EFFECTS OF THE AIR FLOW RATE ON THE OXIDATION OF SELECTED NUCLEAR GRAPHITE GRADES

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1. Instruction.

For a VHTR, graphite oxidation is regarded as a critical phenomenon for degrading the integrity of graphite components under normal or abnormal conditions. The oxidation of a graphite core component can occur by air which may permeate into the primary coolant operation and/or by impurities contained in the He coolant, or by air ingress during a severe accident [1][2].

It is well known that the oxidation properties of a graphite are highly dependent on the source of raw materials, impurities, microstructures (crystallites, pore structure), and on the processing and environmental parameters, such as the forming methods, the coolant type, moisture and impurity content, temperature, flow rate and the oxygen potential of the coolants [3].

A lot of work has been performed on the oxidation of graphite since the 1960s [4], and, for example, in the case of the temperature, a widely accepted oxidation model on the effects of a temperature has already been developed [5]. However, in the case of the flow rate, even for its expected effects in a VHTR, for example, due to the expected changes in the system coolant pressure or in the bypass flow (10-20 % of the total coolant) during an operation [6], no systematic works have been performed for candidate nuclear graphites for VHTR .

In this respect, as a preliminary study, the effects of an air flow rate on the oxidation of NBG-18 and 25 nuclear graphite were investigated.

2. Experimental

2.1 Materials and specimen.

Specimens (cylinder: 1″dia. x1″length) for an oxidation experiment were prepared from NBG-18 and 25 nuclear graphite grades supplied by SGL. Table 1 shows the selected characteristics and properties of the grades. Differences in the source coke and grain size are noted.

Table 1. Characteristics of NBG-18 and -25 Nuclear Graphite Grades.

Grade	Source Coke	Forming Method	Grain Size (㎛)	Density (gcm^{-3})	Ash (ppm)
NBG-18	Pitch	Vibro-Mold	Max. 1600	1.85	<10
NBG-25	Petroleum.	″	Max.60	1.82	<11

2.2 Oxidation Experiments

Oxidation experiments were performed in air by using a graphite oxidation test system which was composed of a vertical tube furnace, 3-zone furnace controller (600-1,100℃), a gas supplier, an analytical balance (capacity: 200g, resolution: 0.001g) and a flow meter (Model: KOFLOC RK-1600: 1 – 10 L/min air).

The system was manufactured by the (draft) ASTM Standard Oxidation Test Method for graphite, and by which present experiments were performed [7]. During a test, 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. Detailed experimental procedures are reported elsewhere [8].

2.3 Oxidized Surface Morphology

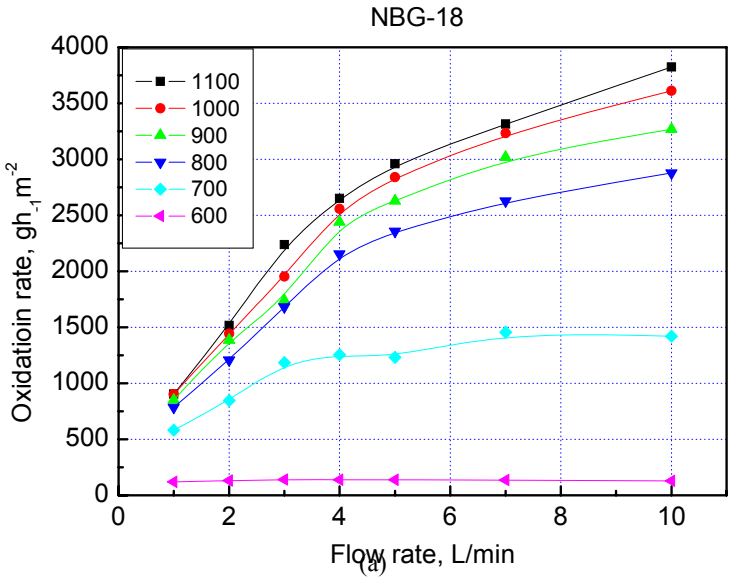
Differences in the oxidized specimen surface morphologies were investigated by the photomicrographs obtained by digital camera since the optical microscope and scanning electron microscope were failed to apply on the oxidized surfaces due to the lower depth of field and the fragile oxide powders formed on the oxidized specimen surface, respectively.

3. Results and Discussion

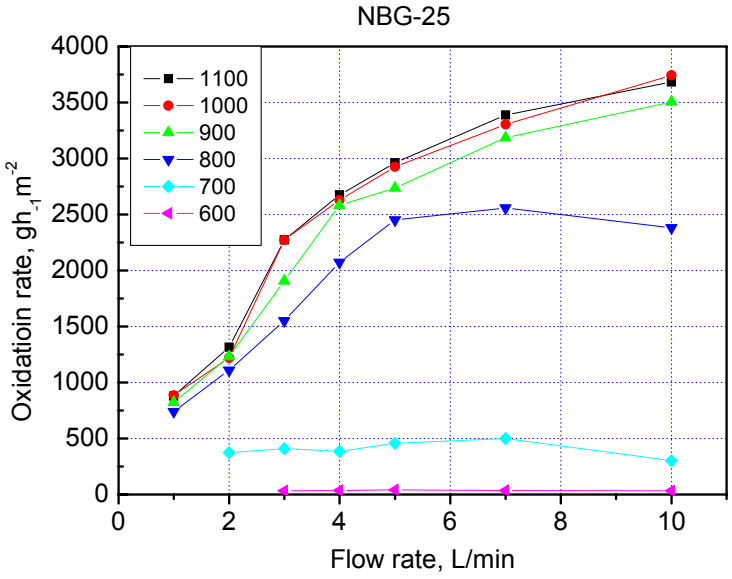
3.1 Effects of Flow Rate (FR) and Temperature on Oxidation Rate (OR).

Fig. 1 shows the effects of FR and temperature on the OR of NBG-18 (a) and NBG-25 (b). It is seen that the FR effects on OR appear as temperature-dependent, i.e., 600℃, 700-800℃, and 900-1100℃.

At 600℃, it is seen both grades show no flow rate effects for the air flow rate examined (1 ~ 10 L/min). From the observation, it is predicted that the flow rate effects may be negligible in the chemical oxidation reaction regime.



(a)



(b)

Figure 1. Relationship between the flow rate and the oxidation rate for 600～1,100℃: (a) NBG-18 (b) NBG-25.

At 700～800℃, while both grades show an apparent FR effects on OR, both grades appeared to show different FR effects on OR. At 700℃, while the FR effects in NBG-18 appeared for 1～3 L/min, the FR effects in NBG-25 appeared for 7～10 L/min. The OR of NBG-18 increased nearly 2 times from 550 to 1,125 $gh^{-1}m^{-2}$ when FR increases from 1 to 3 L/min. For FR > 3 L/min, the NBG-18 showed a relatively small or negligible increase in OR. In case of NBG-25, while a negligible FR effect is seen for the FR of 1～7 L/min, for FR from 7 to 10 L/min, however, the OR decreased about 34 % from 458.7 to 302.2 $gh^{-1}m^{-2}$. Thus, a decrease in OR was observed with increasing FR for 7 to 10 L/min. It is worth noting that the OR of NBG-18 is nearly three times higher than that of NBG-25 for FR > 3L/min.

All the observed differences between the NBG-18 and NBG-25 at 700℃ may be attributed to the differences in the microstructure of the grades and the responsible oxidation reaction mechanism (i.e., in-pore diffusion) at 700℃.

At 800℃, while NBG-18 shows a two step increase in OR with increasing FR for 1-10 L/min, i.e., step I: 1 – 4 L/min (OR: 750-2150 $gh^{-1}m^{-2}$), step II: 5-10 L/min (OR: 2150-2850 $gh^{-1}m^{-2}$), NBG-25 shows a one step increase (FR: 1-5 L/min, OR: 750-2480 $gh^{-1}m^{-2}$) with a little decrease in OR for 5 – 10 L/min FR, Fig. 1 (b). This observation of the decreasing OR with increasing FR at 800℃, is quite similar to the case at 700℃, where the NBG-25 showed a decreasing OR with increasing FR for the same FR range of 7～10 L/min. In Fig. 1 (a) of NBG-18, it is observed that the rate of increase in the OR of step I is about three times larger than that of Step II (466.6 $gh^{-1}m^{-2}/Lmin^{-1}$ vs. 140 $gh^{-1}m^{-2}/Lmin^{-1}$).

For 900-1,100℃, two grades show quite similar FR effects on OR. Thus, the differences in grades of the source coke, the forming method, and the grain size are hardly observed. The observed similarities between the grades in the FR effects on OR for 900-1,100℃ may be attributed to the prevailed oxidation mechanism in the temperature range. It is well known that, for these high temperatures, the reaction rate is governed by the mass transport in the reaction zone, rather than the intrinsic microstructural difference [9] and the oxidation rate is observed to increase as the square root of the FR of air [10]. It is seen that both grades show a 2 step increase: Step I: 1-4 L/min, Step II: 4-10 L/min. The rate of increase in OR per unit flow rate (L/min) is about 533.3 $gh^{-1}m^{-2}/Lmin^{-1}$ for Step I and 183.3 $gh^{-1}m^{-2}/Lmin^{-1}$ for Step II. Again, like the two step increase in OR of NBG-18 at 800℃, it is observed that the step I rate of increase is about three time larger than that of Step II.

Finally, for NBG-18 at 1,100℃, it is observed that the OR has increased by about 4.7 times when FR increases from 1 L/min to 10 L/min, and, at 10L/min FR, the OR at 1,100℃ is 30.4 times that of 600℃. In case of NBG-25 at 1,100℃, while the OR appeared to increase about 4.7 times when FR increases from 1 L/min to 10 L/min, the OR increased 75 times that of 600℃ at 10L/min.

3.2 Comparison of Oxidized Specimen Surface Morphologies.

Fig. 2 shows the photographs of the specimen surfaces oxidized at 700℃ and 1,100℃ for 1～10 L/min FR of air. It is seen that, while the temperature effects are apparent, the flow rate effects within the same oxidation temperature are nearly the same for 1～7 L/min FR particulary for NBG-25 of finer grains. At 700 ℃, however, the NBG-18 of a coarse grain appeared to show an increase in the oxidation of binder phase with increasing FR from 1 to 7.

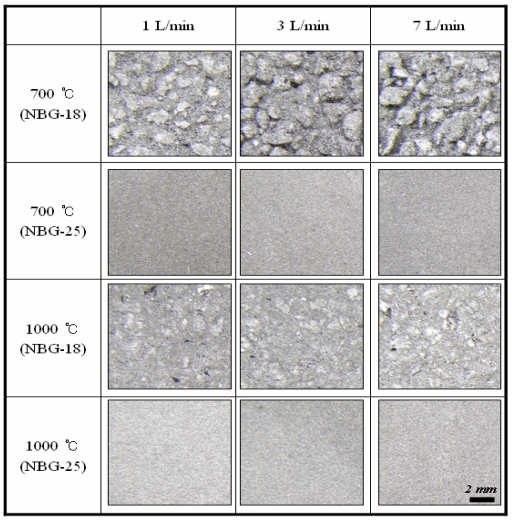


Figure 2. Oxidized surfaces of NBG-18 and NBG-25 (Oxidation Temp.: 700 and 1,100℃, Flow rate: 1, 2, and 7 L/min).

In Figure 2, the oxidation surfaces appeared to reflect the oxidation reaction mechanisms. Thus, while the oxidized surfaces at 700℃ are somewhat rough due to the selective oxidation of surface binder phase (in-pore diffusion mechanism), all the as-oxidized surfaces at 1,100 ℃ show a fine and smooth microstructure (boundary layer mechanism).

4. Conclusion

The FR effects on OR increased with an increase in the temperature. For NBG-18, the OR has increased by about 4.7 times when FR increases from 1 to 10 L/min, and the OR at 1,100℃ increased by 30.4 times that of 600℃ at 10L/min FR. For NBG-25, at 1,100℃, the OR appeared to increase about 4.7 times when FR increases from 1 L/min to 10 L/min, but, the OR appeared to increase 75 times that of 600℃ at 10L/min. Investigation of the oxidized surfaces confirmed again the strong temperature effects on oxidation with a negligible FR effects.

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