



RADIATION EFFECTS ON THE OXIDATION RATE AND ON OTHER
CHEMICAL PROPERTIES OF GRAPHITE

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Radiation effects on graphite have been studied in considerable detail because the extensive use of graphite in nuclear reactors requires a knowledge of these effects. Furthermore, the radiation induced property changes are larger in graphite than in most other materials and therefore facilitate a detailed study of the mechanisms involved.

The properties of graphite are altered by irradiation with fast particles because these produce various lattice defects such as vacancies, interstitial atoms, ions, clusters of both, and possibly dislocations. The relative importance of these various defects in changing the physical properties have been evaluated with reasonable success in previous reports.(1, 2, 3, 4, 5) In the present report, a similar evaluation of chemical property changes will be attempted. Particular attention will be given to the burning rate which is of paramount practical importance. The studies have been carried out independently at Brookhaven National Laboratory (BNL) and Argonne National Laboratory (ANL). Practical considerations were stressed at BNL, where the majority of the experiments on artificial, reactor grade graphite were carried out. At ANL, graphite single crystals and the effects of specific chemical agents other than oxygen, such as ozone, atomic oxygen, halogen, etc., were studied.

Several other studies of irradiation effects on graphite oxidation have already been published. Hurst and Wright,⁽⁶⁾ and Sheard⁽⁷⁾ and co-workers

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have shown that irradiation increases the oxidation rate of graphite in oxygen. These results will be amplified by the BNL contribution to the present study. Sheard⁽⁸⁾ has presented evidence extended by present ANL studies that the accelerated oxidation which occurs during in-pile exposure of graphite may be attributed to ozone formed by ionizing radiation.

EXPERIMENTAL

The BNL studies on unirradiated graphite were carried out on AGOT type graphite. All samples were cut from one large block to reduce sample variation. Irradiated samples (exposed at 25-50°C, to an nvt of 4×10^{20} thermal) were either AGOT or AGHT which showed similar behavior on oxidation prior to irradiation as AGOT graphite. ANL studies were carried out on spectroscopic graphite, KCF graphite, and on natural graphite crystals, purified by standard procedures including halogen treatment at 3000°C. Both Madagascar flake graphite and more nearly perfect Ticonderoga* graphites were utilized as indicated in the text.

Irradiations were carried out in the Brookhaven reactor at fluxes of 1×10^{12} or 4×10^{12} thermal neutron/cm²/sec., in the fast flux facility of the Argonne CP-V reactor at 2×10^{13} thermal, or in the Brookhaven Co⁶⁰ gamma facility. Oxidation reactions during irradiation were carried out in aluminum containers which provided a rigid mounting for the graphite rod samples. The container was inserted into an appropriate furnace, and temperature control of about ± 5 degrees was maintained via a thermocouple inserted into one of the graphite samples. Predried air or oxygen was passed over the samples at a flow rate of 1.5 liters/min. Irradiations at ANL were carried out in sealed capsules of vitreous silica. Ozone was produced by a silent discharge. Atomic oxygen was generated in a vitreous silica system by the high frequency field of a commercial diathermy machine.

RESULTS AND DISCUSSION

The mechanism of the interaction of graphite and oxygen is still subject to considerable controversy, which will be further compounded by extensive as yet unpublished studies at ANL on graphite single crystals. Fortunately a detailed knowledge of the reaction mechanism is not essential for the present study.

Oxidation during simultaneous irradiation in a reactor can proceed by several superimposed processes, i.e., ionization and dissociation of oxygen, effects of accumulated lattice defects, transient effects on graphite surfaces, etc. To separate and isolate these processes, most studies have

*We are indebted to W. Primak of ANL for these crystals.

been conducted outside of reactors after extensive irradiation (section on Post Irradiation Studies) or during gamma irradiation or during exposure to suitable chemical analogues of gamma irradiation. (Section on Ionizing Radiations.)

POST IRRADIATION STUDIES

The oxidation rate of previously irradiated artificial graphite is shown in the appropriate curves of Figs. 1 and 2 by plotting weight loss against time. Comparable results have been obtained at 250°C and 350°C. The rates change with time initially but stabilize at values which are considerably larger for irradiated than for unirradiated graphite. These limiting rates have been collected in an Arrhenius plot (Fig. 3) to indicate that preirradiation decreases the activation energy of the reaction from 48.8 kcal to 36.1 kcal.

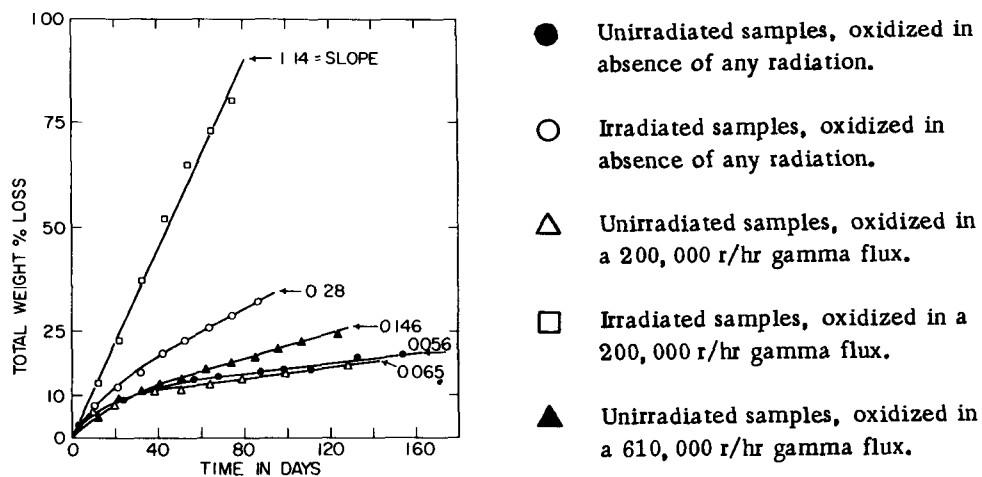
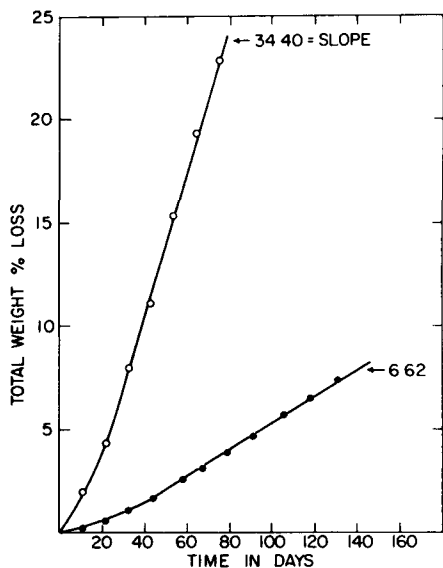


Fig. 1. Percent weight loss vs. time curve for graphite at 300°C. Slopes given as % loss/100 days.



- Unirradiated samples, oxidized in absence of any radiation.
- Irradiated samples, oxidized in absence of any radiation.

Fig. 2. Per cent weight loss vs. time curve for graphite at 400°C. Slopes given as % loss/100 days.

- Unirradiated samples, oxidized in absence of any radiation $E = 48.8$ kcal/mole.
 - Irradiated samples, oxidized in absence of any radiation $E = 36.1$ kcal/mole.
- Samples oxidized in presence of pile radiation
- △ (low flux), $E = 9.0$ kcal/mole
 - × (high flux), $E = 1.6$ kcal/mole.

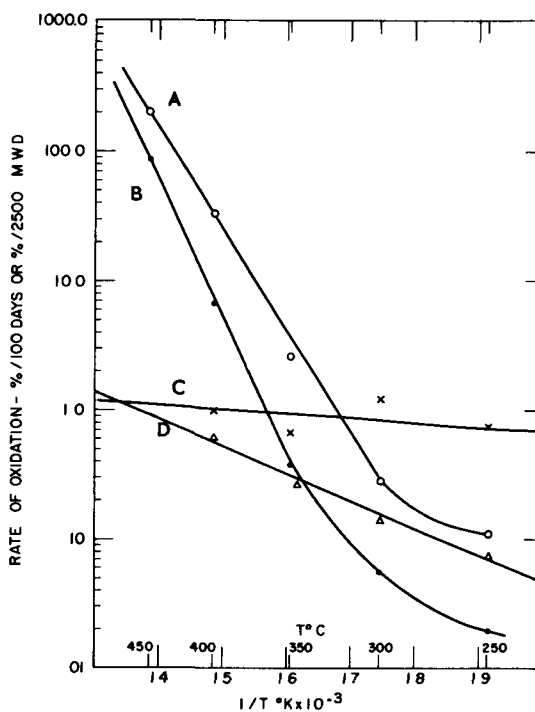


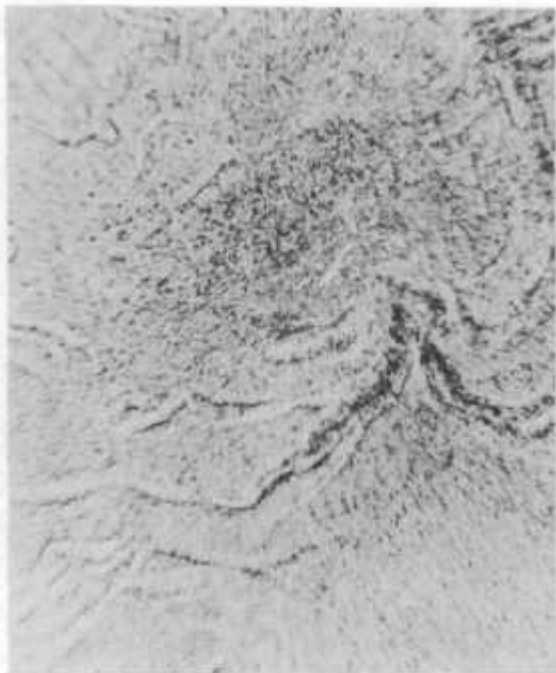
Fig. 3. Rate of oxidation vs. $1/T$ for graphite oxidized under various conditions.

Annealing of this radiation effect was studied by heating samples of unirradiated and of irradiated (4×10^{20} nvt) graphite to 600°C and to 2800°C , and by measuring the subsequent oxidation rates at 300°C . Annealing did not affect the oxidation rate of unirradiated graphite. Irradiated samples preheated to 600°C burned at the same rate as unannealed irradiated graphite, but after annealing at 2800°C , burned at the preirradiation rate, thus indicating that the radiation effect was removed by annealing between 600°C and 2800°C . These experiments indicate that the impurities in unirradiated graphite do not cause catalytic burning: the impurity content was found to decrease during annealing at 2800°C from between 0.05 and 0.1% to about 0.001% without altering the measured combustion rate. The experiments do not exclude the possibility that a catalytically active impurity is introduced during irradiation and removed again by annealing, although this explanation of the results is unlikely in view of the time independence of the oxidation rate and the reproducibility of measurements made on separate samples.

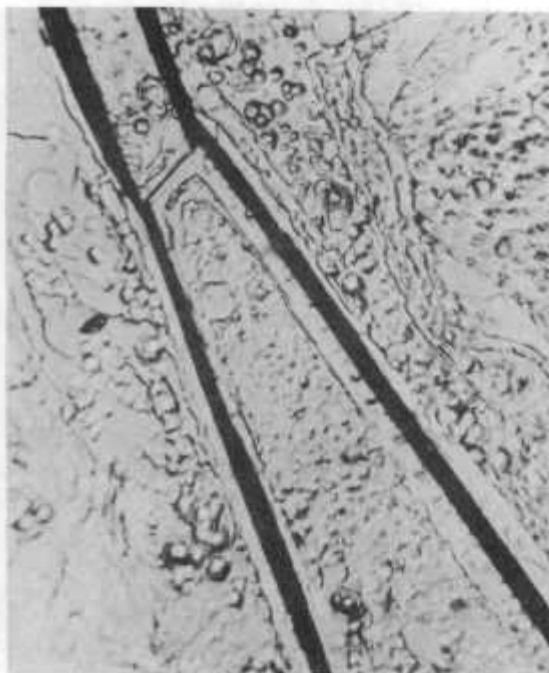
Natural graphite crystals irradiated in the reactor also burn at a higher rate than unirradiated crystals. The increase is about three-fold after an exposure of 5×10^{20} integral nvt, although it is occasionally but not consistently much smaller at the beginning of the combustion and increases to considerably larger values after heavy combustion. Due to various reasons, particularly the very low effective surface area of natural graphite activation energy determinations by Arrhenius plots are not reliable; nevertheless they seem to indicate that the activation energy is not appreciably altered by irradiation. Microscopic examinations reveal that oxidation causes a very pronounced pit formation on the previously smooth cleavage planes of irradiated crystals. (See Fig. 4a.) Unirradiated crystals if free of impurities, burn only at lattice steps and at crystal faces which contain edges of carbon layers, so that their cleavage planes are unaffected by burning except for displacements of the lattice steps. In irradiated crystals, the pits in the cleavage planes, produced by burning are superficially similar to pits produced by chemical impurities or by ozone (to be described later), but differ considerably when examined by the electron microscope* (Fig. 5). The increased burning rate of irradiated crystals can be attributed directly to these pits which increase the effective area for reaction with oxygen. To understand the phenomenon completely it is necessary to find the reason for this pit formation.

Originally the effect was believed to be a catalytic one: although the total impurity content is only about 0.004% it was assumed that reactor exposure converted some of these impurities from catalytically inactive to active ones. In an attempt to confirm this hypothesis, crystals were exposed to heavy gamma irradiation which however, did not activate the impurities to cause pitting on subsequent oxidation. In another experiment, small chips of

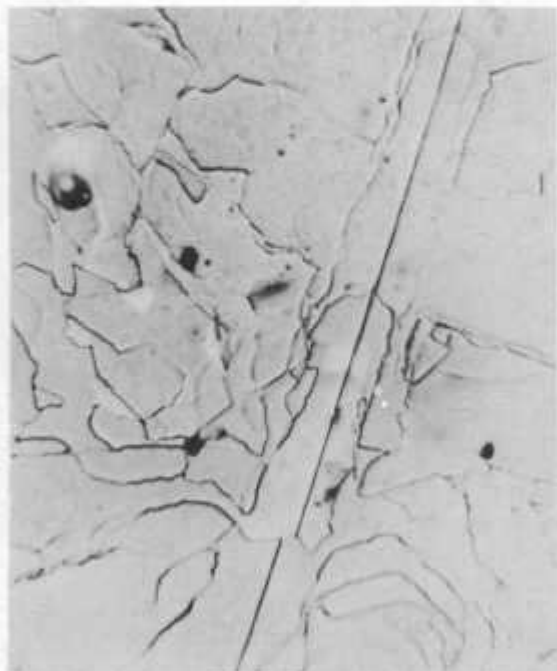
*We are indebted to O. T. Minnick of ANL for assistance with the operation of the Electron Microscope.



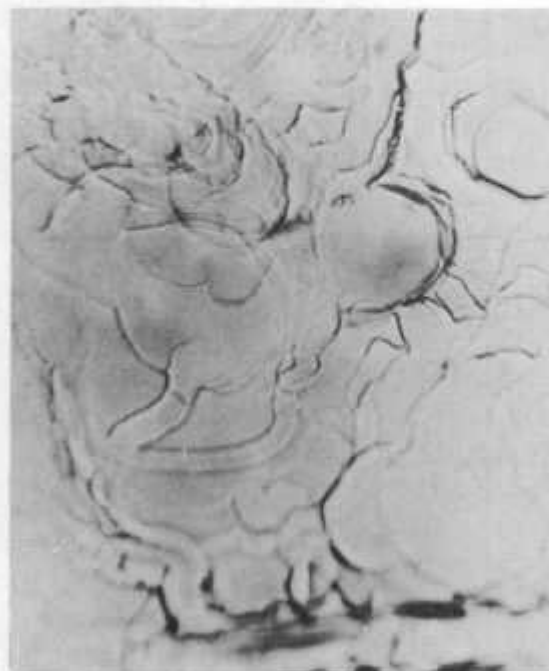
A. Irradiated



B. Irradiated and Annealed at 1100°C

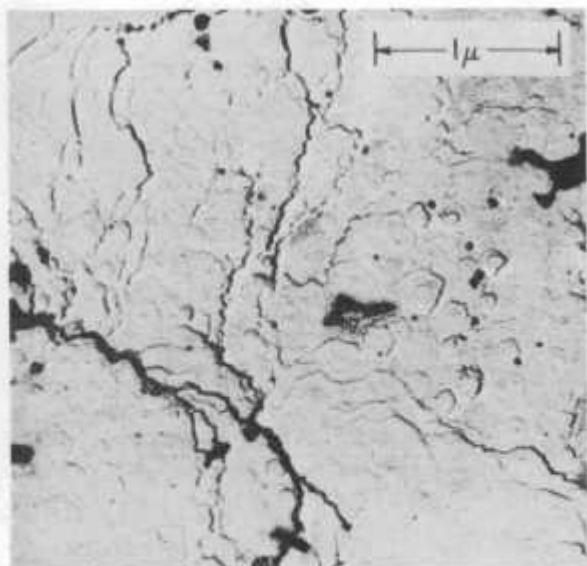


C. Irradiated and Annealed at 1400°C

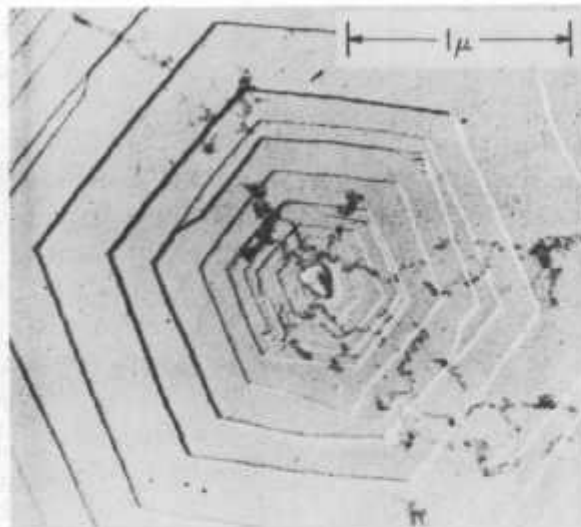


D. Irradiated and Annealed at 1800°C

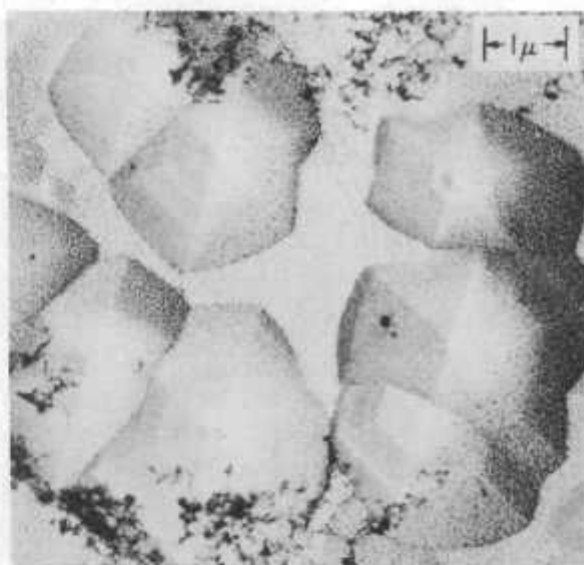
Fig. 4. Surfaces of Irradiated Madagascar Graphite Crystals after Oxidation at 650°C in Oxygen. (400X)



A. Irradiated Madagascar Crystal, burned at 650°C in Oxygen.



B. Unirradiated Ticonderoga Crystal, impurity catalyzed burning at 650°C.



C. Unirradiated Madagascar crystal, burned by atomic oxygen at 10 mm Hg.

Note: Black artifacts such as spheres on crystal A, hazy mottling on crystal B and spotting on crystal C are gold residues from the replication technique.

Fig. 5. Pitting of Graphite Crystals, Electron Microscope Replicas.

of irradiated crystals were placed on unirradiated crystals to allow the hypothetical activated impurity to transfer to the blank crystal; no such transfer was observed. The blank crystal burned without any pit formation whatsoever even after complete oxidation of the irradiated crystals. After annealing at various temperatures in helium, the tendency of irradiated crystals to pit during oxidation disappeared much more gradually than would be expected for thermal inactivation of impurities (Fig. 4). Varying the conditions of irradiation also had no effect on the subsequent tendency to pit, which was similar for crystals irradiated in vacuo, in helium, or even inside of purified graphite capsules within helium filled quartz capsules.

In view of these results, the pit formation on irradiated crystals may be attributed to lattice defects. Of the various lattice defects, vacancies are most probably responsible for pitting, since they are more likely to be attacked by oxygen than intact carbon layers distorted by interstitial atoms or clusters located immediately below the surface. A paradox, which has not yet been resolved completely, concerns the question how pits started at vacancies (and also those pits to be described later which are induced by ozone) manage to grow to microscopically visible size. Indications are at present that the surfaces of most crystals are somewhat poisoned to oxygen attack. Once the surface layer has been broken at a vacancy, oxidation at this site can proceed more rapidly than at adjacent vacancies, so that a visible pit will form. This hypothesis explains why pitting rarely occurs uniformly over the whole crystal surface but generally predominates near surface discontinuities. (See Fig. 4.) It was also observed that occasionally, pit formation was delayed in very perfect, irradiated crystals. The burning rate of these crystals did not differ from unirradiated crystals, until the crystals were exposed briefly to ozone, which induced pitting as will be described later. On subsequent burning in oxygen, the irradiated crystals burned faster and also continued to develop pits. Unirradiated crystals, treated with ozone, burned subsequently at their original rate because the pits which had been initiated by the ozone treatment merely increased in diameter but not in depth and soon disappeared completely by merging.

Without further experiments it is not yet certain whether the enhanced oxidation rate of irradiated artificial graphite can be attributed to the same mechanism which is operative in irradiated natural graphite. This problem will be examined by electron microscope studies of irradiated artificial graphite.

IONIZING RADIATION

Irradiation by gamma rays increases the oxidation rate at 300°C of unirradiated graphite somewhat, but increases the oxidation rate of previously irradiated graphite very considerably. (See Fig. 1.) Woodley⁽⁹⁾ had

observed the first of these effects at room temperature in a closed system and estimated an efficiency of about one carbon atom oxidized per ion pair produced. At 300°C in a flow system, the efficiency is considerably higher, which seems to indicate a chain reaction.

The separate effects of some of the possible intermediates produced in this oxidation were studied at ANL. A long-lived product from gamma-irradiated oxygen is ozone. In ozone, single crystals of graphite showed a characteristic pitting. The burning rate of large Ticonderoga crystals in ozone was not increased by prior neutron irradiation in contrast to the burning rate during gamma irradiation of artificial graphite, which is considerably increased (Fig. 1).

Atomic oxygen is the principal short-lived product from gamma irradiation of oxygen. Experiments to test the effects of atomic oxygen had to be carried out at low oxygen pressure to eliminate secondary effects. In atomic oxygen, natural graphite again pitted at cleavage surfaces. (Fig. 5)

Combustion rates of artificial graphite were carried out in atomic oxygen and in ozone at several temperatures. An Arrhenius plot of the results indicated that the oxidation by ozone occurs with an activation energy of about 14 kcal. (Results below 250°C not shown here.) The oxidation (Fig. 6) by atomic oxygen at an oxygen pressure of 1.0 mm Hg has practically no activation energy; at 10 mm pressure, where presumably some ozone is also formed, an activation energy of 7 kcal was measured.

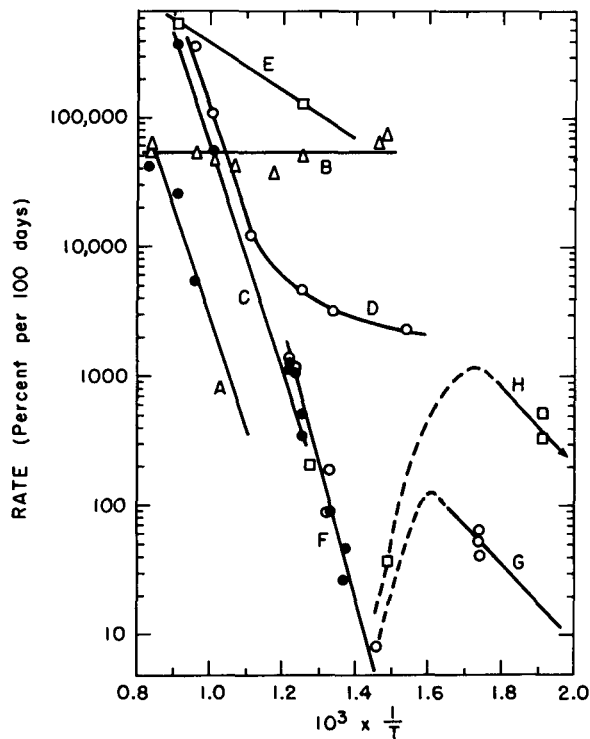


Fig. 6

Arrhenius Plot of Combustion Rates, Artificial Graphites in Activated Oxygen.

- A: Spec. graphite in O₂ pressure 1 mm Hg
- B: Spec. graphite in O₂ pressure 1 mm Hg, high O conc.
- C: Spec. graphite in O₂ pressure 10 mm Hg
- D: Spec. graphite in O₂ pressure 10 mm Hg, low O conc.
- E: Spec. graphite in O₂ pressure 10 mm Hg, high O conc.
- F: KCF in O₂ pressure 760 mm Hg
- G: KCF in O₂ pressure 760 mm Hg, low O₃ conc.
- H: KCF in O₂ pressure 760 mm Hg, high O₃ conc.

IN-PILE OXIDATION

The most interesting and important results were obtained at BNL when the rate of burning during exposure in the reactor was measured. As shown in Figs. 1, 2 and 3, the combustion is accelerated below 300°C by simultaneous irradiation. At higher temperatures, however, the combustion is actually slowed by exposure in the reactor (Fig. 7). Needless to say this effect is of paramount practical importance: if the extrapolation of Fig. 7 to higher temperatures can be confirmed by further experiments, it seems to permit the use of graphite for air-cooled reactors at higher temperatures than those previously estimated from out-of-pile experiments.

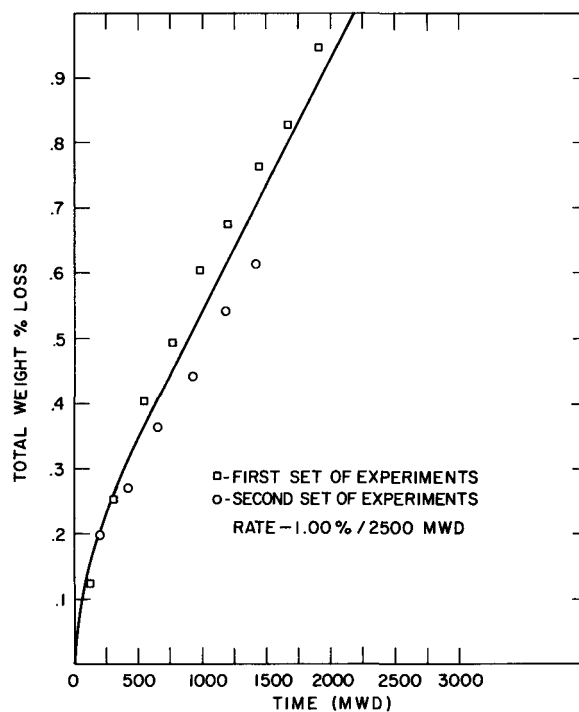


Fig. 7. In-pile Oxidation High Flux using O₂ at 400°C.

The phenomenon obviously requires much further experimentation. To date measurements have been carried out at two different neutron flux intensities (curves C and D, Fig. 3). It should be pointed out that curves C and D were obtained from data at very low (<1%) burn-off, whereas curves A and B were obtained at about 5% burn-off, and would be lower (Fig. 2) if data at low burn-off had been plotted. The phenomenon of inhibition by neutron exposure may therefore be somewhat smaller than Fig. 3 suggests, but nevertheless does exist.

No explanation has as yet been found for this unexpected retardation of oxidation. The retardation can not be attributed to a protective oxide or

other adsorbate produced by activated oxygen, because such an effect would have produced a similar retardation in the ozone and atomic oxygen experiments of Fig. 6.

The observed retardation may conceivably be caused by nonvolatile reaction products such as carbon from dissociation of carbon monoxide within the pore structure of graphite which partially block the access to these pores; such an effect can not, of course, be studied by passing ozone or atomic oxygen over the graphite. To test this hypothesis, natural graphite which is free from internal pores, should be oxidized during exposure in the reactor. It is also obvious that combustion studies during simultaneous gamma irradiation should be extended to higher temperatures to ascertain whether a similar retardation occurs under these conditions.

LAMELLAR REACTIONS OF IRRADIATED GRAPHITE

It has been shown that oxidation reactions are considerably influenced by radiation induced lattice defects, and that the vacancies are probably responsible.

It has been observed that other chemical reactions are also influenced by neutron irradiation. In particular, the large class of lamellar reactions of graphite are usually retarded or even inhibited by prior neutron bombardment. Montet⁽¹⁰⁾ has studied as one particular example, the graphite bisulfate reaction. By measuring galvanometric properties, he has shown that the formation of a lamellar compound proceeds rather slowly in irradiated graphite and causes a simultaneous annealing of radiation damage. As another example, the lamellar reaction of graphite with bromine was found to be nearly completely inhibited by radiation damage. The lattice defects primarily responsible for this inhibition of lamellar reactions seem to be the interstitial atoms and interstitial complexes.

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