II - THERMAL OXIDATION RATE OF PURIFIED GRAPHITE IN AIR - INFLUENCE OF PRE-IRRADIATION

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The oxidation by air of purified nuclear graphite was studied on graphites of which the texture was examined in our first communication.

A - Apparent activation energy of the air-graphite reaction before irradiation

In either dry or damp atmospheres, between 438°C and 620°C, the log V = f (1/T) curves are almost linear and cross at about 530°C. The activation energy values are E = 56±3 Kcal and E = 47 ± 3 Kcal respectively. The overall phenomenon is thus very similar to that observed previously with oxygen (apparent order about 0.7), which was explained by the catalytic action of moisture on the carbon combustion whatever the temperature. However when this latter is raised the catalysis changes into an apparent inhibition caused by the appearance of increasing amounts of CO and H_2 in the micropores.

B - Oxidation at 438°C of purified graphite irradiated under vacuum at 60°C at a dose of 2.10^{20} nvt (E > 1 Mev) -

After being placed in contact with the atmosphere at 25°C, some of these samples were oxidised by damp air at 438°C while others were annealed under a current of argon, again left in contact with air at 25°C for 1 hour and then oxidised.

Thermal oxidation in damp air at 438°C shows a large apparent increase in the initial corrosion rate, measured by the liberation of CO + CO_2, in the case of pre-irradiated graphite (factor of 60). This effect is fairly short-lived and seems to be due to surface oxides thermally unstable at 438°C, it stops at about 0.04 % weight loss, after which the rate is about 4 times higher than that of a non-irradiated sample. Annealing at 630°C or 900°C reduces the initial rate, but after 0.04 % weight loss the value obtained is still 3 times higher than that found with non-irradiated graphite. It is necessary to heat to 1800°C before the graphite is completely healed and the oxidation rate returns to the same value as that of the non-irradiated sample.

An irradiated sample treated in a dry atmosphere, after annealing under argon at 900°C, behaves in a similar way to that treated in a damp atmosphere under the same conditions (similar aspect of curve showing increase in rate with respect to the non-irradiated reference sample). The rate observed in damp air is however higher than that observed in dry air. This conforms with the relationships between the activation energies of reactions in dry and in damp atmospheres.

C - Oxidation at 620°C of graphite irradiated under vacuum (same conditions as B) no longer shows the increase in the initial rate still observable at 510°C, this phenomenon being masked by the rate of oxidation of the sample at this temperature. As with the reference samples, the oxidation rate of an irradiated sample in a dry atmosphere is higher than that observed in the presence of moisture. The ratio after and before irradiation is about 2 in the case of dry oxidation, whereas in a damp atmosphere there is little difference between the oxidation rates.

D - Oxidation at 620°C of purified graphite irradiated in CO_2 at 200°C. Dose = $0.7.10^{20}$ nvt (E > 1 Mev), γ dose = $5.1\ 10^3$ W.h.g^{-1}

A preliminary radiolytic corrosion to 16 % weight loss in a CO_2 atmosphere, at the above temperature and dose, increases the oxidation rate with respect to the results obtained in C. In view of the fact that in this case the irradiation temperature is higher and the dose smaller than in C, the effect of radiolytic corrosion seems clearly proved.

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E - Oxidation at 620°C of purified pyrolytic graphite (Carbone Lorraine) irradiated under vacuum at 60°C, at a dose of 2.10^{20} nvt (E > 1 Mev) *

By using pyrolytic graphite we were free from the influence of the porous texture of the sample during thermal oxidation, and in addition we were able to observe the development of the corrosion figures by electron microscopy.

In all cases a large increase in oxidation rate was observed after irradiation. Here the introduction of moisture into the atmosphere always leads to higher rates than in a dry atmosphere. With non-irradiated pyrolytic graphite the corrosion figures in dry or damp atmospheres are very similar to those observed previously on natural graphite flakes (clean-edged hexagons in the former case, ragged pits in the latter). Pre-irradiation leads to corrosion figures made up of numerous ovoid holes whatever the degree of humidity.

CONCLUSION :

Certain authors ** have observed a decrease in the gap between the rate curves obtained with nuclear graphite before and after irradiation when the thermal oxidation temperature rises. With air we believe that the large decrease in this gap is only partially due to annealing of the defects created by irradiation, and is caused mainly by the presence of moisture inhibiting active sites located in the micropores, this action increasing with temperature. This phenomenon does not occur with pyrolytic graphite which is only slightly porous.

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* The electron microscope study is part of a thesis being prepared by P. Maire

** G.R. Hennig, W. Kosiba and G.J. Dienes, P.J. Robinson and J.C. Taylor
R.E. Nightingale, Nuclear Graphite, p. 415 (1962)