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Nanostructures of carbon in nuclear graphite

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Abstract. A variety of nanostructures of carbon in nuclear graphite were revealed by transmission electron microscopy (TEM) and high resolution TEM. Theses nanostructures include nanosized graphite particles, quinoline insoluble particles, a chaotic structure and a non-graphitizable structure of carbon. The basic structure of these nanostructures was observed to be nanosized packets of graphitic sheets or nanosized graphene.

1. Introduction

Last two decades witnessed intensive studies of carbon nanostructures including fullerenes, carbon nanotubes, carbon nano-onions and carbon nanospheres [1]. All these carbon nanostructures were first grown from vapour with or without a catalyst, except the carbon nano-onions which were first observed by intense electron beam irradiation of carbon soot particles and tubular graphitic structures [2], and were then subsequently grown from vapour [3]. In a microstructure characterization of nuclear graphite by transmission electron microscopy (TEM), a variety of carbon nanostructures were observed which were formed during carbonization and graphitization of pitch. In this paper we report the observation of carbon nanostructures in nuclear graphite, including nanosized graphite particles, quinoline insoluble (QI) particles, a chaotic structure and a non-graphitized structure of carbon. Unlike carbon nanotube and carbon nano-onions which are structurally related to fullerenes, the basic structure units (BSUs) of the carbon nanostructures we observed are nanosized packets of graphitic layers or nanosized graphene.

2. Experimental Procedures

Two different Gilsocarbon graphites (hereafter referred as Gilsocarbon A and Gilsocarbon B) were studied in this work. Gilsocarbon is the isotropic moderator graphite used in the UK nuclear Advanced Gas Reactors (AGR) [4]. Most of the specimens for TEM and high resolution TEM (HRTEM) were prepared by grinding, polishing and ion beam thinning. Some specimens for HRTEM were also prepared by microtome sectioning. A detailed description of the TEM sample preparation is given elsewhere [5]. TEM observations were carried out in a Philips CM 200 microscope operated 200 KV. The HRTEM observations were performed in a Tecnai F30 microscope operated at 300 KV.

3. Results and Discussion

Fig.1 (a) and Fig.1 (b) show a TEM image and a HETEM image of nanosized graphite particles in Gilsocarbon A, with amorphous carbon distributed between them. The size of the graphite crystallites varies from several nanometres to tens of nanometres. It is observed that the graphite particles in Fig.

1 are preferentially oriented. In this case, their graphite basal planes are parallel to the surface of the TEM sample. Crystallites with their graphite basal planes parallel to the electron beam were also occasionally observed and the l_c of these crystallites is about 5 nm. These are regarded as the basic structural unit (BSU) of the graphitized pitch. Because l_c is small, there are inevitably overlaps with crystallites of different in-plane orientations in the observed region. As a result of this overlapping, moiré fringes with different orientations were observed in the areas where the graphite particles have a relatively larger size (>15 nm). In these areas, no amorphous carbon was observed. This structure of nanosized graphite paticles was not observed in Gilsocarbon B.

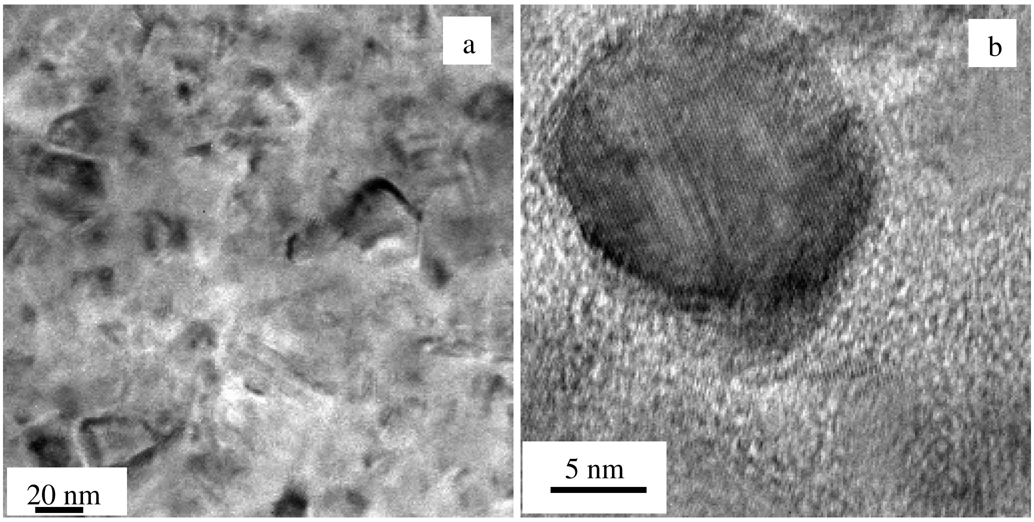

Figure 1. TEM image (a) and HRTEM image of nanosized graphite particles in binder of Gilsocarbon A.

The microstructures of QI particles and a chaotic structure which is associated with the QI particles are shown in Fig. 2, obtained from Gilsocarbon A. Fig. 2(a) shows an agglomeration of four small particles. These particles have a roughly spherical appearance. Such particles have previously been observed in the binder of pitch-bonded graphites and it was proposed that these particles were part of the QI fraction of the coal-tar pitch binder [6]. Hereafter they will be referred as QI particles. QI particles were observed in both Gilsocarbon A and Gilsocarbon B. Higher magnification in Fig. 2(b) reveals that the QI particles consist of concentrically arranged packets of graphitic layers, with the thickness of these packets varying between 2 nm and 50 nm. The packets in a QI particle are in such a configuration that the c-axis of the packets is directed radially towards the centre of the particle. The change of orientation of the packets around the circumference is achieved by a segmented folded structure. This is unlike the structures observed in onion-like carbon structures [2], which show continuous bending of graphite-like layers. The QI particle size varied between from tens of nanometres to approximately 600 nm.

A characteristic structure was observed in some areas surrounded by QI particles (indicated by arrows in Fig. 2(c)). Higher magnification image (Fig. 2(d)) shows that this structure consists of small packets of graphite layers in random orientations. This structure is therefore described as a chaotic structure. It was only observed in Gilsocarbon A. The thickness of these packets varies from 2 nm to about 20 nm. Although the packets in Fig. 2d are randomly arranged, they do have a preferred orientation. For example, it can be seen that the graphite basal planes of all the packets in Fig. 2d are parallel to the electron beam. No (hkl, $l \neq 0$) reflection rings were observed in the electron diffraction patterns taken from the chaotic structure, suggesting that the packets in the chaotic areas have a turbostratic structure. There are many low contrast regions with a size of the order of a few ångstroms in the chaotic structure. These are interpreted as voids or fissures.

The observation that the chaotic structure is associated with the QI particles suggests that the chaotic structure was formed from pitch binder, as QI particles are only found in the pitch. As the QI particles appear to influence graphitization, it is deduced that if there were no QI particles, the pitch, would have formed a well-graphitized structure.

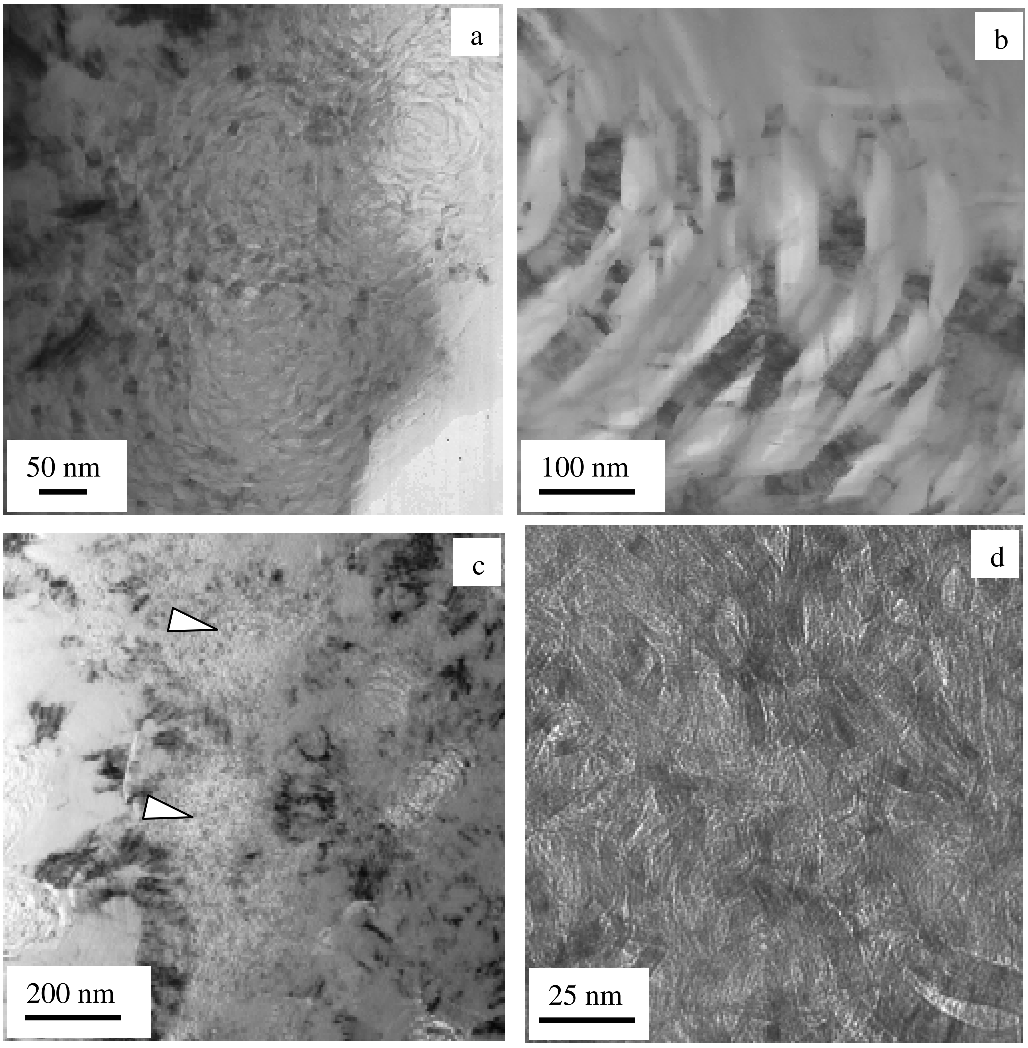

Figure 2. TEM image of an agglomeration of QI particles (a); higher magnification of a QI particles (b); a chaotic structure (arrows indicated) (c) and higher magnification of a chaotic structure (d).

Fig. 3 shows a HRTEM image taken from a non-graphitised region of a Gilsocarbon B sample, which was prepared by microtome sectioning. It is difficult to find any two dimensional lattices with a size larger than 1 nm. Straight or curved lines of white dots can be observed in the image. These lines may be the projection of fragments of straight or curved graphenes. At the lower left of the image, a feature indicated by an arrow can be seen. This feature is apparently formed of three concentric rings. The inner ring is approximately 0.7 nm in diameter and formed of dots. Part of the middle ring appears as a fringe and is mostly formed of dots. Only part of an outer ring can be observed as dots and a fringe. The appearance of this feature is similar to that of an onion-like structure. The distance between rings, however, is about 0.19 nm. This is much less than the reported distance of 0,334 nm between layers in an onion-like graphite sphere [2], which was in agreement with the distance between graphite layers in bulk graphite (d_{002} = 0.334 nm). This onion-like structure with a smaller interlayer distance may be a single structure, or perhaps due to overlapping of two or more curved graphene monolayer fragments in the foil thickness. Further work is being done to resolve this. The basic structural unit (BSU) in the non-graphitised binder is concluded to be graphene fragments.

This paper presents only part of the results from the work of microstructure characterization of nuclear graphite. More detailed descriptions on the microstructure of filler particles and binder in nuclear graphite are given elsewhere [5, 7].

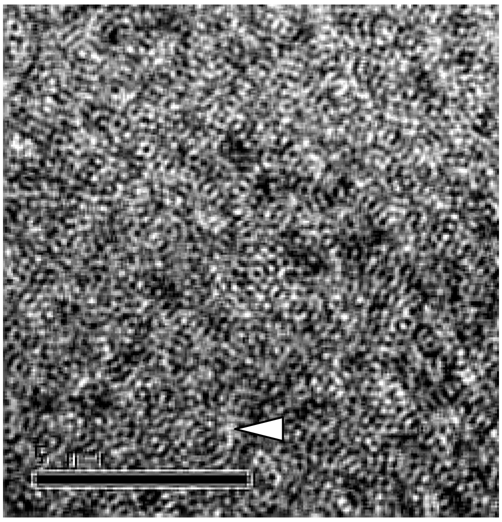

Figure 3. HRTEM image of non-graphitzable carbon, a feature is indicated by an arrow. The scale bar is 5 nm.

4. Conclusion

TEM and HRTEM revealed a variety of nanostructures of carbon in the pitch binder of nuclear graphite. The nanosized graphite particles, the QI particles and the QI particles associated chaotic structure have a BSU of nanosized packets of graphitic layers. The BSU of a non-graphitizable structure is suggested to be fragments of graphenes.

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