Porosity of Nuclear Gade Graphite

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1. Introduction

Nuclear graphite is any of a grade of high purity, high density and near-isotropic graphite specifically manufactured for use as fuel elements, moderator or reflector blocks and core support structures in a high temperature gas cooled reactor (HTGR). According to ASTM 7319-08 [1], the minimum bulk density of a nuclear graphite shall be 1.7 g/cm^3. Considering that the theoretical density of graphite is 2.266 g/cm^3, the volume of a bulk piece of nuclear graphite is occupied by open or closed pores up to 25%. This porosity plays an important role in physical and mechanical properties and thermal oxidation.

In this study, fundamental porosity parameters such as pore size and distribution, pore volume and surface area of nuclear graphites were determined using a mercury porosimeter and compared one another.

2. Experimental

In this study, six grades of commercially available nuclear graphite were used. Typical properties of the graphites are summarized in Table 1.

Table I: Typical properties of the graphites

Grade	Coke source	Forming method	Coke particle size (μm)	Manufacturer
IG-110	Petroleum	Isotatic molding	20	Toyo Tanso
IG-430	Coal-tar	Isotatic molding	10	Toyo Tanso
NBG-17	Coal-tar	Vibrational molding	Max. 800	SGL
NBG-18	Coal-tar	Vibrational molding	Max. 1600	SGL
NBG-25	Petroleum	Isotatic molding	Max. 60	SGL
PCEA	Petroleum	Extrusion	Max. 360	GrafTech

Open pore parameters were quantitatively determined by mercury porosimetry measurements (Micromeritics Instrument Corporation, Model AutoPore IV 9500). The sample size was 12 mm in square and 18 mm in length. The measurements were performed 3 times for each grade. Pressures were increased up to 60,000 psi, corresponding to a pore size of 3.4 nm. A surface tension constant of 485 dynes/cm and a wetting contact angle of 130 degrees were assumed and used in the Washburn equation [2],

$$PD = -4\gamma\cos\theta$$

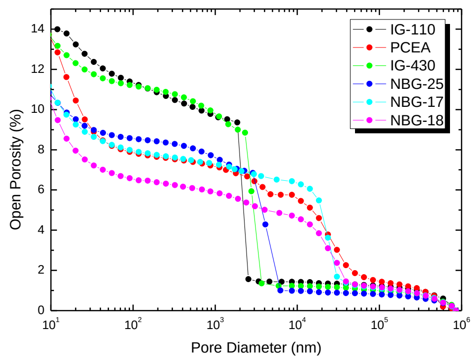
where P is the pressure, D is the pore diameter, γ is the surface tension and θ is the contact angle.

The surface area was also determined for each sample as described in the relationship where S is the surface area in square meters per gram [3].

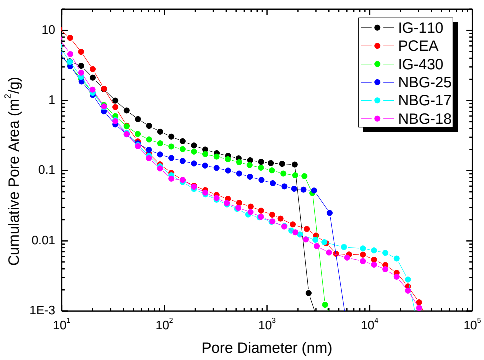
$$S = 0.0225\int_0^{V_{max}} PdV$$

In addition, the open and closed porosity was calculated by measuring the pycnometric density (Micronics, Model Accupyc 1330).

3. Results and Discussion



(a)



(b)

Fig. 1. Open pore spectra: (a) porosity and (b) cumulative pore area as a function of pore entrance diameter

As can be seen in Fig. 1, the open pore spectra showed strong dependence on the density and coke particle size of the graphite. The distribution of pore sizes is very narrow for the fine-grained graphite (IG-

110, IG-430 and NBG-25), while they are relatively broader for the medium-grained graphites (PCEA, NBG-17 and NBG-18). In the fine-grained graphites, major pores were concentrated at about 2~5 μm and they occupied about 8~9 % of the specimen volume. In the medium-grained graphites, major pores were concentrated at about 10~50 μm and they occupied about 5~7 % of the specimen volume. The penetration curves showed an upturn at 10 ~ 40 nm depending on the grade. From the pycnometry results summarized in Table 2, the open porosity was estimated to be about 7.08~13.41%. Considering the higher open porosity at the upturn points compared to the pycnometry results, some of the initially closed pores may become open because of breakage of thin pore walls under too high a mercury pressure [4]. Generally, as the bulk density increased, the cumulative surface area decreased.

Table 2 Total and open porosity

Grade	Bulk density (g/cm^3)	Pycnometric density (g/cm^3)	Total porosity (%)	Open porosity (%)
IG-110	1.772	2.046	21.82	13.41
PCEA	1.801	2.009	20.51	10.35
IG-430	1.803	2.063	20.42	12.57
NBG-25	1.811	2.048	20.06	11.53
NBG-17	1.838	2.012	18.87	8.63
NBG-18	1.852	1.993	18.27	7.08

It is noteworthy that as bulk density increased, the closed porosity decreased, as shown in Fig. 2.

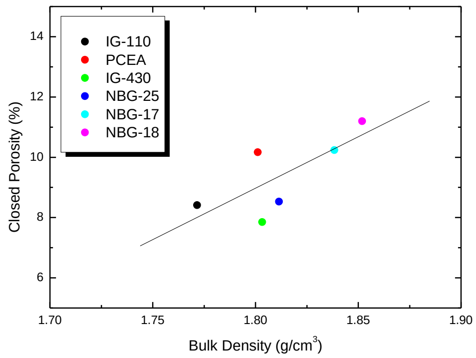


Fig. 2 Closed porosity vs. bulk density

Although cause and effect relationships are difficult to establish, graphite porosity, pore size, and surface area are all physically related to density. Their relationship to density, whether direct or inverse, has implications on the structural properties of nuclear graphite. As the graphite structure increases in density, the smaller pores can be imagined to become more and more occluded until they are isolated from the rest of the pore system. As this process occurs the smaller diameter pores are systematically eliminated until only the larger, less complex pores remain. This also creates a larger amount of closed porosity. Thus, not only does the average pore diameter increase as a result of the elimination of small open pores, but pore surface area is reduced since only pores with less branched structures remain. Mercury porosimetry data on fine-grained graphites reveals a definite relationship between closed porosity and apparent density with the closed porosity increasing as the apparent density increases. The pore size also increases as apparent density increases.

4. Summary

As the coke particle size increased, the pore size distribution became relatively broader. As the bulk density increased, the pore surface area inversely decreased, while the closed porosity increased.

ACKNOWLEDGEMENT

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