Nuclear Engineering and Design 335 (2018) 231–240

Contents lists available at ScienceDirect

Nuclear Engineering and Design

journal homepage: www.elsevier.com/locate/nucengdes

Irradiation resistance study of binderless nanopore-isotropic graphite for use in molten salt nuclear reactors

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ARTICLE INFO

Keywords:
Nanopore-isotropic graphite
Irradiation stability
Microstructure
Mechanical properties

ABSTRACT

Binderless nanopore-isotropic graphite (NPIG) produced from mesocarbon microbeads by isostatic pressing method was irradiated with 7 MeV Xe^{26+} to a total peak dose of 0.1, 0.5, 2.5 and 5.0 dpa. The effect of the irradiation on the microstructure and physical properties of NPIG was then evaluated and compared against the performance of isostatic nuclear graphite (IG-110, TOYO TANSO CO., LTD). Ion-irradiation has a different effect on the microstructure (crystallinity, crystallite size) and mechanical properties (hardness, Young's modulus) of NPIG and IG-110 graphite. At lower irradiation doses, the surface morphology of NPIG was fragmented in a similar way to that of IG-110, but the NPIG gradually balled at 5 dpa. X-ray diffraction results show that NPIG has a lower degree of graphitization than IG-110. Raman studies indicated that NPIG reached saturation at lower doses. The nanoindentation showed that the hardness and Young's modulus of the NPIG and IG-110 increased after irradiation. Transmission electron microscopy images also provide clear evidence for an irradiation-induced increase in the number of basal dislocations and defects. Thus, although NPIG is generally more sensitive to irradiation than IG-110, its hardness is actually less affected.

1. Introduction

Molten salt reactors (MSRs) are a promising new type of high-temperature nuclear reactor that was originally proposed by the Generation IV International Forum due to the advantages offered by their fuel-bearing molten salt cycle capabilities and inherent safety characteristics (A Technology Roadmap for Generation IV Nuclear Energy Systems, 2002). In most nuclear reactors, graphite used as a neutron moderator or reflector due to its superior neutron-moderation properties, high-temperature thermal and mechanical stability, ease of machinability and cost-effectiveness. In a MSR, however, nuclear graphite also used a score-supporting structure, through which flows a molten salt (a mixture of fluorides) that serves as both the fuel and coolant. This creates special requirements in that any seepage of salt into the graphite used can lead to local hot spots easily capable of reaching 1000–1200 °C, which is significant given that the rate at which graphite is damaged increases by a factor of two at anything over 700 °C (Kasten, 1969). However, if the diameter of entrance pores to the internal void structure of graphite is kept within an order of 1 μm or less, then salt penetration into the graphite is restricted by surface tension. The diffusion of fission-product gases (mainly ^{135}Xe-based) into graphite can lead to a significant increase in neutron absorption and a reduced breeding ratio in the reactor (Rosenthal et al., 1972). The removal of Xe^{135} from the core therefore places a further constraint on the pore diameter of graphite, requiring that it be less than 100 nm.

For both the Oak Ridge National Laboratory (ORNL) and our MSR project, a binderless, homogeneous graphite would be a promising and suitable candidate for inhibiting liquid fluoride salt and helium penetration. The process for preparing nanopore-isotropic graphite (NPIG) is a rather special one, as spherical mesocarbon microbeads (MCMBs) containing solid β-resin are used to prepare graphite-matrixes through self-sintering reactions without traditional nuclear graphite materials (e.g., IG-110). Compared to the traditional nuclear graphite, the mechanical properties and microstructure uniformity of the NPIG are

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https://doi.org/10.1016/j.nucengdes.2018.05.027
Received 3 September 2017; Received in revised form 10 May 2018; Accepted 25 May 2018

Table 1
Typical physical and mechanical properties of NPIG and IG-110 graphite.

Property (unit)	NPIG	IG-110
Manufacturer	Our Lab.	Toyo Tanso
Preparation	Isostatic pressing	Isostatic pressing
Avg. grain size (μm)	4	20
Apparent density ($g{\cdot}cm^{-3}$)	1.90	1.77
Anisotropy ratio	~1.05	~1.05
Compressive strength (MPa)	230	79

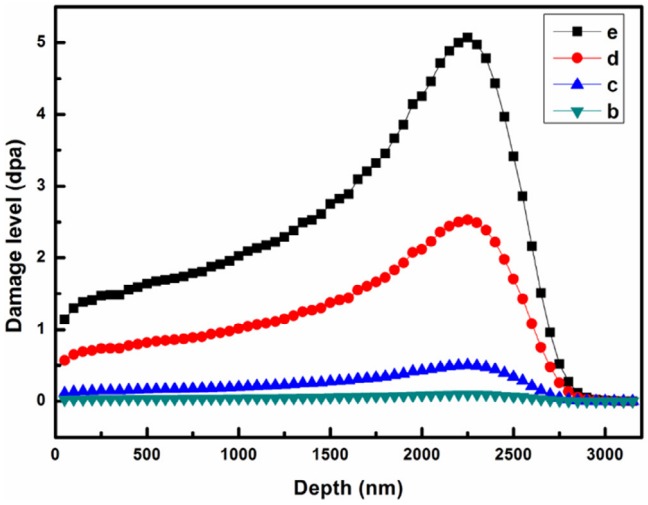

Fig. 1. Depth profiles of damage level (dpa) for irradiated samples (groups b, c, d and e) based on a SRIM2008 estimation. The irradiation fluences for curves b, c, d and e were 1×10^{14}, 5×10^{14}, 2.5×10^{15} and 5×10^{15} ions/cm^2, respectively.

excellent, which leads to the irradiation stability of the graphite. However, the pores of the NPIG are much smaller, and the amounts and sizes of the graphite are much less. There is less space for effectively absorbing the irradiation-induced c-axis expansion of the NPIG which could affect the irradiation behavior of the final graphite products and leads to the poor irradiation stability (Wen et al., 2008; Kane et al., 2011; Mrozowski, 1952; Sutton and Howard, 1962). However, the behavior of NPIG under irradiation, and in particular its crack evolution and difference to traditional graphite, has not been systematically studied yet.

The change in microstructure induced in NPIG by irradiation is important to its successful application in MSRs, but as neutron irradiation can be costly and time consuming, it can be simulated using heavy ion-irradiation to study its effect on the crystallinity and microcrack evolution of graphite. This technique has already been widely adopted in researching the effects of ion irradiation on the microstructure of graphite (He et al., 2014; Zhang et al., 2014). In this study, Xe^{26+} irradiation was used to further understand the effects of irradiation on the mechanical and microstructural properties (insoluble quinoline, cracks, defects) of NPIG compared to IG-110 (petroleum coke).

2. Experimental

2.1. Specimen preparation and irradiation conditions

Near-spherical MCMBs with an elemental composition of C, H, N and a particle size of ~4 μm were produced by the Osaka Gas Company. These were used to form cylindrical bodies with a diameter of 75 mm and a thickness of 40 mm by applying 100 MPa of pressure at room temperature, which were then carbonized under nitrogen at 900 °C for 4 h at a heating rate of 20 °C/h. Graphitization treatment was then performed under an argon atmosphere at a temperature of up to 2800 °C with a heating rate of 100 °C/h and dwelling time of 0.5 h to produce NPIG matrices (Song et al., 2014).

The NPIG specimens and commercially sourced IG-110 were cut into 5 × 5 × 1 mm^{3}pieces for $^{129}Xe^{26+}$ irradiation. Typical physical and mechanical properties of NPIG and IG-110 graphite are listed in Table 1. Before irradiation, all specimens were mechanically polished on metallographic SiC papers to #2000 and ultrasonically cleaned. They were divided into five groups (a, b, c, d and e). Untreated samples (Group a) were kept for the purposes of comparison, and each remaining piece was irradiated only once with $^{129}Xe^{26+}$ ions using a terminal of the 320 kV high-voltage experimental platform at the Lanzhou Institute of Modern Physics, which is equipped with an electron cyclotron resonance ion source.

TEM characterization was performed using a FEI Tecnai G2 F20 microscope, operated at 200 kV. The preparation process of TEM samples is as follows:

(i) cut the samples respectively into two pieces and then clean the surfaces
(ii) glue two pieces into a sandwich using epoxy resin and constant temperature heating for an hour and a half
(iii) polish the sandwich using #2000 SiC paper until it can be included in the copper tube. Fix them using epoxy resin and constant temperature heating
(iv) cut the copper tube into 0.7 mm
(v) after that, the specimen was dimpled to 40 um using a 40 g load, followed by ion-beam thinning with a Gatan PIPSion mill (Ar ions, 5 keV).

A constant energy (7 MeV) of Xe^{26+} ions was adopted to irradiate the samples. The irradiation fluences were 1×10^{14}, 5×10^{14}, 2.5×10^{15} and 5×10^{15} ions/cm^2. The damage level (displacement per atom, dpa) was calculated using the Stopping and Range of Ions in Matter (SRIM). The irradiation damage depth was calculated to be 3 μm. The peak damage was achieved at the depth of 2.3 μm. The corresponding peak doses were 0.1, 0.5, 2.5 and 5 dpa. The corresponding surface doses were 0.02, 0.11, 0.55 and 1.25 dpa, respectively, as shown in Fig. 1.

2.2. Characterization

Scanning electron microscopy (SEM) (LEO 1530VP) was used to monitor any change in the morphological structure of the graphite samples, and their structure before and after irradiation was measured with a Bruker D8 Advance XRD with $Cu_{K\alpha1}$ radiation source (λ = 1.5406 Å) conditioned by two 2.5° Sollerslits and a 0.025 mm Ni mask. The reflected X-ray intensity was collected by a LynxEye XE counter using continuous θ-2θ scans at a tube power of 40 kV/40 mA in a range of 20–70°(2θ), with a step size of 0.02°(2θ) at 0.15 s intervals. Any changes in the defects induced by irradiation were recorded using a Raman spectrometer (XploRA INV, France) at an excitation wavelength of 532 nm and effective penetration depth of about 50 nm. Nano indentation experiments were carried out at room temperature using a diamond Berkovich indenter (triangular based pyramid, produced by Keysight) in continuous stiffness measurement mode using a G200 nanoindenter with a penetration depth of 3 μm. A FEI Tecnai G^2 F20 microscope operated at 200 kV was used for TEM analysis of the samples.

3. Results and discussion

3.1. Crystal structure

Fig. 2 shows the XRD patterns obtained from the pristine NPIG