

## Thermal Oxidation Behaviors of Candidate Nuclear Grade Graphites for VHTR at High Temperatures above 900°C

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### 1. Introduction

In a very high temperature reactor (VHTR), thermal oxidation of graphite components is inevitable due to oxidants impurities from a graphite outgassing and a leakage in a heat exchanger [1]. The mechanical properties of graphite are severely degraded by oxidation, the oxidation of graphite has been widely studied to analyze the safety of the reactors and assess the operational life of core structures [3-6]. The major concern of the safety concept of the VHTR is the limitation of the maximum fuel temperature even in the case of hypothetical accidents to about 1600°C. However, in most cases, the former oxidation researches were performed in the normal operation temperature of the VHTR below 900°C.

In this study, we examined the effect of temperature on oxidation rates of candidate nuclear grade graphites for VHTR using a thermogravimeter.

### 2. Experiments

Two grades of nuclear graphites, IG-110 produced by Toyo Tanso Co. Ltd, Japan and NBG-17 produced by SGL Carbon Group, Germany were used for this study. The main properties of the two grades are summarized in Table 1. The specimen for the oxidation test was a cylinder with the size of  $\phi 8 \times 8 \text{mm}^3$ . The specimens were wiped with lint-free paper to remove dust from a machining and then dried for 2 hours at 110 °C.

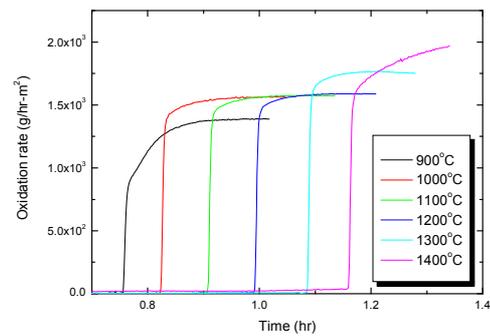
Table 1: Properties of two grades of nuclear graphites

Grade	IG-110	NBG-17
Coke	Petroleum	Coal tar
Forming method	Iso-static	Vibro-mold
Density (g/cm <sup>3</sup> )	1.78	1.81
Average grain size (μm)	20	Max. 900

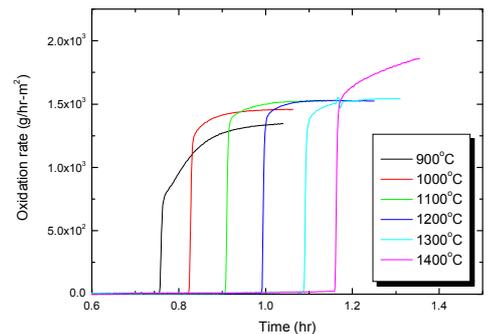
The oxidation tests were performed with the SDTA 851e model thermogravimeter from Mettler Toledo Company. To oxidize the specimen in the boundary layer controlled regime, the test temperatures were selected from 900 to 1400°C at an interval of 100°C. The oxidant was dry air with a flow rate of 60 ml/min. After placing the specimen in the thermogravimeter, the argon gas (99.999%) was purged at a rate of 60ml/min during a heating at a rate of 20°C/min from room temperature to the targeted temperature. The weight was continuously collected every 5sec until the specimen has lost 10% of its original weight

### 3. Results and Discussion

Fig. 1 shows the variation of the oxidation rates as a function of the time. Directly after the dry air was purged into the chamber, the oxidation rates were sharply increased and then reached stable values past a certain incubation time except for 1400°C. As the temperature increased from 900°C to 1000°C, the incubation time decreased significantly. However, there was little in the incubation times between 1000 and 1300°C. Unfortunately, the oxidation data at 1400°C were inadequately accumulated, it can not be determined whether the oxidation rate will reach a stable value or not. The dependency of the oxidation rate on the time was similar for two grades.



(a)



(b)

Fig. 1 variation of oxidation rates as a function of weight loss: (a) IG-110 and (b) NBG-17

In the boundary layer controlled regime above 900°C, the chemical reactivity is so high at the external surface of a specimen that the surface area shrinks without any damage to the interior of the specimen. The oxidation rate is proportional to the surface area of a specimen and thus the oxidation rate decreases with the time (weight loss) at high temperatures. From this point of

view, it is considered that the change of the surface area didn't affect the dependency of the oxidation rate on the oxidation temperature.

The oxidation rates determined by a linear fit of the weight loss plotted against time in the range of a 5 to 10% loss of the original specimen weight are summarized in Table 2. As the oxidation temperature increased from 900 to 1000°C (1100°C for NBG-17), the oxidation rate increased by 12% for IG-110 and 14% for NBG-17, respectively. Between 1000 and 1200°C, the change of the oxidation rates was insignificant. However, the oxidation rates at 1400°C were about 20% higher than those at 1300°C (1200°C for IG-110).

Table 2. Oxidation rates at different temperatures

Temperature (°C)	Oxidation rate (g/hr-m <sup>2</sup> )	
	IG-110	NBG-17
900	1384	1323
1000	1560	1453
1100	1573	1521
1200	1587	1527
1300	1760	1538
1400	1916	1810

It was observed that the oxidation rate reached a stable value after a certain incubation time (weight loss) and increased with the oxidation temperature. While the rate of the chemical reactions is proportional to  $\exp(-A/T)$ , where A is a constant and T is the absolute temperature, the rate of a diffusion is typically proportional to  $T^{0.5}$ . At higher temperatures, the rate of the chemical reactions is very high, the oxidation rate is mainly controlled by the diffusion of the oxidizing gases. Also, the concentration of the oxidant at the specimen surface is so low that CO is mainly produced by the oxidation reactions with oxygen,  $C+1/2O_2 \rightarrow CO$ . For the flow rate of 60ml/min at room temperature, the flow of oxygen was 0.031mol/hr. If all the oxygen were consumed by the  $C+O_2 \rightarrow CO_2$  reactions, for example, the oxidation rates would be 1642g/hr-m<sup>2</sup>, which is much lower than the actual oxidation rates at 1400°C. From this approximate calculation, the increase of the oxidation rate at 1400°C was caused by the enhancement of  $C+1/2O_2 \rightarrow CO$ .

#### 4. Summary

The thermal oxidation behaviors of candidate nuclear grade graphites for VHTR investigated at high temperature above 900°C are summarized as follows.

1. The oxidation rates were reached stable values past a certain incubation time which was dependent on oxidation temperature.
2. As the oxidation temperature increased from 900 to 1000°C, the oxidation rate increased. The values of oxidation rate at 1000~1300°C remained unchanged

however, the oxidation rates at 1400°C increased significantly. The increase of oxidation rate with oxidation temperature is considered to be attributed with the enhanced  $C+1/2O_2 \rightarrow CO$

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