Measurements of Kinetic Parameters of Nuclear Graphite IG-110 for HTGR Air-ingress

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Abstract

In order to investigate the chemical behavior of the graphite during an air-ingress accident in high temperature gas-cooled reactors, kinetic tests on nuclear graphite IG-110 were performed in chemical reaction dominant regime. In the experiment, inlet gas flow rate ranged from 8 to 18 SLPM, graphite temperatures from 540 to 630   and inlet oxygen mole fractions from 3 to 30 %. He/O_2 mixture was used as a reacting gas.

The test section was made of a quartz tube, which has 75 mm diameter and 750 mm length. The specimens with 21 mm diameter and 30 mm length were supported in the center of quartz tube by the ceramic rod. The 15 kW induction heater was used to heat the specimen. The graphite temperature was measured by 2 infrared temperature sensors. The concentration of each component of gas mixture introduced to the gas sampler was analyzed by NDIR (non-dispersive infrared) gas analyzer.
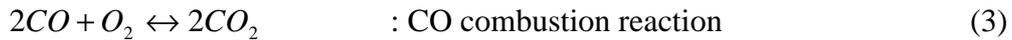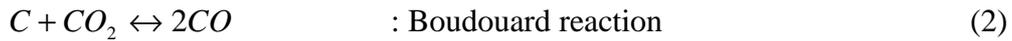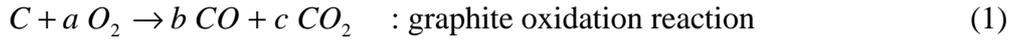
The oxidation rate was calculated from the inlet and outlet concentration of O_2, CO, CO_2. The order of reaction (n) was estimated as 0.75 ± 0.146 with 95 % confidence level. It was not affected by the burn off ratio and oxidation temperature. With activation energy (Ea) data obtained for different oxygen concentration and flow rate conditions, 218 ± 3.76 of Ea was obtained within 95% level of confidence. It was found that the activation energy was not affected by oxygen concentration.

1. Introduction

Air ingress due to a pipe break is a critical event for helium-cooled HTGRs. Following the loss of coolant through the break and coolant depressurization, air will enter the core through the break by molecular diffusion and ultimately by natural convection, leading to oxidation of the in-core graphite structure and fuel. The oxidation of graphite materials by corrosive gases such as oxygen-mixed helium gas is expected to cause the following problems:

(1) Heat-up of graphite material by exothermic reactions
(2) Structural integrity problem caused by the strength losses of the graphite material
(3) Release of toxic gas such as CO and CO_2

The main chemical reactions taking place in HTGRs are known as follows [1].

$$C + a\,O_2 \rightarrow b\,CO + c\,CO_2 \qquad \text{: graphite oxidation reaction} \qquad (1)$$

$$C + CO_2 \leftrightarrow 2CO \qquad \text{: Boudouard reaction} \qquad (2)$$

$$2CO + O_2 \leftrightarrow 2CO_2 \qquad \text{: CO combustion reaction} \qquad (3)$$

The graphite oxidation of Eq. (1) is the main reaction in air-ingress accident. Since the reactions of Eqs. (2) and (3) occur only at high temperature, we ignored all other effects except for the graphite oxidation in our study.

The graphite oxidation reaction can be divided into 3 regimes with the oxidation temperature [1]. At low temperature the reaction velocity is limited by the oxidation reaction rate since the reaction is so slow that the oxygen can penetrate the whole porous graphite with a small concentration gradient. On the other hand, at high temperature the reaction velocity is determined by only mass transfer rate since the mass transfer is too slow compared with the chemical reaction. At the intermediate temperature the reaction rate is affected by both the chemical and mass transfer effects. The transition temperature of each regime is known to depend on the kinetic parameters and mass transfer coefficient. Generally it ranges as follows.

(1) chemical reaction dominant regime (~ 577   )
(2) in-pore diffusion regime (577 ~ 877   )
(3) mass transfer dominant regime (877   ~)

The detail mechanisms of the graphite oxidation have not been revealed yet, but the reaction rate has good agreement with the following Arrhenius equation:

$$R_g\,(kg/s) = C_0 \cdot e^{-\frac{Ea}{R \cdot T}} \cdot P_{O2}^{\;2} \cdot A_e \qquad (4)$$

The value of activation energy has been reported by many previous researchers [2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. However, the order of reaction needs to be investigated experimentally due to lack of studies.

2. Experiment

It has been known that the graphite oxidation reaction is mainly affected by the following factors.

(1) oxidation temperature
(2) oxygen concentration
(3) gas flow rate
(4) humidity
(5) graphite material
(6) size and geometry

In this study, kinetic tests on nuclear graphite IG-110 have been performed in chemical reaction dominant regime focusing on the temperature effect and oxygen concentration effects.

2.1. *Apparatus*

IG-110 nuclear graphite, an isotatically molded, isotropic, fine-grained graphite manufactured by Toyo Tanso Co. Ltd was tested as a sample material. This material is used for the fuel element blocks in the Japanese HTR-10 plant. Specimens were designed based on the GT-MHR core structure with the cylindrical shape of 21 mm diameter and 30 mm length. Figure 1 shows a schematic diagram of the experimental facility. As shown in this figure, the specimen was supported in the center of the test-section on the vertical ceramic rod. The test-section was made of quartz for visual observation and non-contact measurement. The 15 kW induction heater was installed at the outside of the test-section for direct heating of the graphite specimen, and the temperature was monitored by the 2 infrared thermometers. Figure 2 shows a schematic of the test section and the gas flow paths around the specimen. The mixture of highly purified helium and oxygen gases was used as reacting gas. The inlet flow rate and concentration were precisely controlled by 4 mass flow controllers. After being mixed with each other in the mixing tank the gases were introduced to the test section in which a graphite specimen was mounted. The reacted gas was passed through the gas cooling system and then the concentration of each component in the sampled gas was analyzed by the multi-gas analyzer.

The experimental conditions are shown in Table 2. These conditions cover all possible ranges of pressure, gas flow and oxygen concentration in HTGRs during the air-ingress accident. The total pressure was maintained to be 1 atm during the test. Oxidation temperature was controlled by the infrared thermometer and the heater controller within ±1 in the range between 540 and 630   . The gas flow rate for each run varied between 7 and 18 SLPM (standard liter per minute). The oxygen concentration was maintained constantly in the range between 0 ~ 0.32 mole fraction.

Table 2. Experimental Conditions

	Conditions
Temperature ( )	540~630
Flow rate (SLPM)	7 ~ 18
Oxygen fraction	0 ~ 0.32
Graphite material	IG-110

2.2. *Procedure*

Two different kinds of experiment were performed in the present study. To obtain the activation energy and the order of reaction we performed the test increasing the graphite temperature and oxygen concentration under the constant oxygen concentration and temperature condition, respectively. The test was carried out by the following procedure.

(1) Helium gas is injected into the test section with the fixed flow rate.
(2) After the test section is purged, a graphite sample is heated up to the setting temperature by the induction heater.
(3) If the temperature is fixed at the setting temperature, oxygen gas is injected into the test section.
(4) If the concentration of each gas component reaches the steady state, temperature (or concentration) is increased to the next step.
(5) The step (4) is repeated until the last step.

Since the reaction rate is very slow in the chemical reaction dominant regime, it can be assumed that the graphite internal structure dose not change through the above process.

2.3. *Analysis*

From the oxygen species conservation law, we can derive the following equation:

$$R_g(kg/s) = Mc \cdot \frac{\dot{m}_{O2}}{(f_{O2} + f_{CO2} + 1/2 f_{CO})} \cdot (f_{CO2} + f_{CO}) \tag{5}$$

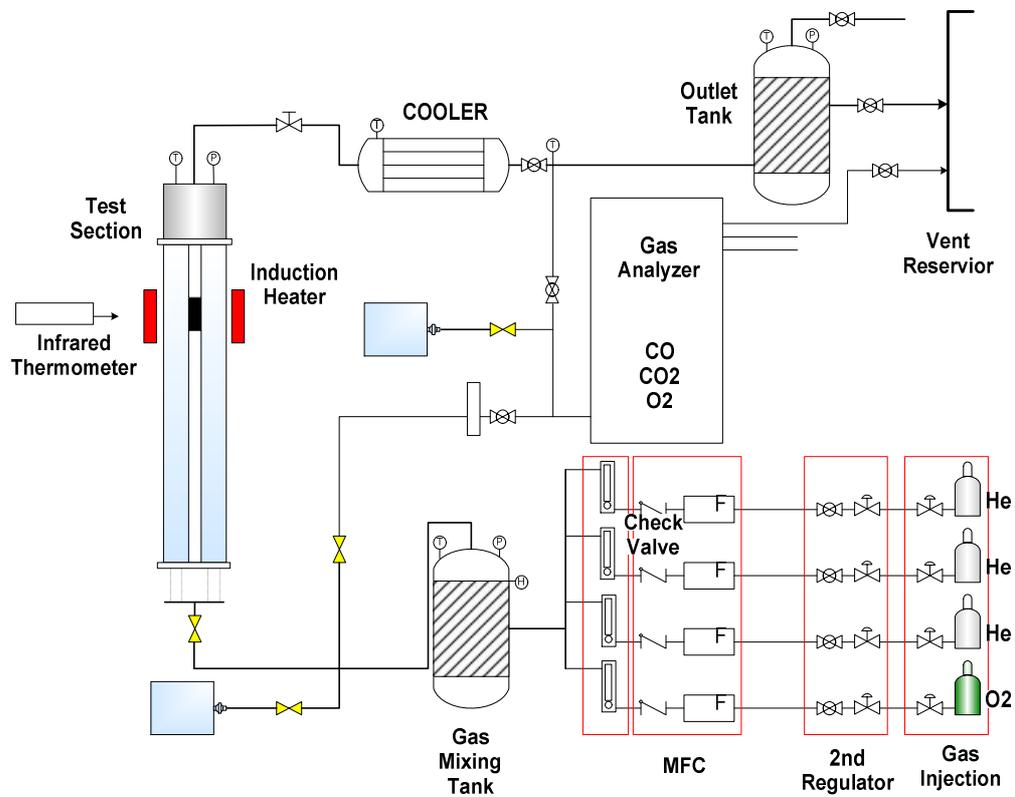In this equation, all variables of the right side are experimentally measured.
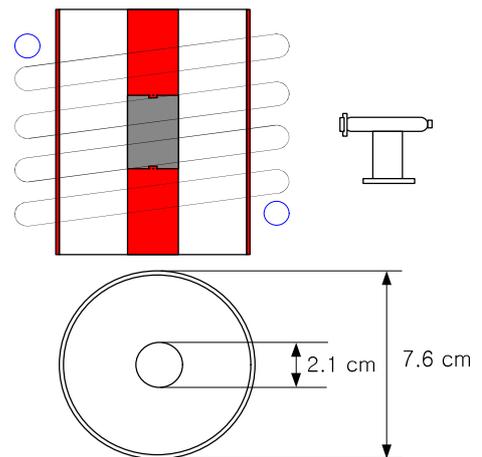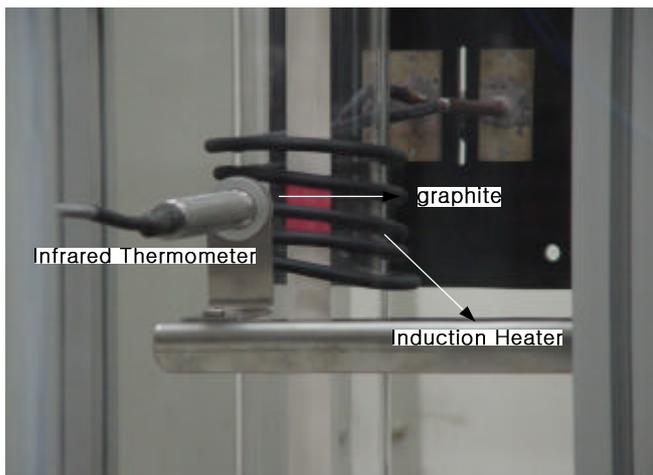
Figure 1. Schematic diagram of experimental facility

Figure 2. Picture and schematics of test section

3. Results and Discussion

In this study, we considered the effects of temperature and oxygen concentration on chemical behavior. The main kinetic parameters concerned with these two effects are the activation energy and the order of reaction. The following results are including the value of each parameter and their characteristics.

3.1. *Activation energy*

3.1.1. *Measurement of activation energy*

A plot of ln R_g against 1000/T is shown in Figure 3. This test was performed at the flow rate of 8 SLPM and mole fraction of 5.05 %. The temperature ranged between 540 and 580 . All data are included in the chemical reaction dominant regime. The flow rate and oxygen inlet concentration were maintained at fixed ones during the test.

This graph has a slope of Ea/R = 25.58, Ea=212.7 kJ/mol within 0.53% of linearity error. As shown in this figure, the linearity of log R_g against 1000/T is very excellent and it means that the Arrhenius model has good agreement with the graphite oxidation rate. This result can be expressed by the following equation:

$$\frac{\partial(\ln R_g)}{\partial(1/T)} = -\frac{E_a(P_{O2})}{R} \tag{6}$$

Totally 33 cases of tests were carried out with different oxygen concentrations, flow rates and burn-offs. Figure 4 shows all the results of the experiment. In this graph, the x-axis represents oxygen concentration and y-axis activation energy. Each symbol represents a different sample number and flow rate condition. The following facts were obtained:

(1) Ea is 218.43± 3.76 kJ/mol within 95% level of confidence.
(2) Ea is not affected by oxygen concentration.
(3) Ea is not affected by the burn off rate.

3.1.2. *Comparisons of the experimental results with the previous works*

The activation energy of graphite oxidation has been studied by many other people as shown in Table 3. Our experimental result is very close to the one given by Fuller[1977], Kawakami[1984], Ogawa[1992]. The over-prediction seems to be caused by some in-pore diffusion regime data included in their analysis. Hino's[1991] result shows large discrepancies with others since his experiment was performed under the unsteady concentration condition.

Table 3. Comparison of experimental results (Ea)

Author	Temp ( )	Oxygen mole fraction	Flow rate (SLPM)	Test method	Ea (kJ/mol)
Fuller [2, 3]	450 ~ 750	0.2	0.496	TGA	201
Kawakami [6]	550 ~ 650	0.2	-	gas analysis	210
Hino [10]	650 ~ 900	0.013	0	TGA	324
Ogawa [4, 5]	700 ~1500	0.05 ~ 0.19	0.2~ 4.5	gas analysis	199.72
KAIST	540 ~ 630	0.03 ~ 3.2	7 ~ 18	gas analysis	218

* TGA : thermo gravimetric analysis

3.2. Order of reaction

3.2.1. Measurement of order of reaction

To measure the order of reaction, the experiment was performed with the temperature and flow rate maintained constantly. Figure 5 is a plot of ln R_g against 1000/T. The slope of this graph stands for the order of reaction. In this test, the resultant value is n=0.741 within 1.2 % of linearity error. We can see that the good linearity of ln R_g against ln P_{O2} is very excellent. This result can be expressed by the following equation:

$$\frac{\partial(\ln R_g)}{\partial(\ln P_{O2})} = -n(T)$$ (7)

Totally 66 cases of tests were carried out with different oxygen concentrations, flow rates and burn-offs. Figure 6 shows all the experiment results of activation energy. In this graph, the x-axis represents the test number and y-axis order of reaction. Each symbol stands for a different sample number and temperature condition. The following results are obtained from the above experiment:

(1) n is 0.75± 0.146 within 95% level of confidence.
(2) n is not affected by the burn off rate.

3.2.2. *Temperature dependency of n*

Temperature independency on the order of reaction is very important for modeling and predicting the graphite oxidation rate. However, it is difficult to be estimated experimentally because the graphite oxidation rate is affected by not only chemical reaction but also the mass transfer effect at high temperature. So in this section, we will prove the independency in the whole temperature range by the analytical approach.

Before starting, we can assume that the graphite oxidation follows the Arrehnius model in high temperature condition only if the sufficient oxygen is supplied. Figure 7 illustrates this assumption. As the mass transfer rate increase, the transition point increases. It is a very reasonable assumption with the intuition of an engineer.

From the result that the activation energy is not affected by oxygen concentration, we have the following relationship:

$$\frac{\partial(\ln R_g)}{\partial(1/T)} = -\frac{E_a}{R} \tag{6'}$$

Solving the above equation yields

$$\ln R_g = f(P_{O2}) - \frac{E_a}{R \cdot T} \tag{8}$$

Substituting Eq. (5) into Eq. (4), we can have

$$\frac{d(\ln R_g)}{d(\ln P_{O2})} = \frac{df(P_{O2})}{d(\ln P_{O2})} = n(T) \tag{9}$$

Solving this equation produces

$$f(P_{O2}) = n(T) \cdot \ln P_{O2} + C_1(T) \tag{10}$$

Then since $f(P_{O2})$ is not a function of temperature, Eq. (7) is written as

$$f(P_{O2}) = n \cdot \ln P_{O2} + C_1 \tag{10'}$$

Substituting the above equation into Eq. (3), we can have

$$\ln R_g = n \cdot \ln P_{O2} - \frac{E_a}{R \cdot T} + C_1 \tag{11}$$

$$R_g = A_0 \cdot e^{-\frac{Ea}{R \cdot T}} \cdot P_{O2}{}^n \tag{12}$$

Equation (12) is the same form as the Arrhenius equation. From Eq. (7), we can see that the

order of reaction is constant with temperature in the whole temperature range.
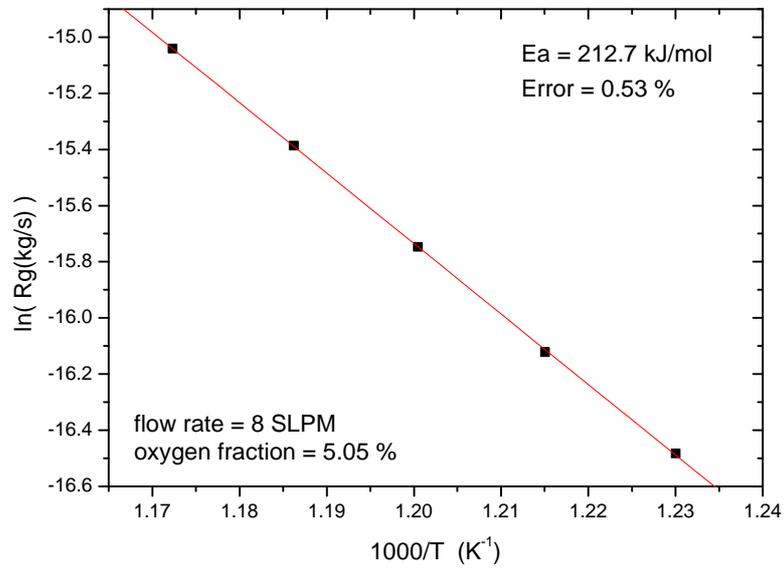

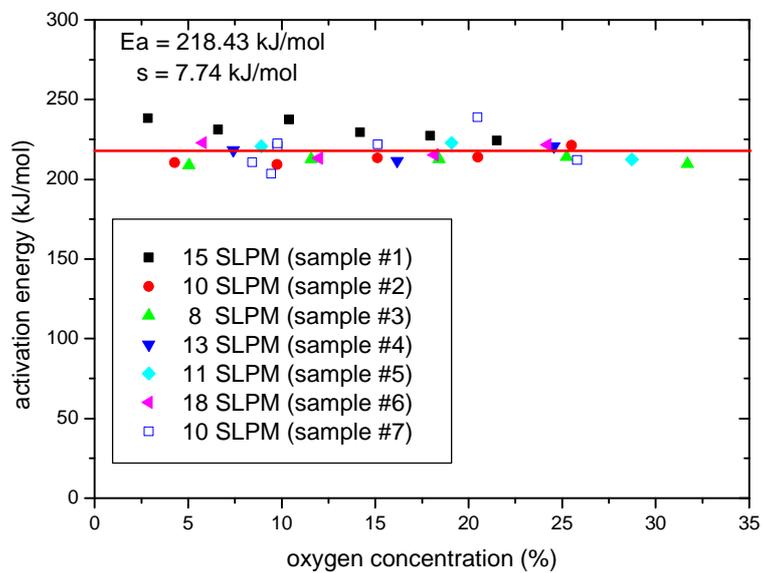Figure 3. Effect of temperature on the graphite oxidation

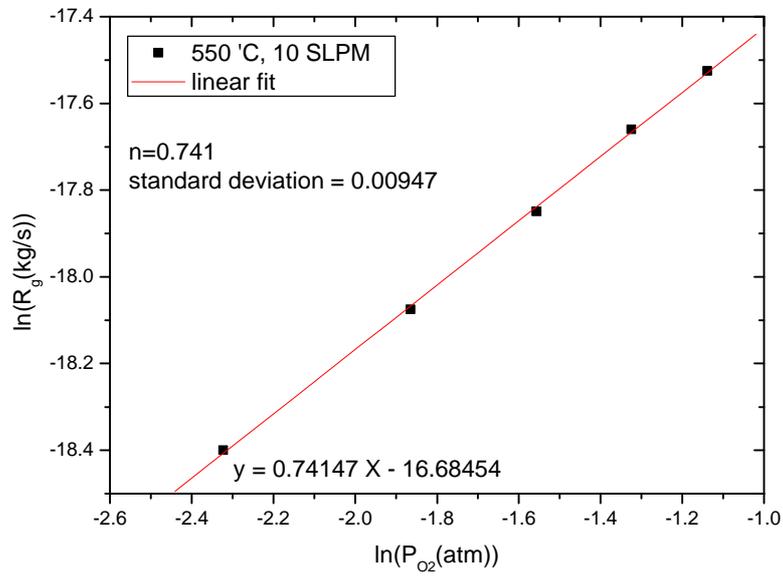

Figure 4. Activation energy (Ea) results of IG-110

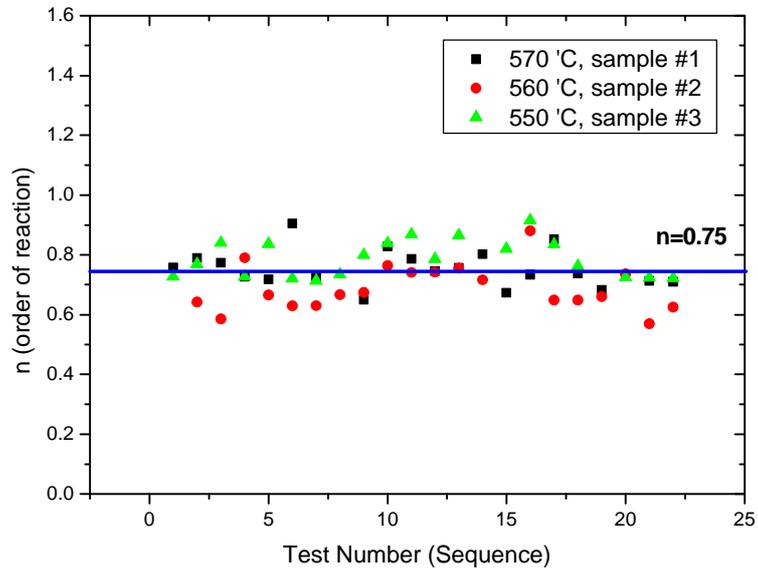Figure 5. Effect of Oxygen concentration on the graphite oxidation
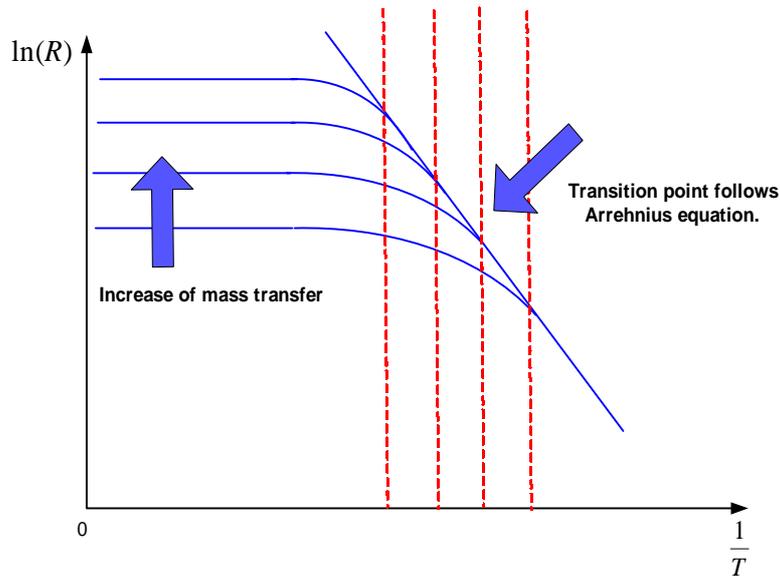

Figure 6. The order of reaction (n)

Figure 7. Transition point change with mass transfer increase

4. Conclusions

The measurements of Chemical behaviors of the nuclear graphite IG-110 were experimentally investigated for the chemical reaction dominant temperature regime. The main conclusions for our experiments are as follows:

(1) Graphite oxidation has good agreement with the Arrhenius model experimentally.
(2) 218.43±3.76 kJ/mol of activation energy was obtained within 95% level of confidence. And it was not affected by oxygen concentration, flow rate and burn off rate.
(3) 0.75±0.146 of the order of reaction was obtained within 95 % level of confidence. And it was not affected by oxygen concentration, flow rate and burn off rate.

To complete the graphite oxidation model, the following studies are required:

(1) the effect of moisture and geometry on the chemical reaction
(2) the effect of mass transfer on the graphite oxidation in mass transfer dominant regime

Nomenclature

R_g graphite oxidation rate (kg/s)
Mc molecular mass of carbon (0.012011 kg/mol)

$\dot{m}_{O2}$ mole flow rate of O2 (mole/s)

f_{O2} mole fraction of O2

f_{CO2} mole fraction of CO2

f_{CO} mole fraction of CO

T temperature (K)

P_{O2} oxygen pressure (atm)

E_a activation energy (kJ/mol)

n order of reaction

R gas constant

A_e reaction area (m^2)

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