Oxidation behaviors of Selected IG and NBG Nuclear Graphite Grades

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1. Introduction

In very high temperature gas-cooled reactor (VHTR), graphite acts as a moderator and reflector as well as a major structural component that may provide channels for the fuel and coolant gas, channels for control and shut down, and thermal and neutron shielding. During operation, the graphite core components are expected to be degraded by neutron irradiation and oxidation due to the high temperature helium coolant containing catalytic impurities. It is known that oxidation of graphite will result in loss of structural integrity, change the thermal conductivity, reduce the fracture toughness and strength of the components.

In view of this discussion, in the present study, the oxidation behaviors of two nuclear graphite grades were investigated to provide information necessary for a safety analysis, an evaluation of integrity and a life-prediction of graphite component, and a graphite selection for the KAERI NHDD project.

2. Experimental

2.1 Materials and specimen

Four nuclear graphite grades, IG-110, IG-430, NBG-18 and NBG-25 were chosen for the present study by considering the manufacturing process (i.e., manufacturing process including the forming method), and the source of the coke, i.e., pitch or petroleum. **Table 1** summarizes the characteristics of the grades.

Table 1
Comparison of Some of the Physical and Mechanical Properties of Nuclear Graphites (IG-110, IG-430) and IG-11 Non-Nuclear Graphite (manufacturer data sheet).

Grade	IG-110	IG-430	IG-11
Coke	Petro.	coal-tar	Petro
Grain Size, mm	0.02	0.01	0.02
Appar. density, g/cm^3	1.77	1.82	1.77
Anisotropy ratio	1.10	1.09	-
Ash content, ppm	<10	<10	479
Impurity, ppm	~ 0.1	~ 0.1	-
E, GPa	9.7	10.6	9.04
Tensile Strength, MPa	27.2	37.8	25.4
Compre. Str., MPa	79	96	86
Ther. Cond., W/mK	129-140	138-147	122

The specimen used for the present oxidation experiment was cylindrical with 25.4 mm in diameter and 25.4 mm in height.

2.2 Determination of oxidation rate

2.2.1 Oxidation test system.

Oxidation rate was determined by using a graphite oxidation test system which was composed of a vertical tube furnace, 3–zone furnace controller, a gas supplier, and an analytical balance (capacity: 200g, resolution: 0.001 g).

During a test, a flow rate of a minimum of 10 liters /min was maintained, and an automated data collection system was used to record the logged specimen weight and temperature data until the specimen had lost about 10 % of its initial weight.

2.2.2 Determination of kinetics: oxidation rate (OR) and activation energy (AE).

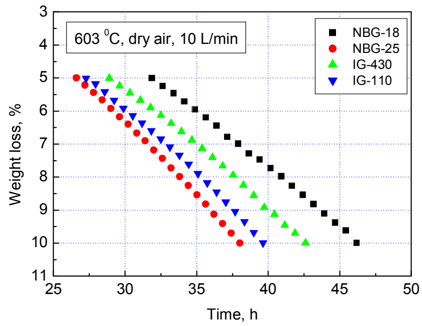
ORs were determined at six temperatures, i.e., 603, 702, 808, 854, 911 and 953 ℃, and the AE was determined for 603 ~ 803 ℃.

These temperatures were chosen to investigate the oxidation characteristics of the grades within the chemical and in-pore diffusion or boundary layer controlled regime [1]. The linear rate of the weight loss between 5% and 10% of the specimen's initial weight was used for a determination of the OR at four oxidation temperatures in units of $g.h^{-1}m^{-2}$. AE was determined in units of kJ/mole from the slope of ln (oxidation rate) vs T^{-1}.

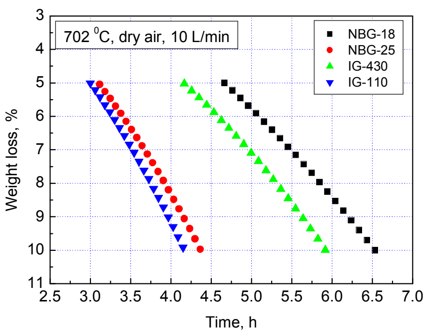
3. Results and Discussion

3.1 Weight loss behavior

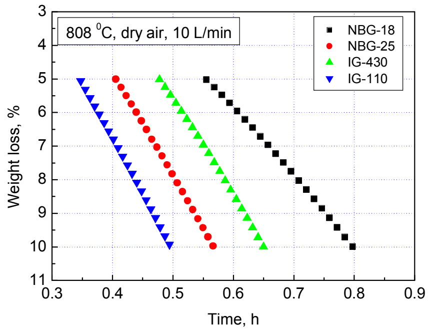
Fig. 1 (A), (B), (C), (D) show the weight loss behavior of the grades at 603, 702, 808, and 911 ℃, respectively. The weight loss behavior appeared to be different according to the type coke. The grades made of petroleum coke, i.e., NBG-25 and IG-110, clearly show a faster weight loss behavior than the grades made of pitch cokes irrespective of a manufacturer. The difference according to the coke appeared to disappear with an increase in the oxidation temperature, **Fig. 1(D). Fig. 1 (C)** (808℃) shows a clear difference in the weight loss behavior between the grades. The order of the weight loss with time in a descending order is IG-110 > NBG-25> IG-430 > NBG-18. It is seen that a change in the weight loss mechanism during an oxidation may have occurred between the



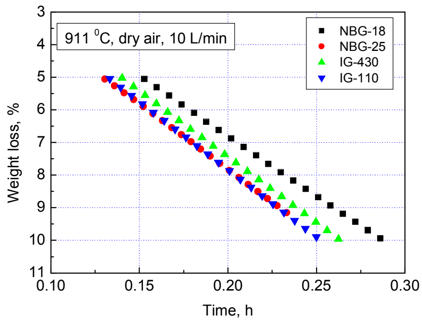
(A)



(B)



(C)



(D)

Fig. 1 ((A), (B), (C), (D)) Weight loss (%) behavior of four nuclear graphite grades (NBG-18, NBG-25, IG-110, IG-430) in dry air (603, 702, 808, 911℃, flow rate: 10 L/min).

temperatures 808 and 911^{0}C. The dominant oxidation reaction before 854^{0}C is thought to be a chemical control and is appeared to be in the middle of transition from the chemical control to the in-pore diffusion or boundary-layer control from 854 to 911^{0}C. It is known that the chemical control is largely controlled by the material-specific factors, and the in-pore or boundary-layer controls are dominantly controlled by the material specific "diffusion" or non-material-specific factor, i.e., the "availability" of oxidant (air), respectively [1].

3.2 Oxidation rate (OR) change with the temperature

Changes of the OR upon an oxidation temperature are seen in **Fig. 2**. While the increase in the OR from 603^{0}C to 702 ^{0}C is not significant, it shows a drastic increase from 702 ^{0}C to 854^{0}C. From 854 ^{0}C to 911℃, no large change in the OR is observed. Even a little decrease in the OR is observed for the three grades except for NBG-18. Thus, all the grades except for NBG-18 show a little decrease in the OR with an increasing temperature. At 911^{0}C, all four grades show an increase in the OR. It is worth noting that NBG-18 consistently shows a minimum value in the OR through out all the test temperatures. The oxidation rates at 854 ^{0}C are roughly 10 ~ 14 times higher than the rates at 702 ^{0}C.

Of these four grades, the NBG-18 of pitch coke showed the least oxidation rate through out the six oxidation temperatures. The present observation for NBG-18 may be attributed to the highest density, the largest grain size, the lowest frequency factor and the lowest open pore density of the grades in a comparison to the other three grades [2].
In addition, a higher density and a larger size of the Mrozowski cracks observed in the petroleum coke graphite may also have contributed to the present observation [3][4][5].

As discussed in 3.1 weight loss behavior, it is confirmed that some changes in the dominant oxidation control mechanism have occurred for 808~911℃, Fig. 2 and 3. From the large differences in the weight loss and oxidation rate behavior between the grades at 808℃, the oxidation at this temperature is believed to be occurred by chemical control.

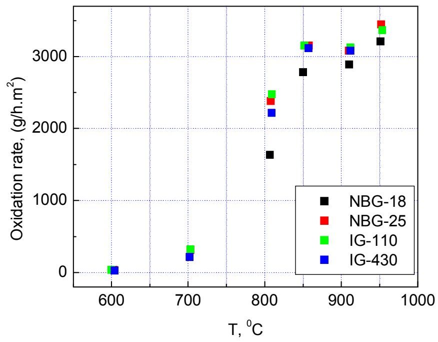


Fig. 2 The oxidation rate change with temperature.

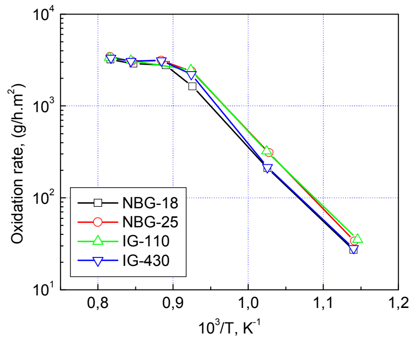


Fig. 3 The Arrhenius plot for an activation energy determination.

3.3 Activation energy

Fig. 3 shows the Arrhenius plot for an activation energy determination, where, the average activation energy of the four grades was determined to be 161.5 ± 7.3 kJ/mol. A gradual change in the slope between 808 and 854 ^{0}C (i.e., decrease in the activation energies) due to the dominant oxidation mechanism was noted. In fig. 3, the expected decrease in the activation energy from above 808℃ is coincident with the assumed change in the oxidation mechanism from a material-dependent to a non material–dependent mechanism.

4. Conclusion

While the four examined nuclear graphite grades showed a highly temperature-sensitive behavior through out the test temperature range of 600 ~ 950℃, differences between the grades were not significant. Thus, over all, the four nuclear grades from the NBG and IG grades showed a similar oxidation behavior. The oxidation rates determined for a 5 ~ 10 % weight loss at the six temperatures were nearly the same except for 702 and 808 ℃, where the pitch coke graphites showed a smaller oxidation rate than the petroleum coke graphites. These effects of the coke type reduced or disappeared with an increasing temperature. The average activation energy determined for 608 ~ 808℃ was 161.5 ± 7.3 kJ/mol, showing that the dominant oxidation reaction occurred by a chemical control.

References

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