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Letter to the Editor

Experimental study on the reaction between nuclear graphite IG-110 and carbon dioxide

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Abstract

With nuclear graphite IG-110, we measured various kinetic parameters and reaction rates of the C/CO_2 reaction. As a result, its activation energy is 295 ± 8 kJ/mol and the order of reaction is 0.9. It turns out that the rate of C/CO_2 reaction is much smaller than the rate of the C/O_2 reaction which is dominant in HTGR air-ingress below 1400 °C. Finally, we propose the following rate equation for the C/CO_2 reaction of IG-110:

$$r_{C\text{–}CO_2}(\mathrm{kg/m^3s}) = 3.95 \times 10^3 \cdot \exp\left(-\frac{290\,000}{R \cdot T}\right) \cdot (p_{CO_2})^{0.9}.$$

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1. Introduction

The graphite in high temperature gas cooled reactors reacts with various gases in accidents involving the air-ingress. Among these reactions, the most important is the oxidation reaction (C/O_2 reaction), which is caused by the oxygen gas in the environment. Until recently, many researchers have studied the reaction of C/O_2 [1–10] and obtained excellent results. However, relatively, little attention has been given to other reactions. The reaction of graphite and CO_2 gas (C/CO_2 reaction) is among those neglected reactions. The reaction of the C/CO_2 is written as follows:

$$C + CO_2 \rightarrow 2CO \tag{1}$$

This equation shows that the C/CO_2 reaction produces CO gas as a main product, which is known toxic. Furthermore, since this reaction can damage the structural integrity, investigation on this reaction is necessary for better analysis of the air-ingress.

2. Experiment

Fig. 1 shows our experimental facility. First, we obtained the reaction rate by analysis on the

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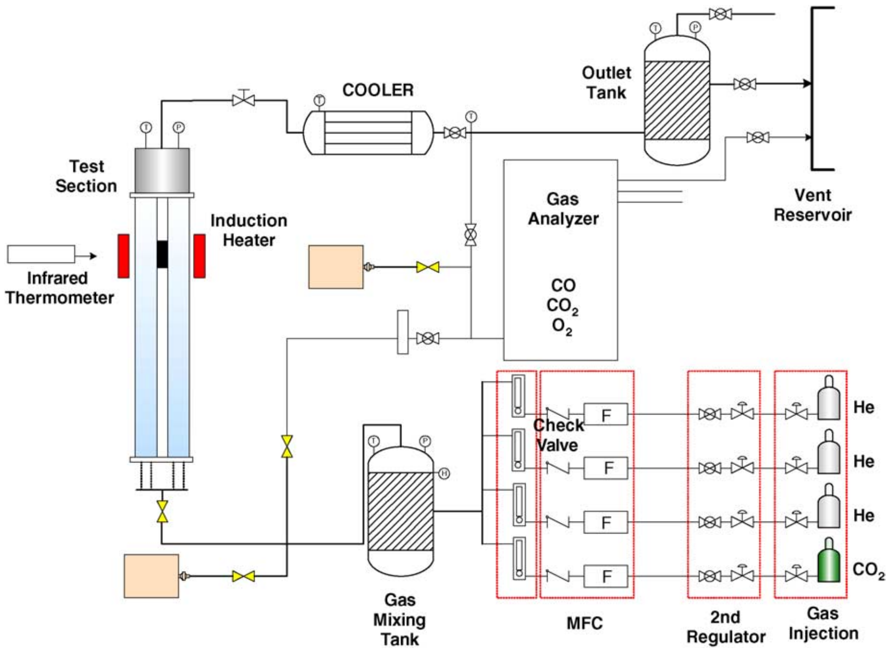

Fig. 1. Schematics of experimental facility.

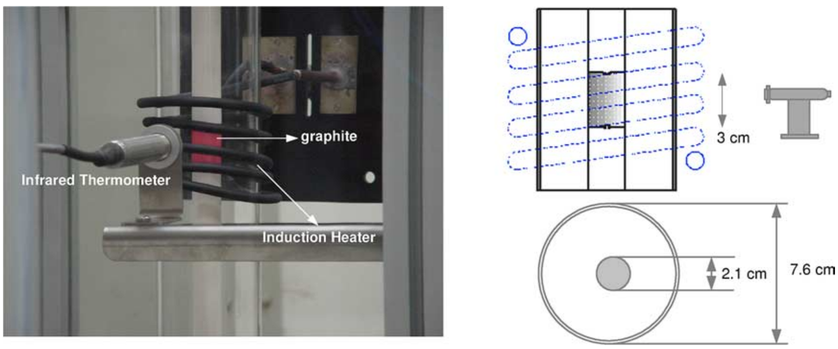

Fig. 2. Test-section.

concentrations of O_2, CO and CO_2 species. Fig. 2 shows the test section. The specimen was supported by a ceramic rod and heated by a induction heater. We then measured its surface temperature with an infrared thermometer. The test specimens made of IG-110 graphite, which is an isostatically molded, isotropic fine-grained and halogen purified, were machined to 2.1 cm in diameter and 3 cm in length. The mixture gas of helium and CO_2 was used as a reacting gas and injected at the bottom of the test section, which was made of a quartz tube. This experiment was conducted in the temperature range between 600 °C and 1400 °C, and in the mole fraction of CO_2 between 5% and 20%.

3. Results and discussion

To investigate the reaction of C/CO_2, we measured kinetic parameters: an activation energy (E_a) and an order of reaction (n). Fig. 3 illustrates the effect of temperature on the reaction rate. In this graph, which is generally called as Arrhenius plot, the x-axis represents 1000/T and y-axis represents the logarithm of the reaction rate. This figure shows a linear trend of the data between the two main parameters: 1000/T and a log of the reaction rates, and it confirms that the Arrhenius model is globally well representing the reaction of C/CO_2 in our conditions. The activation energy can be obtained

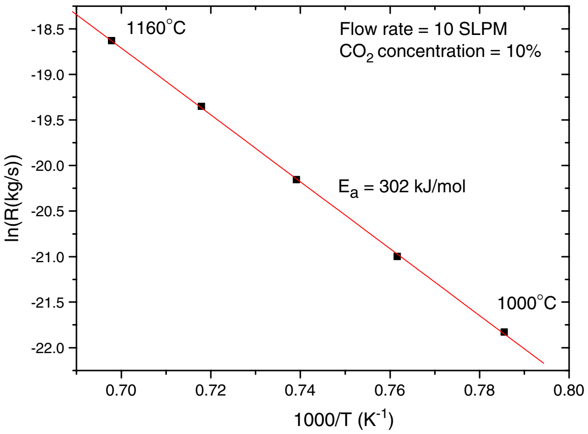

Fig. 3. Effect of temperature on reaction rate.

from the slope of this graph and we repeated the same tests seven times for more confidence. By applying a statistical method, we determined the value of activation energy as 295 ± 8 kJ/mol within 95% confidence level. Although we tried to measure the reaction from 600 °C, we could not detect it below 1000 °C due to its slow rate of reaction. Fig. 4 illustrates the rates of reaction at the temperature between 1000 °C and 1400 °C at the mole fraction of CO_2 between 5% and 15%. This figure shows that the effect of CO_2 concentration is much smaller than the effect of temperature. On the basis of the experimental data, the value of the order of reaction was calculated as 0.9. Fig. 4 also shows that there is no transition in the reaction rate data, and it confirms that the rate of the C/CO_2 reaction is not affected by mass diffusion in our experimental conditions. We expect that the mass diffusion effect would occur at a higher temperature.

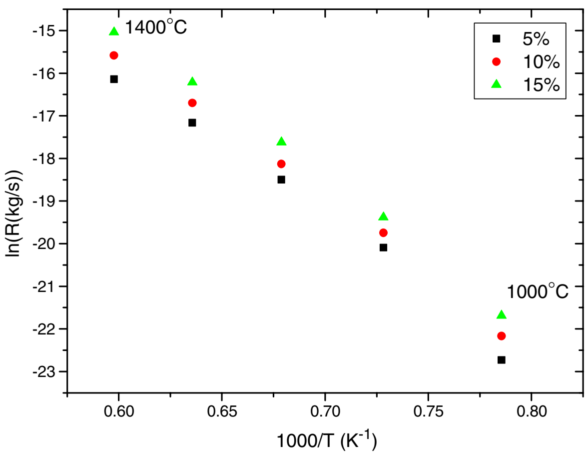

Fig. 4. Reaction rate of C/CO_2.

Fig. 5 compares the rates of reactions between the C/CO_2 and the C/O_2, which is the dominant reaction in HTGR air-ingress. For this comparison, we measured the rates of the C/O_2 reaction with the same method as the C/CO_2 reaction. The experimental temperature ranged between 700 °C and 1500 °C, and the CO_2 mole fraction was 2.5–20%. This figure shows that the rate of the C/CO_2 reaction is much smaller than the rate of the C/O_2 reaction. The differences between them are very large at low temperature, but the differences are reduced as the temperature increases due to the limitation of the C/O_2 reaction by mass diffusion effect. Based on the trend of Fig. 5, we deduces that both of the reaction rates would be comparable around 2000 °C. To quantitatively compare the rates of the two reactions, the following value was calculated from experimental data:

$$f(\%) = \frac{R_{C\text{–}CO_2}}{R_{C\text{–}O_2}} \times 100, \tag{2}$$

where f is a relative percentage of C/CO_2 reaction compared to the C/O_2 reaction, and $R_{C\text{–}CO_2}$ and $R_{C\text{–}O_2}$ are the rates of C/CO_2 and C/O_2 reaction, respectively. Fig. 6 shows the f value versus temperature. In our experimental conditions, the rate of the C/CO_2 reaction was less than 3% of the C/O_2 reaction. It means that the reaction of C/CO_2 reaction is generally negligible in the reactions between graphite and gases. However, for the special situation where the portion of O_2 gas is very small, on the basis of our experimental data, we propose the following rate equation:

$$r_{C\text{–}CO_2}(\mathrm{kg/m^3 s}) = 3.95 \times 10^3 \cdot \exp\left(-\frac{290000}{R \cdot T}\right) \cdot (p_{CO_2})^{0.9}, \tag{3}$$

where r_g is a volumetric rate of C/CO_2 reaction, R is a gas constant, T is temperature (K), and p_{CO_2} is a partial pressure (Pa) of CO_2. Since the IG-110 graphite has a lot of pores in the inside and the effect of inside reaction is more dominant than the external surface reaction, the correlation for C/CO_2 reaction can be expressed by a volumetric reaction as in Eq. (3) when the rate of reaction is slow enough. This equation is a general type of Arrhenius equation and it agrees well with our experimental data with RMS error of ±5%.

To investigate the effect of degree of burn-off, thermo-gravimetric analysis (TGA) test was

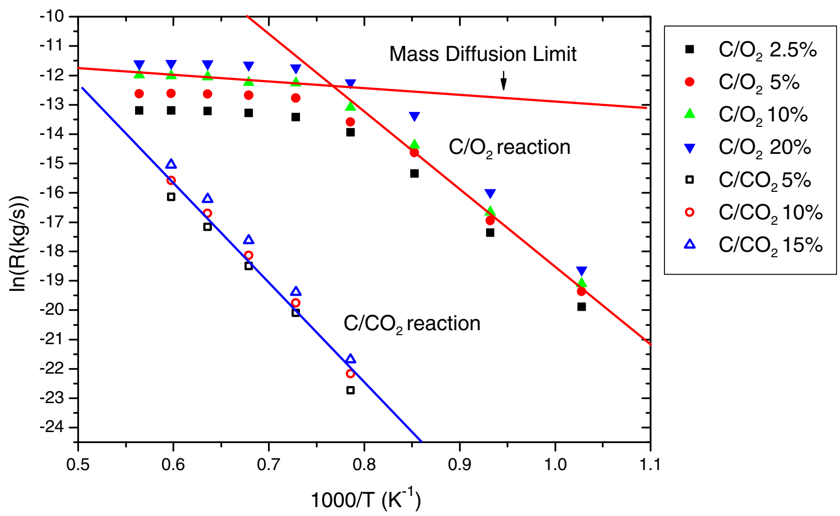

Fig. 5. Comparisons between C/CO_2 reaction and C/O_2 reaction.

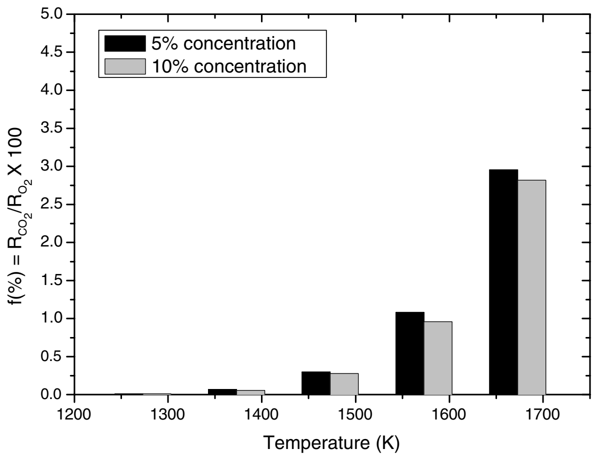

Fig. 6. Comparison between C/CO_2 reaction and C/O_2 reaction.

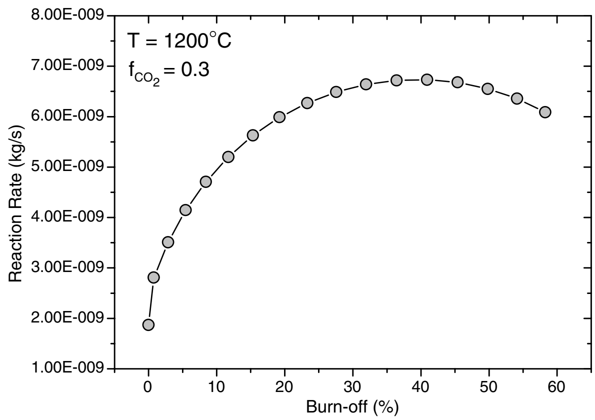

Fig. 7. Changes of the reaction rate with degree of burn-off.

performed at 1200 °C with initial mass of 39.59 mg. The result is illustrated in Fig. 7. As shown in this figure, the rate of reaction increases with degree of burn-off, and after passing through the maximum, the rates decline. The maximum rate was observed at the burn-off degree of 35–40%. This pattern is very similar to that of C/O_2 reaction reported by Fuller and Okoh [5]. It deduces that the similarity exist also in the changes of internal structure with burn-off between C/O_2 and C/CO_2 reactions. The rate equation for C/CO_2, Eq. (3) was obtained for the induction period, and it represents only initial reaction rate. Therefore, for better prediction in the wide ranges of burn-off, more researches are required.

4. Summary and conclusions

In this experiment, we measured various kinetic parameters and reaction rates for the C/CO_2 reaction. The activation energy is 295 ± 8 kJ/mol and the order of reaction is 0.9. As the C/CO_2 reaction is much smaller than the C/O_2 reaction when the temperature is lower than 1400 °C, the effect of C/CO_2 reaction is negligible when both of the reactions occur at the same time below the graphite temperature of 1400 °C. As temperature increases, the differences between them reduced due to the mass diffusion effect of the C/O_2 reaction. On the basis of the trend, we deduced that the reaction of C/CO_2 would be comparable to the reaction of

C/O_2 around 2000 °C. Finally, we propose the following rate equation:

$$r_{C\text{–}CO_2}(\mathrm{kg/m^3s}) = 3.95 \times 10^3 \cdot \exp\left(-\frac{290000}{R \cdot T}\right) \cdot (p_{CO_2})^{0.9}.$$

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