

FORMATION OF RHOMBOHEDRAL CRYSTALLITE IN PLATELET GRAPHITE NANOFIBERS

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Introduction

Graphite crystallizes in both hexagonal (2H) and rhombohedral (3R) systems. It is known that the 3R modification in graphite occurs locally by grinding of 2H crystal, and disappears by annealing at high temperature or decomposition of its intercalation compounds [Boehm 1955]. It was reported that the 3R phase content in artificial graphite, which was estimated from the integrated intensities of X-ray powder patterns, was increased by increasing the grinding time using ball-mill and saturated ca. 30% even at prolonged period [Inagaki 1973]. These observations suggest that the 3R stacking of carbon layers is meta-stable phase. Recently, the 3R modification in graphite has attracted attention as the cathode material for the Li-ion battery and as an intermediate for the cubic-diamond formation from graphite [Flandrois 1996, Guerin 1999, Yang 2001].

In this study, we found that the graphite nanofibers (GNFs) with high content of 3R phase could be synthesized by CVD method from CO/H₂ mixture with Fe ultra fine particles as a catalyst. The stability of 3R phase in GNFs was also examined.

Experimental

GNFs were synthesized by CVD method using a closed circulating apparatus. Ultra fine powder of Fe (20 nm of average diameter) was used as catalyst. When the reaction temperature (500-600 °C) reached in vacuum, 80% CO and 20% H₂ mixture was started to flow over the catalyst powder by means of a magnetic circulation pump equipped in the circulation loop. The total pressure of the reactant gas mixture at the beginning of the reaction was 76 kPa. After 100 hr of reaction, ca. 1g of GNFs was obtained from 100 mg of catalyst. The GNFs thus prepared was immersed in concentrated HCl for 1 day to eliminate spent catalyst. The samples were examined by scanning electron microscope (SEM), transmission electron microscope (TEM) and X-ray powder diffraction (XRD).

Results and Discussions

From the SEM observation (Figure 1.), the purified samples contained only nanofibrous morphology and no other form of carbons such as amorphous or particles were found. High resolution TEM images showed that the lattice fringes of carbon layer stacking along the c-axis coincided with the fiber axis. Since the XRD showed 3-dimensional ordering of graphite crystallite mentioned later, the samples was regarded as “graphite” nanofibers (GNFs) with platelet texture. The selected area electron diffraction gave a series of 00*l* spots along the longitudinal direction of GNFs more than *l* = 10 with several *hk*0 spots, indicating the high crystallinity and preferential orientation of the carbon layer stacking.

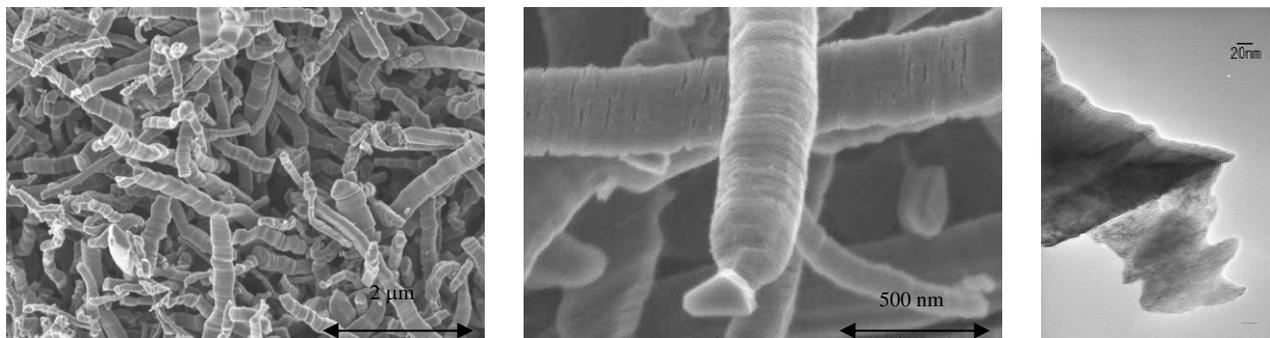


Figure 1. Scanning electron microscope and transmission electron microscope observation of graphite nanofiber with platelet texture synthesized at 550 °C. (left and middle: SEM, right: TEM)

XRD pattern of the GNF synthesized at 550 °C showed the development of 3-D structural ordering with both hexagonal (2H) and rhombohedral (3R) modification of graphite (Figure 2.). The diffraction lines of 101, 012, 104, 015 from 3R phase were observed without superposition on the 2H diffractions, although the 003, 006, 110 and 113 lines from 3R located at the

same positions with 002, 004, 110 and 112 lines from 2H phase, respectively. Applying the standard procedure of X-ray diffraction measurements on carbon materials by the Japan Society for the Promotion of Sciences (JSPS) [Iwashita 2004], the crystal parameters with 0.3358 nm of d_{002} , 0.2461 nm of a_0 and the crystallite sizes of ca. 50 nm for both $L_c(002)$ and L_a for 2H phase were obtained. Therefore, 2H phase in GNF obtained at 550 °C has almost ideal crystal parameters of graphite.

The 3R phase in GNFs was formed between 530 and 600 °C of reaction temperature and its diffraction intensity was the strongest for the samples synthesized at 550°C. For the evaluation of graphite polymorph (2H and 3R) contents from the integrated intensities of X-ray powder diffraction, the different equations (corrections) were found in the literature [Flandrois 1996, Ruland 1968]. For the calculation of polymorph contents from the integrated intensities by two components, it must be taking account the multiplicities of interested diffractions and the unit cell volumes of both phases, besides the corrections by Lorenz-polarization, absorption and atomic scattering factors for the observed diffractogram. The integrated intensities for 101 diffractions from both 2H and 3R phases were obtained by the peak fitting program using pseudo-Vogt function on the corrected diffractogram. Finally, the 3R phase content in GNFs synthesized at 550 °C was estimated about 55 vol% according to the Ruland's equation.

When the GNF synthesized at 550 °C was treated at high temperature up to 2800 °C in flowing argon, the diffraction intensities from the 3R phase were decreased. However, the diffractions of 3R structure had never been disappeared by the treatment of 2800 °C for 30 min and the diffractograms of GNFs heat-treated at 2500 and 2800 °C were the almost same. On the other hand, the grinding of GNFs by using the vibration mill caused a drastic change in morphology and crystallinity in a few minutes. From the SEM observation, it was revealed that the milling decreased the length of GNFs remarkably, but not affected the diameter of the GNFs. The 3R phase diffractions disappeared in 2 min of milling, although the 2H one was unchanged even after 10 min of milling time. These results seemed to suggest the thermal stability and the mechanical instability of the 3R phase in GNFs.

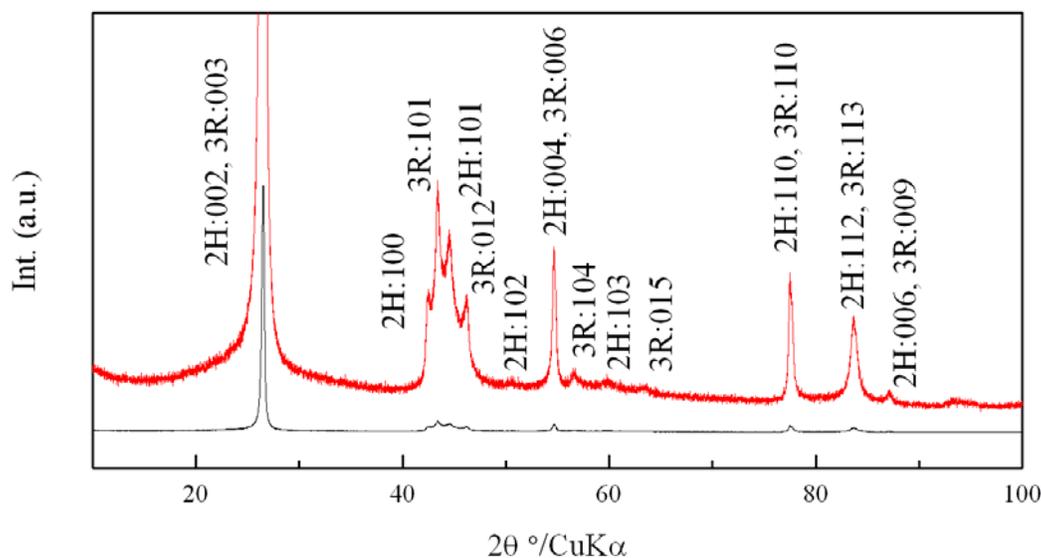


Figure 2. X-ray powder pattern of GNF synthesized at 550 °C containing both hexagonal and rhombohedral modification of graphite.

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