

Oxidation Behavior of Fine-Grained Isotropic Nuclear Graphites

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1. Introduction

In high temperature gas-cooled reactors (HTGRs), graphite has been widely used as a moderator, reflector and fuel block for its excellent moderating power, mechanical properties and machinability. The graphite structures may be oxidized due to oxygens from the leakage in the heat-exchanger tube and graphite outgassing [1]. Therefore, the oxidation of graphite is very important for analyzing the safety of the reactors and assessing the operational life of core structures. All the nuclear graphites are being manufactured from the two kinds of cokes, i.e., petroleum and coal-tar pitch coke, and the impurity levels are different among the fuel block, reflector and supporting structure so that the type of coke and level of impurity should be considered to analyze the oxidation behavior of nuclear graphite [2]. In this study, to investigate the effects of coke types and impurity levels on the oxidation behavior, the thermogravimetric experiments were performed on three kinds of fine-grained isotropic nuclear graphites.

2. Experimental

Three kinds of fine-grained isotropic nuclear graphites, IG-11, IG-110 and IG-430 made by Toyo Tanso, were used for this study. The IG-11 and 110 are made of petroleum cokes, and the IG-430 is made of coal-tar pitch cokes. Typical properties of the materials are summarized in Table 1. The IG-110 is manufactured adding the halogen treatment process to the IG-11 to decrease the impurities such as Na, K, Ca, Cu, Ti, Fe, Mo, Cr, Co, Ni and V, however the properties of IG-11 and IG-110 are nearly the same except for ash contents. The sample size was $5 \times 5 \times 10 \text{mm}^3$ for oxidation tests.

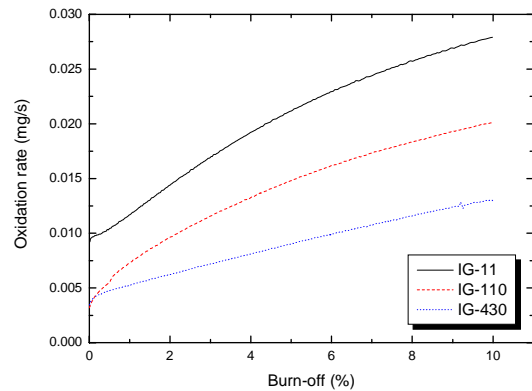
Table 1 Typical properties of IG-11, IG-110 and IG-430

Grade	IG-11 (IG-110)	IG-430
Coke	petroleum	coal-tar
Avg. grain size(μm)	20	10
Porosity(%)	18	14
Apparent density(g/cm^3)	1.77	1.82
Anisotropic ratio	1.10	1.09
Ash content	< 0.1% (<10ppm)	< 10ppm
Impurity (ppm)	0.001-0.1	0.001-0.1

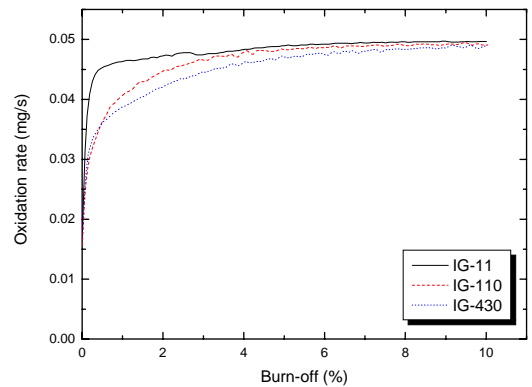
The thermogravimetric analysis experiments were performed using the TG-SDTA 851 model thermobalancer from the Mettler Company. The oxidation temperatures were selected as 750 and 900°C to oxidize the samples in the in-pore diffusion

controlled regime and the boundary layer controlled regime, respectively [3]. The oxidant was ambient air with a flow rate of 60ml/min. After the specimen was placed in the thermobalancer, the nitrogen was used to sweep the specimen at a flow rate of 20ml/min at 25°C for one hour. Then, the specimen was heated at a heating rate of 10°C/min from 25°C to the oxidation test temperature in nitrogen.

3. Results and discussion



(a) 750°C



(b) 900°C

Fig. 1 Variation of oxidation rates at (a) 700 and (b) 900°C as a function of burn-off.

Fig. 1 shows the variation of oxidation rates at 750 and 900°C as a function of burn-off, respectively. At 750°C, the oxidation rates increase gradually with burn-off and vary with the graphite grade while, at 900°C, the oxidation rates remain nearly constant level

regardless of the grade above the 5% burn-off.

It is well known that the oxidation reaction at 750°C of in-pore diffusion controlled regime is slow and partially bulky that the oxidation in this regime may be affected by the density, porosity, impurity level and microstructure of the graphite [2]. The increase of the oxidation rate with a burn-off may be attributed to the increase in the additional fresh surfaces which are believed to be resulted from the opening of closed pores at the interior [4].

At 900°C of boundary layer controlled regime, it is known that the chemical reactivity is so high that all the oxidizing gases react at the exterior free surface irrespective of the interior microstructure. Thus, the oxidation in this regime is considered to be insensitive to the type of coke and the level of impurity [5].

As seen in Fig. 1 (a), the oxidation rate of IG-11 at 750°C is about 50% higher than that of highly purified IG-110. From this result, it is understood that the impurities in IG-11 catalyze the oxygen-carbon reaction and thus enhance the oxidation rate compared to the purified IG-110 [3, 6]. It was also observed in Fig.1 (a) that although IG-110 and IG-430 are both high purity, isotatically molded, isotropic, fine-grained nuclear-grade graphites, the oxidation rate is higher in IG-110 than IG-430. Part of the reason for the difference may be attributed to the higher porosity of IG-110 (18%) than IG-430 (14%).

3. Conclusion

(1) At 750°C, IG-11 shows a higher oxidation rate than IG-110 possibly due to the higher content of impurity in IG-11.

(2) Part of the reason for the higher oxidation rate of IG-110 than IG-430 may be attributed to its higher porosity than IG-430.

(2) At 900°C, the oxidation rates were nearly the same in all the graphites since the oxidation reaction occurs at the exterior free surface irrespective of the interior microstructure.

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