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A study of the relationship between microstructure and oxidation effects in nuclear graphite at very high temperatures

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HIGHLIGHTS

- Oxidation rate of IG-110 and IG-430 in air and helium at temperatures ranging from 700 to 1600 °C determined.
- Significant increases in oxidation rate observed at temperature higher than 1200 °C.
- Post-oxidation surface morphology assessed by scanning electron microscopy.
- Percentage volume reduction of filler particles quantified.
- Discussion of possible intrinsic factors influencing nuclear graphite oxidation.

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ABSTRACT

Graphite is used in the cores of gas-cooled reactors as both the neutron moderator and a structural material, and traditional and novel graphite materials are being studied worldwide for applications in Generation IV reactors. In this study, the oxidation characteristics of petroleum-based IG-110 and pitch-based IG-430 graphite pellets in helium and air environments at temperatures ranging from 700 to 1600 °C were investigated. The oxidation rates and activation energies were determined based on mass loss measurements in a series of oxidation tests. The surface morphology was characterized by scanning electron microscopy. Although the thermal oxidation mechanism was previously considered to be the same for all temperatures higher than 1000 °C, the significant increases in oxidation rate observed at very high temperatures suggest that the oxidation behavior of the selected graphite materials at temperatures higher than 1200 °C is different. This work demonstrates that changes in surface morphology and in oxidation rate of the filler particles in the graphite materials are more prominent at temperatures above 1200 °C. Furthermore, possible intrinsic factors contributing to the oxidation of the two graphite materials at different temperature ranges are discussed taking account of the dominant role played by temperature.

1. Introduction

Most nuclear reactors currently in operation are Generation II or III reactors. To improve the safety and energy conversion efficiency of nuclear reactors, intensive research efforts are being devoted to Generation IV nuclear systems. Amongst Generation IV nuclear reactor designs, the Very High-Temperature Gas-Cooled Reactors (VHTRs) are attracting significant commercial interest. VHTRs have drawn considerable attention because of their high operating temperature (900 °C) and electricity generating efficiency (>45%), improved safety and redundancy, low environmental impact and fuel consumption, less radioactive waste, more compact components and other external benefits [1].

In a VHTR, nuclear-grade graphite is used as the moderator and as a structural material and it will be exposed to a reactor grade helium environment at high temperatures ranging from 600 to 1100 °C. This helium environment is highly inert and is essential in order to prevent the oxidation of graphite and metallic structures.

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However, trace amounts of impurities, such as oxygen and water vapor, which are inevitably present in reactor grade helium, are expected to influence graphite oxidation during normal operations of VHTRs [2]. In addition, during a severe loss-of-coolant accident (LOCA), the fuel temperature in a VHTR is likely to reach 1600 °C [3] and atmospheric air may ingress into the reactor core. Graphite exposed to an oxygen-rich environment, is bound to immediately experience serious oxidation at high temperatures. Therefore, a comprehensive investigation of the oxidation mechanisms of graphite in various gaseous environments at elevated temperatures is essential for reliable predictions of graphite behavior under such conditions [4].

Numerous studies have shown the existence of three regimes of graphite oxidation based on temperature: Regime I chemical (<550 °C), Regime II in-pore diffusion (550–800 °C) and Regime III boundary layer or mass transport (>800 °C) [14]. In addition, oxidation kinetics and associated temperature effects for artificial graphite at temperature ranges between 600 and 2500 °C have been reviewed, mainly by Okada & Ikegawa [5] and Ong [6]. Graphite materials undergo the following three main oxidation processes [5–7]:

Graphite oxidation reaction

$$C + aO_2 \rightarrow bCO + cCO_2 \quad (1)$$

Boudouard reaction

$$C + CO_2 \rightarrow 2CO \quad (2)$$

CO combustion reaction

$$2CO + O_2 \rightarrow 2CO_2 \quad (3)$$

Since transport control (Regime III) was widely accepted as the oxidation process above 800 °C, Okada and Ikegawa [5] assumed that the same number of the oxidizing agent molecules were transported to the graphite surface at all temperatures above 800 °C and suggested a transition of the type of reaction at higher temperatures [5]. Ong [6] made the assumption that the number of carbon atoms removed from the surface is changed and theoretically calculated the oxidation rate change when the main reaction product changes from CO_2 to CO at high temperatures [6]. However, Ong pointed out that additional experimental data were required for more careful assignments in the temperature range 1100–2500 °C. Furthermore, the materials used by Okada & Ikegawa [5] and Ong [6] were semi-isotropic graphites which differ from isotropic graphite used for VHTRs, and there is no experimental evidence that the behavior or rate of oxidation of different graphite grades (isotropic and semi-isotropic) will be the same. Based on this work, several studies analyzed the gasification of nuclear graphite only by measuring the product ratio of CO and CO_2 using gas chromatography [5–12]; mass loss was not measured in these studies.

The experimental results for nuclear graphite gasification [7–12] and subsequent oxidation kinetic models [7,13,14] have shown characteristics similar to those for classic oxidation kinetics of porous materials [15], i.e. three regimes for the control process of graphite oxidation depending on the temperature, for temperatures up to 800 °C.

The studies providing experimental data for graphite oxidation at temperatures higher than 1200 °C are not in agreement. For example, Sun *et* al. [16] found that the oxidation rate of IG-110 increases with increasing temperature at the range between 1000 and 1200 °C, while Kim *et* al. [7] showed a sharp increase in oxidation rate above 1000 °C and a plateau was reached at 1400 °C for IG-110. However, Fuller *et* al. [8] agreed with the three regimes of control process, showing that the oxidation rate is saturated above 800 °C, also for IG-110. Hence, these experimental data cannot substantiate the assumed equations from Ong [6] and they also reveal the uncertainty associated with the method using gas chromatography.

It is suggested that the evaluation of reaction rate based on gasification and kinetic models takes account only of the net rate of the graphite-oxygen reaction mechanism, known as the effective reaction rate [14], and neglects the microstructural characteristics of graphite. A more representative approach would describe the oxidation mechanism at the microscale, including the structure of pores and filler particles. On the other hand, the accuracy of CO measured by gas chromatography may be substantially poorer, because the molar mass of CO is similar to that of N_2.

Numerous studies on the oxidation behavior of nuclear grade graphite with measurement of mass loss are summarized in Table 1 [17–23]. However, data for isotropic graphite at very high temperatures are still limited. Temperatures of graphite components associated with the ingress of air during a LOCA accident may reach as high as 1600 °C. Past research efforts on graphite oxidation have generally focused on temperatures below 1100 °C based on the assumption that the oxidation rate would become steady and stay unchanged at 900 °C and higher [17,18,23]. In these references [14,24], it is claimed that mass transfer control would be the major oxidation mechanism of graphite, leading to a steady rate at temperatures higher than 900 °C.

There are studies with oxidation temperature higher than 1200 °C. Lee et al. carried out oxidation of the IG-110 and NBG-18 graphite at 1600 °C, but they did not report the effect of oxidation temperature on graphite oxidation rate; particularly for temperatures between 1200 and 1600 °C, the oxidation rate was not reported [19,21]. Huang *et* al. and Yang *et* al. also investigated the oxidation behavior of nuclear graphite (IG-110 and NBG-18) at elevated temperatures ranging from 700 to 1600 °C [20,22]. They found that in atmospheric environments the oxidation rates of these two graphite materials appeared to become constant at temperatures between 900 °C and 1200 °C but started to increase rapidly again at temperatures greater than 1200 °C. The trends in graphite oxidation, reported in the literature, are quite different over the temperature range 1200–1600 °C. Noticeably, the oxidation mechanism, especially for the microscale of graphite with the structure of pores and filler particles, above 1200 °C has not been discussed previously.

In order to fully understand the oxidation characteristics of graphite materials at elevated temperatures up to 1600 °C in both reactor grade helium and atmospheric environments, two candidate nuclear grade graphite materials (IG-110 and IG-430) for future VHTR applications were selected and extensive oxidation tests were conducted over a wide range of temperatures. Results for mass changes of the graphite specimens and possible oxidation mechanisms based on microstructure for different temperature ranges are reported and discussed. The lowest oxidation temperature used in this study is 700 °C. Although lower oxidation temperatures are used as a reference and cross-comparison with the literature, this work focuses on the temperatures typically associated with Regime III, i.e. oxidation occurs at the exterior surface. Hence, investigation of the surface microstructure has been used to analyze the oxidation behavior at different temperatures.

2. Experimental details

This study investigates the oxidation behavior of two graphite materials and the corresponding changes in the microstructure in dry air and in helium environments at temperatures ranging from 700 to 1600 °C.