Fuel 180 (2016) 743–748

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Wettability of natural microcrystalline graphite filler with pitch in isotropic graphite preparation

Kuan Li[a], Ke Shen[b], Zheng-Hong Huang[a,d,*], Wanci Shen[a], Guangzhi Yang[c], Junhe Yang[c], Feiyu Kang[a,b]

[a] *State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China*
[b] *City Key Laboratory of Thermal Management Engineering and Materials, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, Guangdong, China*
[c] *School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China*
[d] *Key Laboratory of Advanced Materials (MOE), School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China*

HIGHLIGHTS

- Study of filler-pitch interaction during isotropic graphite preparation.
- Wettability of microcrystalline graphite with pitch was studied.
- Effect of crystalline orientation and degree of graphitization on pitch wetting behavior was examined.

ARTICLE INFO

Article history:
Received 3 March 2016
Received in revised form 18 April 2016
Accepted 21 April 2016
Available online 27 April 2016

Keywords:
Microcrystalline graphite
Petroleum coke
Contact angle
Wettability

ABSTRACT

Natural microcrystalline graphite (MG), which shows highly graphitized structure and near-isotropic material properties, can be used as filler material in isotropic graphite preparation. The final properties of graphite artifacts are largely determined by the interaction between pitch and filler particles during kneading. To achieve a better understanding of the wetting mechanism of MG filler, wetting behavior of pitch on substrates with different crystal structures was studied by measuring their contact angles. The results showed that both crystalline orientation and degree of graphitization of substrates could significantly influence the pitch wettability. Edge planes of graphite surface showed better wetting capacity than basal planes. And cokes obtained at very high temperature with highly graphitized structure tended to prevent pitch from wetting. Further wetting test showed that MG substrate was totally wetted by pitch drop, and its wetting time was shorter than coke. The wetting behavior of MG was related to its unique crystalline structure and surface morphology, and beneficial to the mechanical strength of MG-based isotropic graphite.

1. Introduction

Isotropic graphite has been widely used as neutron moderator, reflector and structural materials in nuclear systems such as in high-temperature gas-cooled reactors (HTR) [1,2]. Fast neutron irradiation creates crystal defects and causes inconsistent dimensional change in with-grain direction and against-grain direction [3,4]. The irradiation lifetime of graphite significantly influences the lifetime of a pebble-bed HTR, for the graphite component in pebble-bed HTR is non-replaceable. Nuclear graphite with high graphitization degree and low isotropy ratio (close to 1.00) shows a better dimensional stability under neutron irradiation, and in turn a longer lifetime in the reactor. Generally, these properties of graphite artifact are distinctly dependent upon the nature of filler particles. Both petroleum coke and pitch coke are most commonly used as fillers for nuclear graphite due to their well-graphitized property.

Natural microcrystalline graphite (MG) has been taken into account as a new filler material due to its unique microstructure. Firstly, MG is formed by randomly oriented micro-crystallites, leading to a near-isotropic structure of graphite particles [5]. This kind of structure is beneficial for the isotropic property of final graphite artifacts. Secondly, MG shows a perfect graphitic structure and a high degree of graphitization, which will enhance the irradiation performance of graphite. Additionally, an irradiated nuclear graphite recycling test which uses nuclear graphite blocks as raw material for making fresh graphite shows positive results in

---

[*] Corresponding author at: State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China.

E-mail address: zhhuang@mail.tsinghua.edu.cn (Z.-H. Huang).

http://dx.doi.org/10.1016/j.fuel.2016.04.091
0016-2361/

density, strength, thermal conductivity and coefficient of thermal expansion (CTE) [6], validating the use of graphitized fillers in producing isotropic graphite with suitable properties.

The wetting behavior of filler with pitch is another important factor that will influence the final properties of artificial graphite [7–11]. During the graphite manufacture, filler particles and coal-tar pitch are mixed together at temperatures above the pitch softening point in order to form a homogenous paste. Therefore, good wettability is essential to establish strong interfacial bonding between filler and pitch [12]. It has been illuminated that surface tension, viscosity and chemical composition of pitch are important factors during this interaction [8,13]. Also, several studies about coke wetting behavior [9–11,14] show that certain functional groups, enough porosity and pre-graphitic order of fillers are necessary for pitch to wet the filler particles. However, the wetting behavior of pitch with highly crystallized carbon, including MG, have not been reported yet.

Therefore, the first aim of this paper is to show the wetting behavior of pitch with MG powders, using petroleum coke as comparison. Also, MG was used as filler material to produce isotropic graphite sample, and its mechanical strength was evaluated. Then compacted natural graphite blocks with different crystalline orientation were used as substrates to evaluate the different wetting capacity of graphite basal planes and edge planes. And petroleum cokes heat-treated at different temperatures were chosen to examine the effect of degree of graphitization on pitch wettability. Finally, the wetting behavior of MG was explained based on its particular crystalline micro-structure and particle surface morphology.

2. Experimental

2.1. Materials

In this study, natural MG, petroleum coke and natural flake graphite (FG) powders were used as raw materials. The coke was obtained from green coke by calcining at 1000 °C. A commercial coal-tar pitch was selected as binder. The main properties of MG, coke, FG and pitch are listed in Tables 1 and 2, respectively.

Natural FG powders were compacted into substrate samples in different ways, in order to form different crystalline orientations of graphite. FG-WG and FG-AG were both obtained from compression molding samples. WG means with-grain or transverse direction, while AG means against-grain or axial direction. FG-ISO was obtained from isostatic pressing samples. FG-WG, FG-AG and FG-ISO samples were then polished for the wetting test. Coke1400, Coke1900, Coke2400 and Coke3000 were obtained from petroleum coke heat-treated at 1400 °C, 1900 °C, 2400 °C and 3000 °C as substrates of the wetting tests. Some properties of different cokes were listed in Table 3.

Table 1
Properties of MG, coke and FG.

Properties	MG	Coke	FG
Carbon yield (%)	99.71	99.66	99.91
Moisture (%)	0.04	0.11	0.02
Ash (%)	0.25	0.23	0.07
Tap density (g cm^{-3})	0.85	0.67	1.02
Porosity (%)	7.12	7.49	4.7
Particle size[a] (μm)	12.7	11.4	9.6

[a] D_{50}, particle diameter at 50% in the cumulative particle size distribution.

Table 2
Properties of coal-tar pitch.

Properties	Coal-tar pitch
Ash content (%)	0.84
Quinoline insoluble (%)	8.50
Toluene insoluble (%)	30.41
Softening point (°C)	110
Carbon yield (%)	39.59

Table 3
Properties of cokes heat treated at different temperatures.

Type of coke	Porosity (%)	d_{002} (Å)	(002) FWHM (°)
Coke	7.49	0.3454	2.3944
Coke1400	7.40	0.3451	2.2214
Coke1900	6.28	0.3434	0.6476
Coke2400	4.29	0.3389	0.2942
Coke3000	3.58	0.3366	0.2430

2.2. Pitch/substrates wetting test

The wetting behavior of pitch on different substrates was studied by a spreading drop test [8–11,14–15]. In this test, about 15 mg pitch powders were molded into a cylindrical pellet with about 3 mm in diameter and 2 mm in height. MG or coke powders were compacted into the groove on a glass sheet to form a granular substrate, and the surface of each granular bed was made as smooth as possible. The substrate was then placed on a hot plate, which was already set to the target temperature for the wetting test. The pitch pellet was then carefully positioned on the substrate, and directly molten into a droplet. The images of the liquid drop can be captured by a CCD camera. And the change of contact angle with time can be obtained from these images. For each wetting test, wetting curve was plotted from the point where pitch sample began to melt into an ellipsoid.

2.3. Isotropic graphite preparation

Filler (including MG and coke) powders were mixed with 30 wt.% coal-tar pitch at 200 °C, which was higher than the softening point of pitch to ensure a good fluidity of pitch. The mixture was then ground and sieved to −80 mesh green powders. Cold isostatic pressing process at 200 MPa was used to produce cylindrical blocks of approximately 60 mm in diameter and 80 mm in height. After forming, the densities of MG and coke green bodies are 1.74 and 1.55 g cm^{-3}, respectively. Carbonization was carried out at 1000 °C. Impregnation and re-carbonization were taken for two times to increase the graphite densities up to 1.70 g cm^{-3}. The graphite blocks were finally heat-treated at 3000 °C in Ar atmosphere.

2.4. Mechanical strength of graphite blocks

The graphite blocks were cut into specific specimens for mechanical property test. Density of the samples was measured by the Archimedes principle. Flexural strength of the samples (5 mm × 10 mm × 50 mm) was measured using four-point bending test.

3. Results

Changes of pitch contact angle on MG and petroleum coke substrate as a function of time at 180 °C and 200 °C were shown in Fig. 1. And the variation of pitch drop on MG substrate at 180 °C with time was shown in Fig. 2. The wetting temperatures were set to be higher than pitch softening point and lower than the initial decomposition temperature of pitch. In general, the contact angle of pitch decreased with increasing time and temperatures. Pitch could completely wet both MG and coke substrates after a