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Original Article

Study on the Recycling of Nuclear Graphite after Micro-Oxidation

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A B S T R A C T

In this paper, a feasible strategy for the recycling of nuclear graphite is reported, based on the formation mechanism and the removal of carbon-14 by micro-oxidation. We investigated whether ground micro-oxidation graphite could be used as a filler to make new recycled graphite and which graphite/pitch coke ratio will give the recycled graphite outstanding properties (e.g., apparent density, flexural strength, compressive strength, and tensile strength). According to the existing properties of nuclear graphite, the ratio of graphite to pitch coke should not exceed 3. The recycled reactor graphite has been proven superior in density, strength, and thermal conductivity. The micro-oxidation process enhances the strength of the recycled graphite because there are more pores and unsmooth surfaces on the oxidized graphite particles, which is beneficial for the access of the pitch binder and leads to efficient joint adhesion among the graphite particles.

1. Introduction

As a moderator, reflector, and fuel matrix, graphite has been widely used in gas-cooled reactors (e.g., advanced gas-cooled reactor, MAGNOX, high-temperature gas-cooled reactor) and the Russian Reaktor Bolshoy Moshchnosti Kanalniy (RBMK) nuclear reactor. At the end of a reactor's life, a significant number of nuclear graphite components are disposed of, which creates radioactive materials management issues such as storage, transportation, and burial. Each storage method has its associated costs and environmental implications. How to dispose of this radioactive waste? A potential solution to the irradiated graphite management issue is to remove the main radioisotope and recycle the graphite [1]. Carbon-14 (^{14}C) is produced in the reactor graphite because of neutron reactions. It is the most significant long-lived radioisotope of concern because of its 5,730-year half-life [2]. To recycle this graphite, it is important to remove ^{14}C from the irradiated graphite components. This may reduce the cost of disposal and even allow recycling of this very pure nuclear grade

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material. Pyrolysis and oxidation have been suggested as ^{14}C decontamination methods [3]. Fachinger et al [4] have demonstrated the concept of thermal treatment of irradiated nuclear graphite in the presence of steam or oxygen. In this work, we perform a micro-oxidation process to remove ^{14}C that is concentrated on the irradiated nuclear graphite surface and on the surfaces of pores. The inner pores in the bulk graphite become the outer surface after crushing. In this manner, we can oxidize ^{14}C that is located in the bulk graphite. After performing the micro-oxidation process, we studied the viability of recycling nuclear graphite and investigated which graphite/pitch coke ratio could yield outstanding properties of the recycled graphite. As a prelude to working with irradiated graphite, the laboratory scale graphite fabrication process line was optimized. The recycled graphite was obtained by the conventional graphite preparation process (i.e., grinding, oxidizing, mixing, molding, baking, impregnating, and graphitizing). Our results indicate that the recycling process is viable.

2. Materials and methods

2.1. *Micro-oxidation process*

The micro-oxidation experimental scheme and equipment used is shown in Fig. 1. The powder of CT-25 graphite (Chengdu Carbon Co., Ltd., Sichuan, China), which was produced by an isostatic molding method with an average particle size of 25 μm, was placed in a ceramic crucible in a quartz tube furnace. Nonirradiated graphite was used because of laboratory constraints. The inert gas argon, which was mixed with a volume ratio of 5% oxygen, flowed through the graphite sample at a flow rate of 300 cm^3/min. The nuclear graphite powder was oxidized in the furnace at 550°C and the oxidation was set to the extent of 5% weight loss.

A drying bottle with cooler was used to cool the off gas and remove the excess water. Gas chromatograph equipment was placed after the cooler system to analyze the concentrations of carbon monoxide (CO) and carbon dioxide (CO_2). Titanium dioxide (TiO_2) is a famous catalyst or catalyst support used in many fields [5–7]. In this paper, copper(II) oxide/TiO_2 (CuO/TiO_2) was used as a catalyst to oxidize the small amounts of CO to CO_2. The following washing bottles were filled with sodium hydroxide for retaining CO_2.

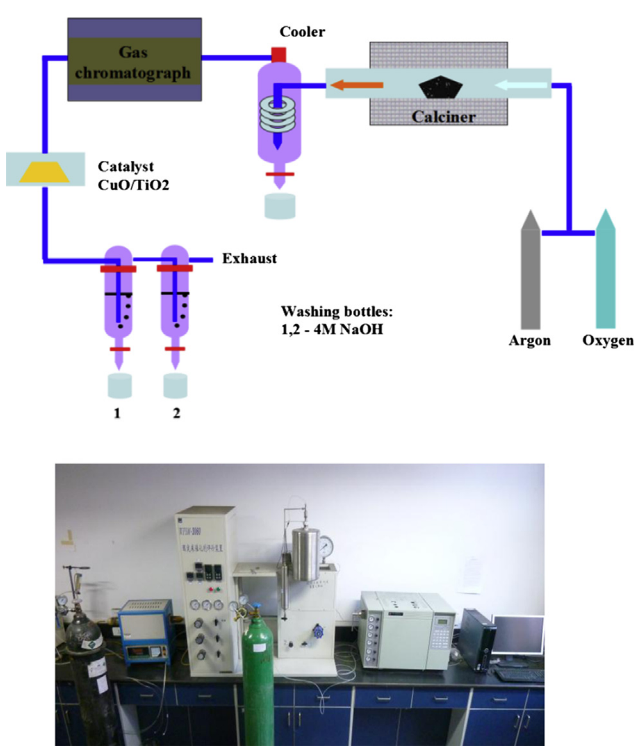

Fig. 1 – Experimental scheme and equipment of micro-oxidation of graphite. CuO, copper(II) oxide; NaOH, sodium hydroxide; TiO_2, titanium dioxide.

2.2. *Graphite recycling*

The graphite recycling process is identical to the flow diagram in Fig. 2. The steps were followed as closely as possible. Ground graphite (oxidized and nonoxidized) and pitch coke were ground to the appropriate particle size (mean size, 20 μm) and mixed in different proportions as the filler. The purpose of this task was to investigate whether the ground micro-oxidation graphite could be used as a filler to make new or recycled graphite and to study the effect of the graphite/pitch coke proportion on the performance of graphite. For comparison, the blending of nonmicro-oxidation graphite powder and pitch coke were also studied. All recycled graphite samples consisted of 72% filler and 28% coal tar pitch binder. According to the ASTM D7219-08, Standard Specification for Isotropic and Near-isotropic Nuclear Graphite (Annual book of ASTM Standards, 2009), the recycled graphite block with a size of Φ220 mm × 280 mm is then characterized, measuring apparent density, thermal conductivity, coefficient of thermal expansion (CTE), compressive strength, tensile strength, flexural strength, etc.

3. Results and discussion

3.1. *Micro-oxygenation graphite properties*

During the oxidation process, carbon atoms on the graphite surface and in the pores interact with adsorbed oxygen

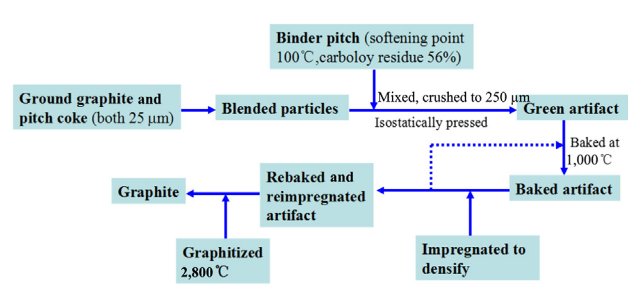

Fig. 2 – Flow diagram for the production of nuclear graphite.