



Original Article

Study on the Recycling of Nuclear Graphite after Micro-Oxidation

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ABSTRACT

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.

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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 (¹⁴C) 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 ¹⁴C 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

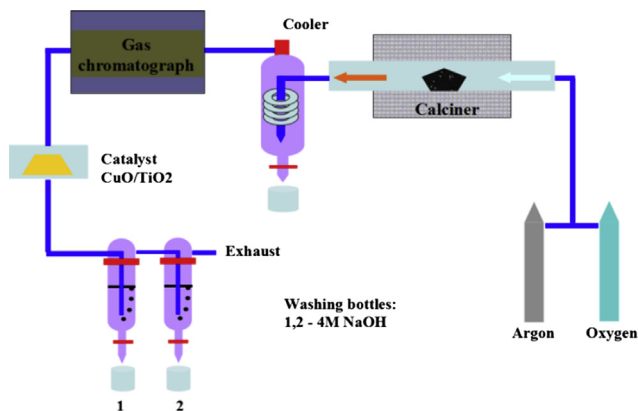


Fig. 1 – Experimental scheme and equipment of micro-oxidation of graphite. CuO, copper(II) oxide; NaOH, sodium hydroxide; TiO₂, titanium dioxide.

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 (CO₂). Titanium dioxide (TiO₂) is a famous catalyst or catalyst support used in many fields [5–7]. In this paper, copper(II) oxide/TiO₂ (CuO/TiO₂) was used as a catalyst to oxidize the small amounts of CO to CO₂. The following washing bottles were filled with sodium hydroxide for retaining CO₂.

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 $\Phi 220 \text{ mm} \times 280 \text{ mm}$ 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

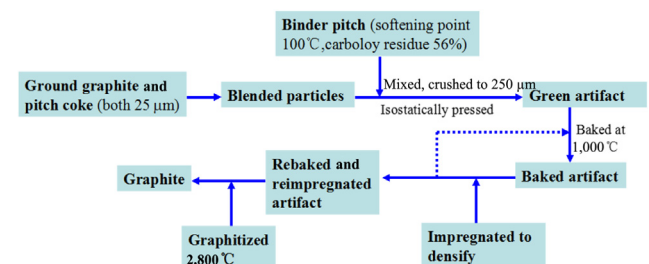


Fig. 2 – Flow diagram for the production of nuclear graphite.

complexes to create CO and CO₂ gases [8]. This is an effective way to remove a significant fraction of ¹⁴C, which tends to be concentrated on the irradiated graphite surface and pores [9]. Graphite gasification occurs by three steps: (1) oxygen adsorbs onto the graphite surface; (2) the adsorbed oxygen reacts with surface carbon sites; and (3) the newly formed carbon-oxygen species desorb. A possible pathway of oxidation of graphite to CO and CO₂ has been modeled by density functional theory calculation [8]. The oxygen (O₂) molecules dissociate and adsorb at defect sites to form adsorbed products. The C–O bond at less stable adsorption sites is etched away to form CO gas at typical temperatures. The energetic newly formed CO molecules react with O atoms at the center site and the bridge site to form CO₂ gas (Fig. 3).

The CO and CO₂ concentration is tested by the gas chromatograph. At low temperature, twice as much CO₂ is released as CO. At high temperatures (i.e., ≥550°C), the CO₂ concentration is approximately 10%, whereas the CO release is <4% (Fig. 4). Because the carbon–carbon bonds are weakened by the chemisorptions of oxygen on neighboring quinone or semiquinone complexes, most of the CO₂ desorbs easily whereas the activation energy required to remove CO from the quinone complex is quite high [9,10]. Therefore the low CO concentration is attributable to the high activation energy. The CuO/TiO₂ catalyst is set to help oxidize CO to CO₂ and thus reduces CO concentration as the temperature increases (Fig. 5).

Fig. 6 shows the surface appearance of graphite before and after micro-oxidation at 550°C. The graphite surface has more pores after micro-oxidation. The samples used in Fig. 6 are 5 mm × 5 mm × 5 mm in size. After the samples were oxidized, the size remained unchanged to 5% weight loss and up to 10% weight loss. The main reason for the weight loss is the expansion of the pores in the sample. The oxidation appears primarily in the pores of the graphite at 550°C. This result is in accordance with the results of other literature reports [11]. Micro-oxidation is an effective way to remove ¹⁴C that is concentrated in the pores and outer surfaces of irradiated graphite.

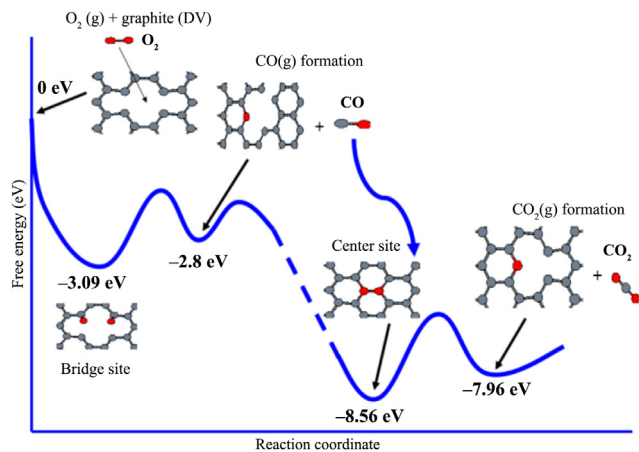


Fig. 3 – Reaction pathways of the O₂ desorption processes to form CO and CO₂ gases at defect sites. CO, carbon monoxide; CO₂, carbon dioxide; O₂, oxygen.

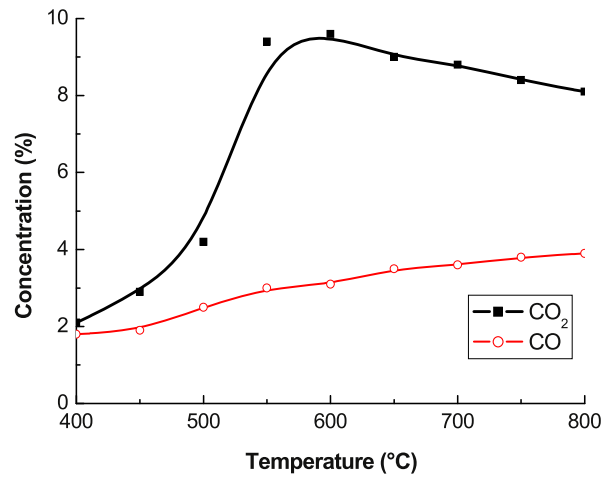


Fig. 4 – CO and CO₂ concentrations for graphite oxidation at different temperatures. CO, carbon monoxide; CO₂, carbon dioxide; O₂, oxygen.

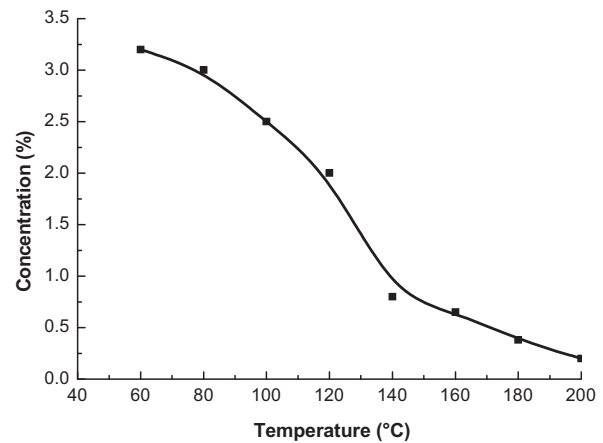


Fig. 5 – CO concentrations after reaction with the CuO/TiO₂ catalyst. CuO, copper(II) oxide; TiO₂, titanium dioxide.

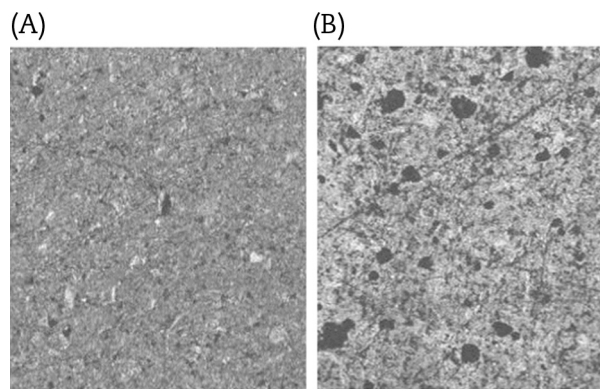


Fig. 6 – Optical microscopy micrographs of the graphite surface. (A) Before and (B) after micro-oxidation [temperature, 550°C; 5%O₂ + argon (Ar)].

Table 1 – The properties of CT-25 graphite.

Coke	Pitch coke
Average filler size (μm)	25
Forming method	Isostatic pressing
Apparent density (g/cm^3)	1.83
Flexural strength (MPa)	39
Compressive strength (MPa)	80
Tensile strength (MPa)	26
CTE for temperature, 20–500°C ($10^{-6}/^\circ\text{C}$)	≤ 4.1
Anisotropy of CTE	1.05
Thermal conductivity (W/mK)	133
Ash (ppm)	<100
CTE, coefficient of thermal expansion.	

3.2. Recycled graphite properties

3.2.1. Determine the ratio of graphite/pitch coke

Table 1 shows the properties of CT-25 graphite. All data are similar to those of IG110 nuclear graphite. Fig. 7 shows the average apparent density for all recycled graphite samples. The red dots represent the density of recycled graphite composed of micro-oxidation graphite powder using pitch coke as the filler, and the black squares represent the density of the original ground graphite with pitch coke. The letter “R” stands for the mass ratio of graphite powder to pitch coke. If the value of R is 3, then the sample has a 3:1 ratio of graphite/pitch coke. If the filler was only composed of pitch coke (i.e., 100% pitch coke), the apparent density of the graphite was $1.83 \text{ g}/\text{cm}^3$. As shown in Fig. 7, the apparent density of the recycled graphite decreases as the amount of graphite powder increases. This indicates that the addition of pitch coke as a filler can improve the graphite density. Pitch coke exhibits severe volumetric shrinkage during graphitization, which results in a high density. Severe volumetric shrinkage is unfavorable because it may lead to internal stress and more cracks in the graphite artifact. Therefore, adding graphite powder effectively reduces volume contraction because the compact graphite powder inhibits volume shrinkage [12].

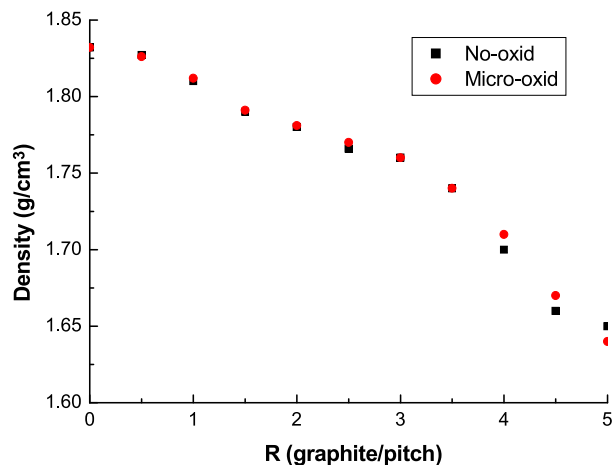


Fig. 7 – Average apparent density of recycled graphite. Micro-oxid, micro-oxidation; No-oxid, no oxidation; R, mass ratio of graphite powder to pitch coke.

In Fig. 7, the density of the “micro-oxide” sample is not different from that of the “nonoxide” samples at the same R ratio. Based on the apparent density, the recycled graphite samples with an R value <3 have a higher density ($\geq 1.76 \text{ g}/\text{cm}^3$). Density is an important performance parameter for nuclear graphite: the higher the density, the better the neutron-moderating effect. Compared to the density of IG110 nuclear graphite, the apparent density of the currently developed nuclear graphite is $>1.76 \text{ g}/\text{cm}^3$.

The compressive strength, flexural strength, and tensile strength of the recycled graphite are shown in Fig. 8. The apparent density has no obvious difference; however, the “micro-oxide” strength is significantly larger than the “non-oxide” strength, and the strength of the recycled graphite decreases as the amount of graphite powder increases. Compared to bending and tensile strength, there is less difference in compressive strength between the “micro-oxide” and “nonoxide” samples. According to the existing properties of nuclear graphite, the R = 3 sample for “micro-oxide” has a satisfactory mechanical property. Its tensile strength, compressive strength, and bending strength are 22 MPa, 60 MPa, and 31 MPa, respectively.

Other physical properties of the R = 3 sample of “micro-oxide” are as the following: the CTE (for a temperature of 20–500°C) is $3.82 \times 10^{-6}/^\circ\text{C}$, the anisotropy of CTE is 1.06, and the thermal conductivity is 103 W/mK. We concluded that to reuse irradiated graphite, the first step is to oxidize it to remove the ^{14}C . The micro-oxidation process removes ^{14}C , and enhances the strength of the recycled graphite. Another factor is that there is a limit for using the graphite: in our experiment, the ratio of graphite powder and pitch coke should not exceed 3.

3.3. Permeability studies

For the same ratio of graphite to pitch coke, performing micro-oxidation on the graphite powder results in higher strength in the final recycled graphite. One explanation is that more pores and unsmooth surfaces are present in the graphite particles after oxidation, and this gives rise to more binder pitch contacting with or filling into the graphite filler, resulting in higher interfacial adhesion strength.

To determine the reason behind the different performances of recycled graphite, permeability studies have been performed [13]. Fig. 9 reports the permeability of different graphite fillers to coal tar pitch. The micro-oxidation graphite interestingly exhibits nearly three times the permeability of nonmicro-oxidation ground graphite. Pictures of pitch binder permeating a graphite matrix at different temperatures are shown in Fig. 10. A coal tar pitch column is located on the surface of the graphite matrix. As the temperature increases, the pitch column tends to become soft and permeates the graphite matrix. Fig. 10A shows the permeation process on a micro-oxidation graphite matrix. Nearly all of the coal tar pitch penetrates into the graphite matrix when the temperature increases to 190°C; however, the situation is different for pitch on a nonmicro-oxidation graphite matrix. The pitch cannot penetrate into the nonmicro-oxidation matrix as easily as in the micro-oxidation graphite matrix.

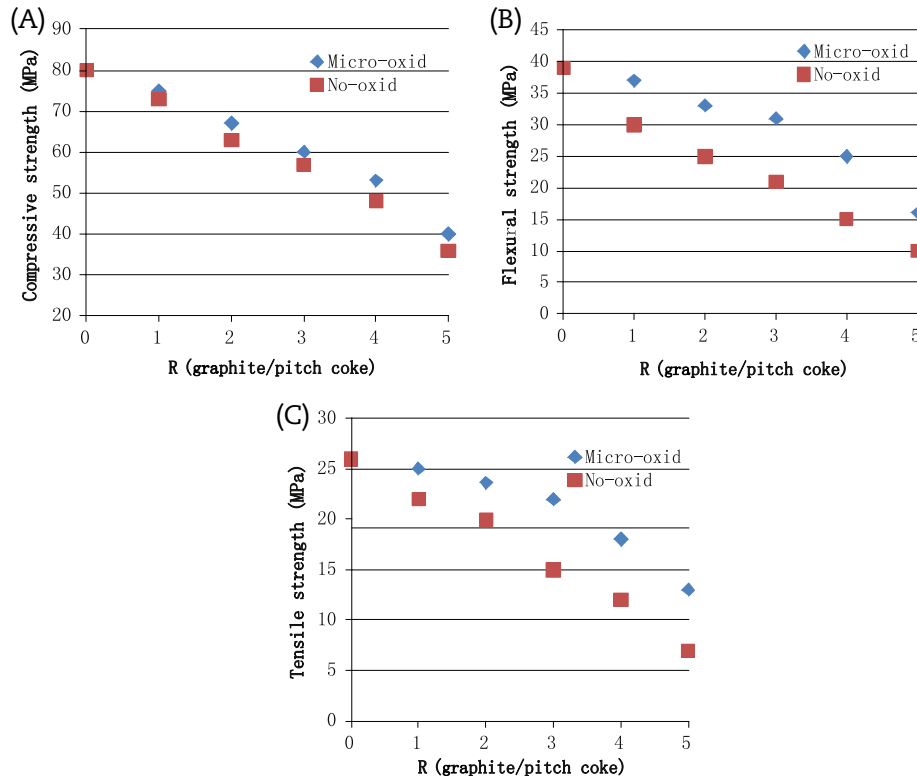


Fig. 8 – Effect of graphite/pitch coke ratio on various properties. (A) Compressive strength, (B) flexural strength, and (C) tensile strength of recycled graphite. Micro-oxid, micro-oxidation; No-oxid, no oxidation.

All results elucidate that micro-oxidation graphite exhibits high permeability for coal tar pitch. This is attributable to the fact that oxidation results in more pores and unsmooth surfaces for these graphite particles, which allows the binder pitch to bind with graphite particles more easily and thereby enhance permeability. Research by Choi et al [14] shows that oxidation increases the pore size of IG110 graphite and produces active groups on the graphite surfaces. Furthermore, the specific surface area is significantly increased in IG-110 after oxidation.

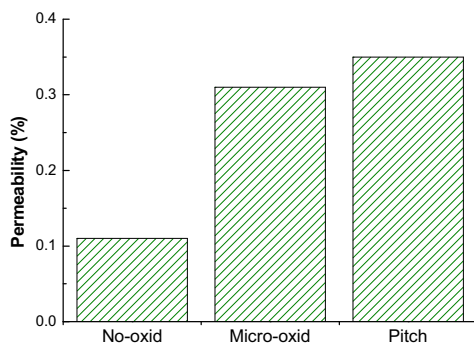


Fig. 9 – Permeability of different graphite fillers and pitch coke to binder pitch. Micro-oxid, micro-oxidation; No-oxid, no oxidation.

Fig. 11 is a schematic drawing of binder pitch binding to graphite particles. The graphite particles are surrounded by binder pitch. For graphite particles without micro-oxidation with smooth surfaces and few pores, the pitch binder cannot easily wet the graphite. As a result, the binder pitch and graphite particles have a poor adhesion strength. When the graphite powder is oxidized, pores and unsmooth surfaces naturally remain on the particles; therefore, pitch binder can permeate the pores to bind graphite particles more tightly. For this reason, micro-oxidation graphite samples exhibit high mechanical strength.

In summary, to reuse irradiated graphite, the first step is to oxidize it to remove the ¹⁴C that is concentrated in the pores and outer surface. The micro-oxidation process removes ¹⁴C and enhances the strength of recycled graphite. Another factor is that there is a limit for using graphite: our experiment indicates that the ratio of graphite powder and pitch coke should not exceed 3.

Mechanical properties, such as compressive strength, flexural strength, and tensile strength, were characterized. The R = 3 samples of “micro-oxide” have satisfactory mechanical properties with tensile strength of 22 MPa; compressive strength of 60 MPa; flexural strength of 31 MPa; and thermal properties such as CTE ($3.82 \times 10^{-6}/^{\circ}\text{C}$), thermal conductivity (103 W/mK), and anisotropy of CTE (1.06).

Permeability studies are performed to determine the reason for the outstanding performance of recycled graphite composed of micro-oxidation graphite powder. An

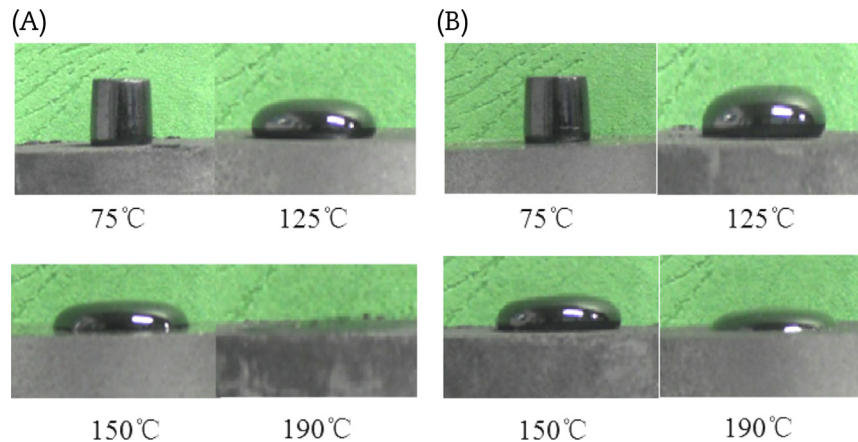


Fig. 10 – Photographs of binder pitch permeating the graphite matrix. (A) The micro-oxidation graphite matrix and (B) the nonoxidation graphite matrix.

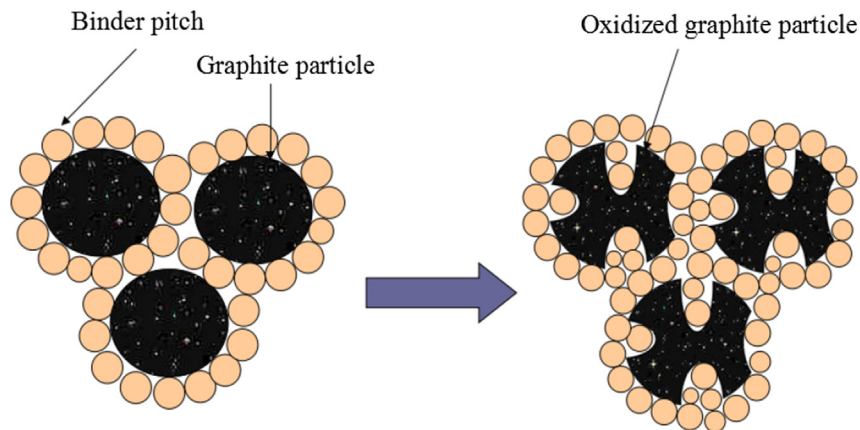


Fig. 11 – Schematic diagram demonstrating pitch binding to graphite particles before (left) and after oxidation (right).

explanation is the production of a greater number of pores and unsmooth surfaces for the graphite particles to interact with after oxidation. This factor gives rise to more binder pitch contacting with or filling into the graphite filler, and thereby results in greater interfacial adhesion strength.

Conflicts of interest

All contributing authors declare no conflicts of interest.

Acknowledgments

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REFERENCES

- [1] T.D. Burchell, P.J. Pappano, Recycling irradiated nuclear graphite—a greener path forward, *Nucl. Eng. Des.* 251 (2012) 69–77.
- [2] X.L. Hou, Rapid analysis of ^{14}C and ^3H in graphite and concrete for decommissioning of nuclear reactor, *Appl. Radiat. Isot.* 62 (2005) 871–882.
- [3] M.S. El-Genk, J.P. Tournier, Development and validation of a model for the chemical kinetics of graphite oxidation, *J. Nucl. Mater.* 411 (2011) 193–207.
- [4] J. Fachinger, W.V. Lenza, T. Podruhzina, Decontamination of nuclear graphite, *Nucl. Eng. Des.* 238 (2008) 3086–3091.
- [5] A. Fujishima, X. Zhang, D.A. Tryk, TiO_2 photocatalysis and related surface phenomena, *Surf. Sci. Rep.* 63 (2008) 515–582.
- [6] S. Hu, F. Li, Z. Fan, The influence of preparation method, nitrogen source, and post-treatment on the photocatalytic activity and stability of N-doped TiO_2 nanopowder, *J. Hazard. Mater.* 196 (2011) 248–254.
- [7] J. Liu, L.M. Dong, W. Guo, T.X. Liang, W.S. Lai, CO adsorption and oxidation on N-doped TiO_2 nanoparticles, *J. Phys. Chem. C* 117 (2013) 13037–13044.

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- [8] J. Liu, L.M. Dong, C. Wang, T.X. Liang, W.S. Lai, First principles study of oxidation behavior of irradiated graphite, *Nucl. Instrum. Methods Phys. Res. B* 352 (2015) 160–166.
- [9] T.E. Smith, S. Mccrory, M.L. Dunzik-Gougar, Limited oxidation of irradiated graphite waste to remove surface carbon-14, *Nucl. Eng. Techn.* 45 (2013) 211–218.
- [10] A. Montoya, T.T. Truong, F. Mondragon, T.N. Truong, CO desorption from oxygen species on carbonaceous surface: 1. Effects of the local structure of the active site and the surface coverage, *J. Phys. Chem. A* 105 (2001) 6757–6764.
- [11] P. Wang, C.I. Contescu, S.Y. Yu, T.D. Burchell, Pore structure development in oxidized IG-110 nuclear graphite, *J. Nucl. Mater.* 430 (2012) 229–238.
- [12] G. Haag, D. Mindermann, G. Wilhelmi, H. Persicke, W. Ulsamer, Development of reactor graphite, *J. Nucl. Mater.* 171 (1990) 41–48.
- [13] W.K. Fischer, U. Mannweiler, F. Keier, R.C. Perruchoud, Anode for the Aluminium Industry, R&D Carbon Ltd, Switzerland, 1995, pp. 169–181.
- [14] W.K. Choi, B.J. Kim, E.S. Kim, S.H. Chi, S.J. Park, Oxidation behavior of IG and NBG nuclear graphites, *Nucl. Eng. Des.* 241 (2011) 82–87.