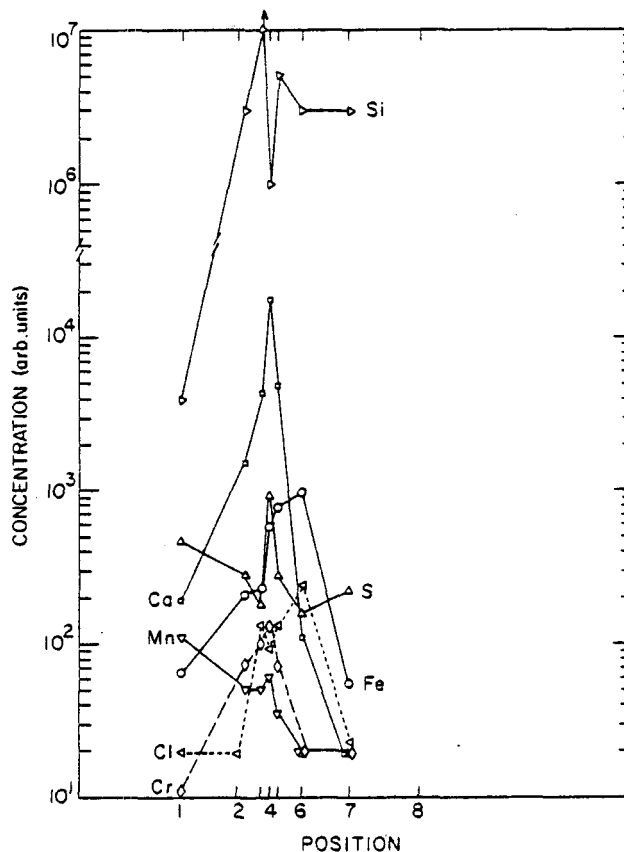


Fig. 4. The experimentally determined concentrations of impurities that collected on a sight tube during a heat-up of H-451 graphite.

Acknowledgements

C. I. Anderson and E. Reilly assisted in sample preparation and analysis. The proton microprobe was developed under Contract No. EY-76-C-02-0016 with the Division of Basic Energy Sciences, Department of Energy and the experimental results were obtained in work sponsored by the Nuclear Regulatory Commission.

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