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Change of properties after oxidation of IG-11 graphite by air and CO_2 gas

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Abstract

Artificial graphite is typically manufactured by carbonization of a shaped body of a kneaded mixture using granular cokes as a filler and pitch as a binder. It undergoes a pitch impregnation process if necessary and finally applying graphitization heat treatment. The effect of thermal oxidation in air or a CO_2 atmosphere on IG-11 graphite samples is investigated in this study. The results show a localized oxidation process that progressively reveals the large coke particles with increasing level of overall weight loss in air. The surface of the graphite was peeled off and no change was found in the specific gravity after air oxidation. However, the specific gravity of graphite was continuously decreased by CO_2 oxidation. The decrease in the specific gravity by CO_2 oxidation was due to CO_2 gas that progressed from the surface to the interior. The pore shape after CO_2 oxidation differed from that under air oxidation.

1. Introduction

Polycrystalline graphite is widely used in reactors, especially in the very-high-temperature gas-cooled reactors (VHTR) because of its excellent nuclear properties (excellent solid moderator and good irradiation performance), high thermal conductivity, good mechanical properties at high temperatures, good machining characteristics, good corrosion resistance and a mature manufacturing process [1]. Nuclear graphite is very high in chemical purity to avoid absorption of low energy neutrons and activation of the impurities [2]. High-dimensional stability is also required for nuclear graphite to withstand the both the high temperatures and the high flux of neutrons [3]. On the negative side, during operation, fast neutron irradiation and radiolytic oxidation produce dimensional and material property changes that can generate significant component stresses, and promote cracking and damage accumulation, and which can lead ultimately to failure [4].

The graphite in VHTR reacts with various gases in accidents involving air-ingress. Among these reactions, the most important is known as oxidation reactions, which are caused by the oxygen gas in the environment [5]. Reactions of graphite with the oxygen in air, carbon dioxide, water vapor and hydrogen have been studied in detail [6].

(1) $C\ (Graphite) + O_2\ (g) \leftrightarrow CO_2\ (g)$: $\Delta H = -394.4$ kJ/mol
(2) $C\ (Graphite) + CO_2\ (g) \leftrightarrow 2CO\ (g)$: $\Delta H = 171.5$ kJ/mol
(3) $C\ (Graphite) + H_2O\ (g) \leftrightarrow CO\ (g) + H_2\ (g)$: $\Delta H = 135.6$ kJ/mol
(4) $C\ (Graphite) + 2H_2\ (g) \leftrightarrow CH_4\ (g)$: $\Delta H = -88.6$ kJ/mol

These reactions may be chemical or diffusion in nature, or may be both, in varying degrees. Although air is mentioned as the reactant, it is the reaction with oxygen that is dominant, compared to carbon dioxide and steam [6]. According to Su and Perlmuter [7], this effect is attributable to an initial increase in the reaction-surface area as the pore

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walls gasify. Later, the pore walls grow larger and join each other and the surface area decreases.

The oxidation of graphite at different temperatures is controlled by three mechanisms: the chemical mechanism at temperatures below 500 °C, the in-pore diffusion-controlled mechanism at temperatures between 500 and 900 °C and the boundary-layer controlled mechanism at temperatures over 900 °C [1,8]. First, a reaction between graphite and oxygen occurs very slowly at a low temperature. The concentration of oxygen and the resulting oxidation are nearly uniform through the depth of the penetration in this region. The oxidation rate is solely controlled by chemical reactivity in this region [1,8]. Second, the in-pore diffusion-controlled region is between the chemical region and boundary-layer controlled region. The oxidation rate is controlled by a combination of these two regions. The concentration of oxygen and the burn-off of the graphite block vary exponentially in depth [1,8]. Third, the chemical reactivity is high enough for oxygen to react at the surface of the hot graphite body. The oxygen attacks the exterior surface of the graphite block and changes the geometry of the graphite body without damaging the interior [1,8].

Carbon dioxide gas adsorbs on the graphite surface at high temperatures. The adsorbed gas creates the oxygen-containing compound C=O on the surface of the graphite and evolves the CO gas. The reaction of the C/CO_2 is written as follows: $C + CO_2 \rightarrow 2CO$. The oxygen-containing compounds changes CO gas continuously on the surface of graphite. As a result, the repeated gasification reactions by CO_2 create the oxidation of graphite.

2. Experimental

2.1. Properties of IG-11 graphite

The main parameters of the graphite IG-11 used in this research are listed in Table 1. The nuclear graphite IG-11 was produced by Toyo Tanso Co. Ltd., Japan. The IG-11 graphite was quasi-isotropic fine-grained nuclear graphite produced using the cold isostatic press method. The typical impurities of IG-11 nuclear grade graphite are given in Table 2. The main impurities that existed are given in ppm (weight based) units of Ti, V, Al, Fe, Si, and B.

Table 1
Typical physical properties of the IG-11 nuclear grade graphite

Property	Value
Bulk density (g/cm^3)	1.77
Electrical resistivity (μΩ m)	11
Flexural strength (MPa)	39
C.T.E. (10^{-6}/°C)	4.6
Comp. strength (MPa)	78
Porosity (%)	18
Total ash (ppm, weight based)	<20
Ave. grain size (μm)	10

2.2. Oxidative conditions and measurement of the fracture properties of the oxidative graphite

Oxidation by air and CO_2 oxidations of the as-received IG-11 nuclear grade graphite were performed in a muffle furnace under a natural state of air and in a tube furnace under a stream with CO_2 of 900 cc/min. The samples were heated at 10 °C/min from room temperature to maximum heat treatment temperatures in the range of 500–1100 °C.

The strengths of all IG-11 graphite specimens ($W20 \times H10 \times L80$ mm) were measured using a three-point flexural test method with the Instron 4204 device (Instron Co., USA). The samples were tested at a constant crosshead displacement rate of 0.5 mm/min. For the specimens the distance between the support points was 60 mm.

Microstructures of the as-received IG-11 nuclear graphite and oxidized graphite were observed by SEM (Model: S-200, Hitachi Co., Japan). The specific gravity of the specimens was measured by an electro-densimeter (Mirage Co., Ltd., Japan).

3. Results and discussion

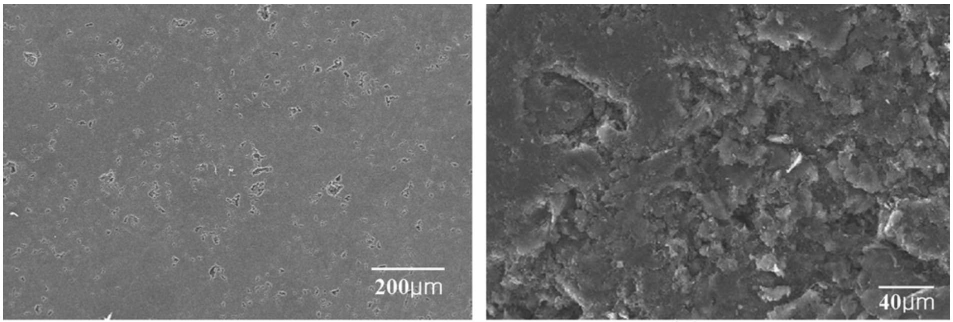
3.1. Changes in the microstructures before and after oxidation of the IG-11 nuclear grade graphite

The surface of the as-received graphite IG-11 is shown in Fig. 1. Many pores are observable in the surface of the IG-11 graphite (Fig. 1(a)). From the microstructures of Fig. 1(b), IG-11 graphite confirmed that petroleum pitch was used as a binder as the edges of the binder phase were round in shape.

Figs. 2 and 3 show SEM micrographs of the oxidized surface structures from the air and CO_2 oxidations, respectively. The micrograph reveals that the as-received graphite has a fairly smooth surface shown in Fig. 1(a). On the other hand, oxidized graphite has a very rough surface shown in Figs. 2 and 3, indicating that the cokes used are revealed from the interior. By increasing oxidation temperatures and holding times, the cokes particles are revealed in the surfaces of the oxidized graphite. This phenomenon shows the differences in microstructures made from cokes and binder pitch after the graphitization temperature treatment during the manufacturing process.

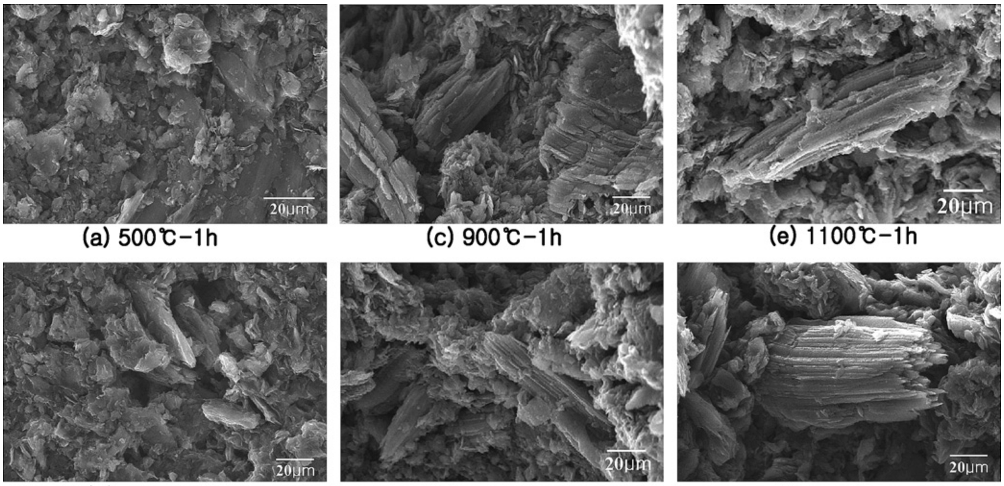
Table 2
Typical impurity of IG-11 nuclear grade graphite

Impurity	B	Na	Al	Si	K	Ca	Ti	V	Cr	Mn	Fe	Cu	Ni
ppm (wt)	1.4	<0.05	0.08	0.70	<0.10	0.04	0.60	0.23	<0.07	<0.03	0.07	<0.08	<0.10



(a) (b)

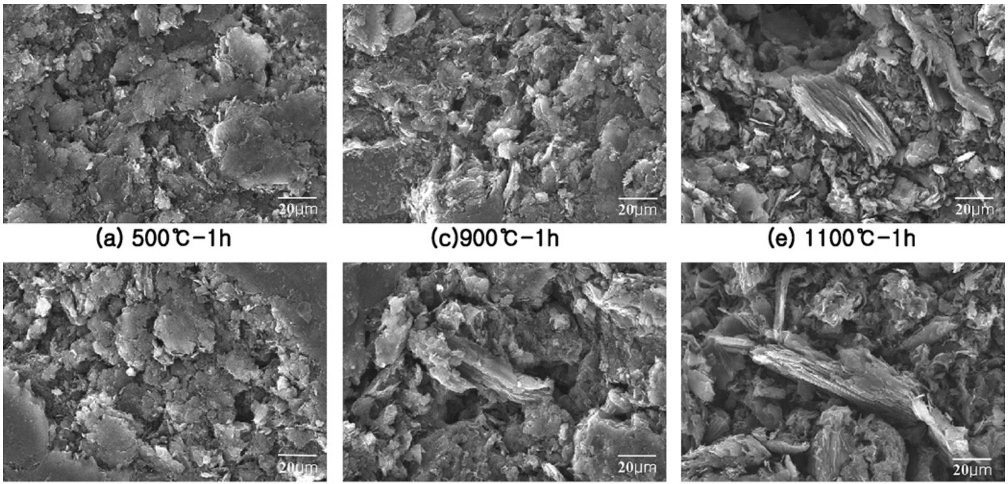
Fig. 1. SEM micrographs of the IG-11 graphite surface (a) low magnification and (b) high magnification.



(a) 500℃-1h (c) 900℃-1h (e) 1100℃-1h

(b) 500℃-3h (d) 900℃-3h (f) 1100℃-3h

Fig. 2. SEM micrographs of air-oxidized IG-11 graphite.



(a) 500℃-1h (c)900℃-1h (e) 1100℃-1h

(b) 500℃-3h (d) 900℃-3h (f) 1100℃-3h

Fig. 3. SEM micrographs of CO_2-oxidized IG-11 graphite.

The graphite structures made from cokes have higher oxidation resistance than that of graphite structures made from binder pitch after an oxidation process. The differences in the microstructures in the micrographs showed the oxidation resistance distinction after the oxidation processes.

3.2. Changes in the weight and specific gravity after oxidation of the IG-11 nuclear grade graphite

Fig. 4 shows the changes in the shape of the IG-11 graphite. Severe shape changes were observed after air oxidation in a range of 900–1100 °C. The corners of the

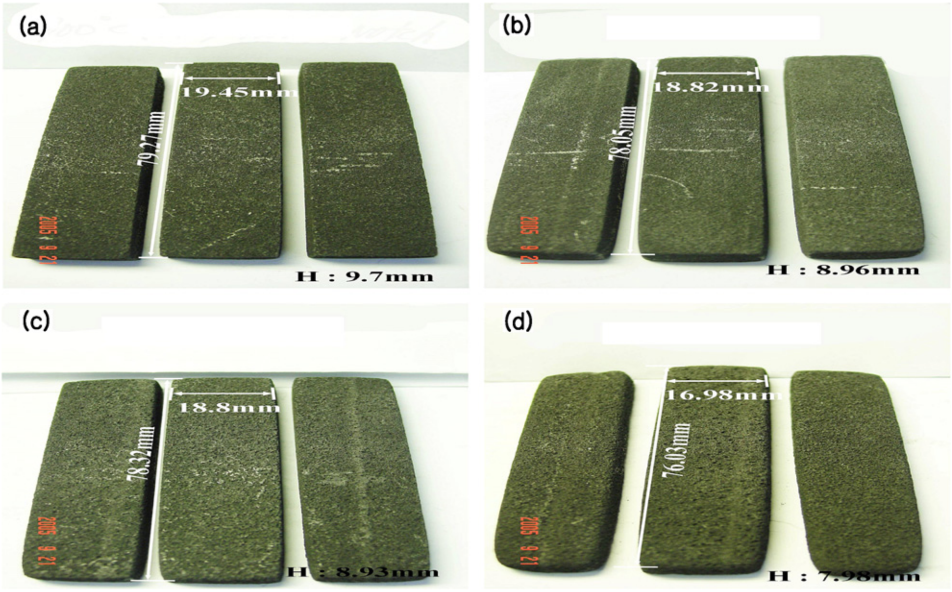


Fig. 4. Changes in shape after air oxidation (a) 900 °C for 1 h (b) 900 °C for 3 h (c) 1100 °C for 1 h and (d) 1100 °C for 3 h.

oxidized graphite were rounded through this process shown in Figs. 4(b)–(d). At high temperatures, the chemical reactivity is sufficiently high for all of the oxygen gases to react at the surface of the hot graphite body. The concentration of oxygen varies greatly at the graphite surface [8]. Many cratered-like pores were created after air oxidation on the surface. Fig. 5(a) shows the original shape along with the dimensions. However, no changes in shape occurred after CO_2 oxidation shown in Fig. 5(b).

The changes in the weight and specific gravity after air oxidation are shown in Table 3. During the air oxidation, the weight reduction was 10.9% and 46.0% at the 900 °C for 1 h and 1100 °C for 3 h, respectively. However, the specific gravities were not changed after air oxidation compared with the specific gravity of the as-received graphite. Therefore, from these facts, oxidation was limited at the graphite surface as a result of the air oxidation. In contrast, nearly no change in the reductions of weight and specific gravity were observed with CO_2 oxidation at 900 °C (Table 4). Reductions in the weight and specific gravity occurred simultaneously, however, at 1100 °C. During CO_2 oxidation, a weight reduction of 2.5% and 10.7% at 1100 °C for 1 h and 1100 °C for 3 h, respectively, was noted. More-

Table 3
Weight and specific gravity changes after air oxidation

Sample	Weight change (g)			Specific gravity (g/cm^3)		
	Before	After	Ratio (%)	Before	After	Ratio (%)
900 °C/1 h	28.59	25.47	−10.91	1.81	1.84	0.02
900 °C/3 h	28.42	21.37	−24.81	1.79	1.87	0.04
1100 °C/1 h	28.30	21.53	−23.93	1.79	1.82	0.02
1100 °C/3 h	28.47	15.37	−46.02	1.80	1.81	0.01

Table 4
Weight and specific gravity changes after CO_2 oxidation

Sample	Weight change (g)			Specific gravity (g/cm^3)		
	Before	After	Ratio (%)	Before	After	Ratio (%)
900 °C/1 h	28.38	28.36	−0.07	1.79	1.79	0.00
900 °C/3 h	28.54	28.49	−0.18	1.80	1.80	0.00
1100 °C/1 h	28.53	27.82	−2.49	1.80	1.77	−1.67
1100 °C/3 h	28.39	25.35	−10.71	1.79	1.73	−3.35

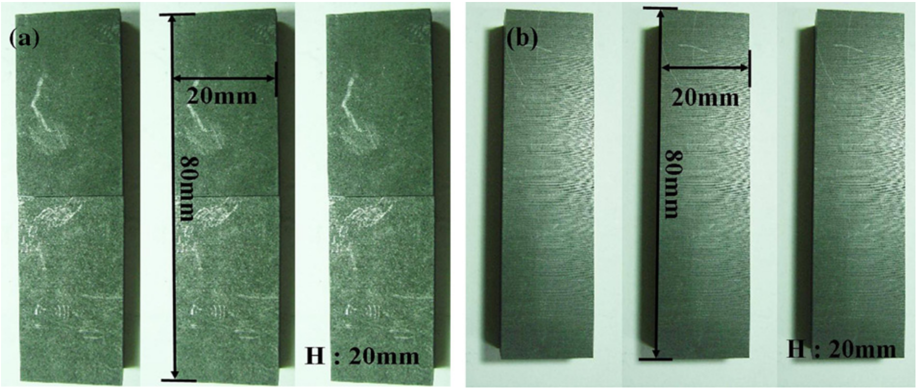


Fig. 5. Changes in shape after CO_2 oxidation (a) before oxidation and (b) after oxidation.

over, a reduction was noted in the specific gravity of 1.67% and 3.35% at 1100 °C for 1 h and 1100 °C for 3 h, respectively. This implies that weight and specific gravity changes occurred although the volume was not changed after the CO_2 oxidation. Thus, the interior of the graphite was oxidized under the CO_2 oxidation, in particular, as compared with the oxidization of the surface by air oxidation.

Fig. 6 shows the interior of the CO_2 oxidized graphite. The interior pore sizes are shown to be larger than those at the mouth of the pore are (Fig. 6(a)). CO_2 gas as an oxidant was attacked the interior of the graphite rather than the surface. The oxygen in the air may not have penetrated into the interior of the graphite due to the chemical reactivity with air at the surface of the hot graphite body. CO_2 gas has sufficient mobility in the porous structure of graphite to penetrate deeply inside the body, at temperatures where oxygen is all consumed in a surface limited reaction because of its higher reactivity. Fig. 6(b) shows that the oxidizing attack by CO_2 is severe at the interior of the graphite block and changes the geometry of the graphite body without damaging the material at the exterior.

3.3. Changes in the bending strength after the oxidation of the IG-11 nuclear grade graphite

Comparing the results of the three-point bending test, the strength of the oxidized graphite samples by both oxidation types was reduced severely at high temperatures. The measuring of the strengths was very difficult for the air oxidation sample at 1100 °C due to the severe change in the shape of the specimen. After air oxidation, the strengths were reduced more than in the case with CO_2 oxidation under the same conditions. Oxidation temperatures were also more important than oxidation times in both oxidation cases. During air oxidation, the strengths were reduced continuously, while almost no change occurred through CO_2 oxidation at 500 °C. Comparing the as-received sample and a sample that underwent oxidation at temperatures over 1100 °C in air, the specimen with oxidation at temperatures over 1100 °C would break as easily as a cookie. However, changes in the specific gravity after oxidation showed different results as shown in Table 5.

Table 5
Change of weight, bending strength, and specific gravity of the IG-11 graphite

Condition		Weight change (%)		Bending strength (MPa)		Specific gravity change (%)	
		Air	CO_2	Air	CO_2	Air	CO_2
As-received		0	0	39.2	39.2	0	0
Oxidation	500 °C/1 h	−0.11	−0.01	36.7	37.2	0.34	0.00
	500 °C/3 h	−0.22	0.00	24.5	35.7	4.47	0.00
	900 °C/1 h	−10.28	−0.00	27.1	35.2	1.10	0.00
	900 °C/3 h	−23.30	−0.56	20.1	35.1	4.47	−0.56
	1100 °C/1 h	−22.04	−2.55	17.4	27.1	1.68	−1.67
	1100 °C/3 h	−41.98	−10.91	11.5	14.0	0.56	−2.79

Almost no change in the specific gravity was shown as a result of air oxidation. However, the specific gravity greatly changed after CO_2 oxidation. As mentioned early, the differences in the shape change and pores formation after the oxidations led to this phenomenon. Specifically, the surface oxidation occurred with the air oxidation due to the change in the shape of the graphite specimen. However, the pores were created in the interior rather than on the surface without changing the shape of the graphite specimen shape in the CO_2 oxidation.

4. Conclusions

The shapes and weight of graphite samples were severe changed from air oxidation. However, oxidation indications were not shown on the surface of specimens after CO_2 oxidation. Therefore, the shape of samples was no changed from CO_2 oxidation. Weight changes of CO_2 oxidation in the graphite samples have shown the little rather than air oxidation. The graphite microstructures transformed from the binding pitch showed the oxidation first compared to the graphite structure transformed from cokes in the air oxidation process. The oxidized graphite formed a C=O functional group after air oxidation.

The bending strengths were reduced up to 52% after air oxidation at 1100 °C for 3 h. No change in the weight was shown, but the bending strengths were reduced by nearly

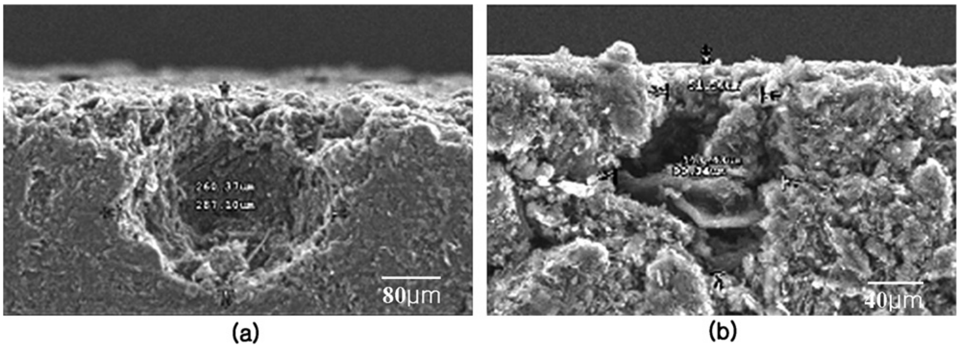


Fig. 6. Pore shape created by oxidation after CO_2 oxidation (side view).

6% after oxidation at 900 °C. The bending strengths were greatly reduced after CO_2 oxidation at 1100 °C for 3 h. The weight changes with CO_2 oxidation at 1100 °C for 3 h were very similar to those that occurred with air oxidation at 900 °C for 1 h. A reduction in strength of 63% in CO_2 oxidation as compared with the reduction with air oxidation of 25% was observed. Thus, the weight reduction resulted from the surface peeling in the air oxidation. The oxygen in the air may not have penetrated into the interior of graphite. However, CO_2 gas has sufficient mobility in the porous structure of graphite to penetrate deeply inside the body, at temperatures where oxygen is all consumed in a surface limited reaction. The oxidation was created from the interior of the graphite hence the weight change for the graphite was relatively small, but the strength of the graphite was reduced greatly via CO_2 oxidation.

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