

Microstructure and molten salt impregnation characteristics of a micro-fine grain graphite for use in molten salt reactors

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Abstract: The microstructure and molten salt impregnation characteristics of a micro-fine grain isotropic graphite ZXF-5Q from Poco Inc. was investigated. The microstructural characteristics of the pores caused by gas evolution, calcination cracks, Mrozowski cracks, and the crystal structure were characterized by optical microscopy, mercury porosimetry, helium pycnometry, transmission electron microscopy, X-ray diffraction and Raman spectroscopy. Results show that the ZXF-5Q has uniformly-distributed pores caused by gas evolution with very small entrance diameters ($\sim 0.4 \mu\text{m}$), and numerous lenticular Mrozowski cracks. Molten salt impregnation with a molten eutectic fluoride salt at 650 °C and 1, 3 and 5 atm, indicate that ZXF-5Q could not be infiltrated even at 5 atm due to its very small pore entrance diameter. Some scattered global salt particles found inside the ZXF-5Q are possibly formed by condensation of the fluoride salt steam during cooling.

Key Words: Molten salt reactor; Graphite; Molten salt impregnation; Microstructure

1 Introduction

The first nuclear reactor, designated as CP-1, achieved a self-sustaining nuclear chain reaction in 1942^[1]. The group of scientists led by Enrico Fermi selected graphite as the moderator material because it was the only suitable material available at that time^[1]. Since then, graphite has been used in many reactors as a moderator and reflector owing to its excellent neutron-moderating ratio just behind heavy water, a high stability, high chemical compatibility and high-temperature strength^[1-3]. Hence, although fast neutron irradiation significantly damages the graphite by changing its dimensions and physical properties^[4-6], nuclear grade graphite is still widely applied. Today, it is mainly used in the high-temperature gas-cooled reactor (HTGR) and molten salt reactor (MSR).

The MSR is one of the six Generation IV reactors^[7]. It is a high-temperature reactor that features circulating molten fluoride salts as fuel and has been successfully operated at the Oak Ridge National Laboratory (ORNL) in the 1960s^[7,8]. Graphite is mainly used as the neutron moderator to control the flow patterns of the fuel salt in the MSR^[8]. The requirements for the graphite material are a high stability against radiation-induced distortion and non-penetrability by the fuel-bearing molten salt. Graphite is a porous material and its pores can be easily impregnated with the molten fuel salt in a high pressure environment^[8-10]. A seepage of the fuel salt into the graphite leads to the formation of local hot spots, which significantly damage the graphite, thereby reducing the service life of the graphite components^[8]. Studies at ORNL suggested that the impregnation is closely related to the pressure environment and the pore diameter^[8,9]. If the entrance pore diameters of the graphite, i.e. the neck of the

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open pore, are sufficiently small, molten salt penetration into the graphite can be restricted. Historically, grade CGB graphite^[11] has been successfully used in previous MSR experiments. The small entrance pores ($<0.4\ \mu\text{m}$) help preventing molten salt impregnation. However, the high irradiation anisotropy (extrusion molding method) makes it not suitable for reactors. Most of the commercially available nuclear graphite materials are highly isotropic and show a good radiation-resistance^[12,13]. Unfortunately, the entrance pore diameters of these graphite candidates (e.g., NBG-18 and IG-110 graphite) cannot meet the requirements for the MSR^[8]. Therefore, sealing the pores in the nuclear graphite material or selecting a new graphite material that can meet the requirements for our MSR project is particularly important.

Recently, we tried several methods to modify the graphite material, e.g., isotropic pyrolytic carbon coating^[14-16] and binderless nanopore-isotropic graphite (NPIG)^[17] research. In addition, experiments were performed to find commercially available graphite that could prevent the impregnation with molten salt. In general, graphite produced from finer grains exhibits finer pores. We have studied many grades of fine grained isotropic graphite commercially available, such as ETU-10/ETU-15 (Ibiden, Japan), DS4/E+40 (Mersen, France), and AXF-5Q/ZXF-5Q (Poco, USA). According to the differences in grain size, these graphites can be divided into super-fine (grain size below $50\ \mu\text{m}$, e.g., ETU-10), ultra-fine ($<10\ \mu\text{m}$, e.g., AXF-5Q/DS4/E+40), and micro-fine ($<2\ \mu\text{m}$, e.g., ZXF-5Q) grained graphite. We have found that only micro-fine grained graphite has the entrance pore diameters below $1\ \mu\text{m}$ and, therefore, could prevent the molten salt impregnation in a relative high-pressure environment. As a consequence, micro-fine grained graphite is promising candidate for the MSR.

However, there is only little information available on micro-fine grained graphite, especially concerning its irradiation and impregnation behavior. As shown by previous studies, the irradiation and impregnation behavior of graphite materials is closely related to their microstructure^[14-19], such as gas-evolved pores, calcination cracks, Mrozowski cracks, and the crystal structure of the materials. It was reported that calcination cracks and Mrozowski cracks in filler particles are highly connected to the initial volume shrinkage of nuclear graphite under high-temperature irradiation^[2,5,20]. In addition, there is a strong correlation between the diameters of the neck of the pores and the impregnation behavior of the graphite^[9]. A detailed investigation of the microstructure of the micro-fine grained graphite will be helpful to understand its irradiation and impregnation behavior. Furthermore, molten salt impregnation tests are essential to find a promising candidate graphite material for a future application in a MSR^[9]. Therefore, we also investigated the molten salt impregnation characteristics at different pressures.

In this study, the microstructure of micro-fine grained isotropic graphite ZXF-5Q was characterized by optical microscopy (OM), mercury porosimetry, helium gas

pycnometry, transmission electron microscopy (TEM), Raman spectrometry, and X-ray diffraction (XRD). The molten salt impregnation characteristics were investigated by impregnating the graphite samples with a molten fluoride salt at $650\ ^\circ\text{C}$, and 1, 3, and 5 atm. Afterwards, the samples were studied by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

2 Experimental

2.1 Materials

The ZXF-5Q graphite was investigated in this study and compared with nuclear grade IG-110 graphite. ZXF-5Q is a typical micro-fine grained isotropic graphite while the IG-110 is a conventional super-fine grained isotropic nuclear graphite used in the HTGRs. The typical physical and mechanical properties of the ZXF-5Q and the IG-110 graphite are compared in Table 1. Both of them were manufactured by isostatic pressing method, which exhibit a low anisotropy ratio (below 1.1) and a high density. The difference between the two graphite materials is the particle size. The average grain size of ZXF-5Q graphite ($\sim 1\ \mu\text{m}$) is much smaller than that of IG-110 graphite ($\sim 20\ \mu\text{m}$), resulting in smaller gas-evolved pores (see Fig. 1). This suggests that molten salt impregnation could be more likely prevented by using ZXF-5Q. Furthermore, ZXF-5Q is mechanically stronger than IG-110 and can better meet the reactor requirements accordingly.

Table 1 A comparison of the typical physical and mechanical properties of ZXF-5Q and IG-110 graphite.

Samples	ZXF-5Q	IG-110
Manufacturers	Poco	Toyo Tanso
Preparation	Isostatic pressing	Isostatic pressing
Avg. grain size (μm)	1	20
Apparent density (g cm^{-3})	1.78	1.77
Anisotropy ratio	<1.1	<1.1
Young's modulus (GPa)	14.5	9.7
Tensile strength (MPa)	79.3	27.2
Compressive strength (MPa)	175.8	79.0

2.2 Characterization

The analysis of the surface morphology was performed by optical microscopy (OM) (Zeiss, Germany). The OM specimens were hand-polished using 1200 grit sand paper and then placed into a vibratory polisher filled with a $0.05\ \mu\text{m}$ Al_2O_3 water-based suspension for 5 h. Mercury porosimetry was performed using a mercury intrusion porosimeter (AutoPore IV 9500) to obtain the entrance pore diameter distribution. The total and open porosity were then calculated based on the apparent and the pycnometric density. The pycnometric density was measured using a helium gas

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