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The effect of magnetic field on the catalytic graphitization of phenolic resin in the presence of Fe–Ni

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ABSTRACT

The effect of an externally applied magnetic field on the Fe–Ni catalyzed graphitization of phenolic resin was investigated. The Fe and Ni doped phenolic resin was first carbonized at 800 °C and then graphitized at different temperatures (800–1200 °C). Both the carbonization and graphitization were carried out in a magnetic field and the crystal structure was characterized by X-ray diffraction and transmission electron microscopy. The externally applied magnetic field was found to promote the graphitization and to improve the orientation of the hexagonal carbon layers. In the presence of Fe–Ni, a high degree of graphitization could be achieved by applying a magnetic field. This resulted in a d_{002} of 0.3355 nm and full-width at half maximum (FWHM) value of 0.103° after a 1200 °C heat treatment. In comparison, the absence of a magnetic field resulted in a d_{002} of 0.3358 nm and FWHM of 0.305°.

1. Introduction

The addition of inorganic or organic additives accelerates graphitization of carbon materials at lower temperatures. It also brings about a transformation of a disordered carbon structure into the ordered structure of hexagonal graphite [1]. Refractory-metal carbides such as TiC (titanium carbide), ZrC (zirconium carbide), VC (vanadium carbide), and WC (tungsten carbide) [2–4], as well as elemental Fe, Ni, B, Si, Ti, Zr, etc. [5–16] have been researched in this context. One of the most effective catalysts for the graphitization of amorphous carbons [17–21] is Ni, which shows catalytic graphitization of amorphous carbon films at ≈700 K [10]. The graphitization of amorphous carbon by supported Ni particles has been investigated by Anton [22,23] using *in situ* transmission electron microscopy. Graphitization by Ni particles occurs through nucleation of graphene at the interface at certain sites that act as steps or kinks on the Ni surface [24]. The diffusion of carbon and Ni atoms at the Ni surface/interface result in the transformation of amorphous carbon into graphite, leaving graphitized carbon behind the propagating Ni particles. The driving force for this phenomenon is the difference between the adhesive force of amorphous carbon and graphite to metal. Amorphous carbon shows a higher adherence to metal than does the (0 0 1) plane of graphite.

Based on these findings, it can be deduced that propagation of metal particles with an external-applied magnetic field could achieve a directional graphitization of carbon materials. There have been a number of applications of magnetic fields in carbonization or graphitization for improvement of the mechanical and physical properties of carbon materials. For example, Pol et al. [25] reported on a magnetic field guided formation of long carbon sausages by pyrolysis of mesitylene. They proposed that the magnetic field directed an interaction between small carbon spheres formed by pyrolysis. In a later paper, the effect of the intensity of a magnetic field on the shape of carbon filaments was investigated [26]. Sung et al. [27] applied a high magnetic field during carbonization to increase the strength of carbon fibers. They concluded that the appearance of carbon surface defects was suppressed in a

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high magnetic field resulting in carbon fibers with enhanced strength. Ito et al. [28] imposed a high magnetic field during the graphitization of polyacrylonitrile (PAN)-based carbon fibers and obtained a 30% increase in fiber strength. This increased strength was attributed to the magnetic energy difference due to the magnetic anisotropy of a six carbocyclic ring and of flaws on the fiber. These studies drew attention to the effect of a magnetic field on the orientation of carbon atoms during carbonization and graphitization. However, the real impact of this technique was limited by the weak magnetic anisotropy induced, which primarily arose from defects in the carbon structure. Consequently, a very high magnetic field was needed to achieve the observed results.

In the current study, an external magnetic field was used to direct the orientation of Fe and Ni particles during the carbonization and graphitization of a phenolic resin. The mechanism of the magnetic field-induced catalytic graphitization is further discussed in terms of our findings.

2. Experimental

2.1. Sample preparation

Samples were prepared by homogeneously pulverizing phenolic resin together with Fe–Ni powder (200 mesh). The sample was carbonized at 800 °C for 2 h, then graphitized at different temperatures (800–1200 °C) in a tube furnace under the protection of a nitrogen atmosphere (purity of 99.99%), with or without an applied magnetic field. A 45 mT magnetic field was generated by a pair of rare-earth magnets (Nd–Fe–B) spaced 10 cm apart. Fig. 1 shows the experimental apparatus. The heating rate of both the carbonization and graphitization was 1.3 °C/min. The experimental conditions are listed in Table 1.

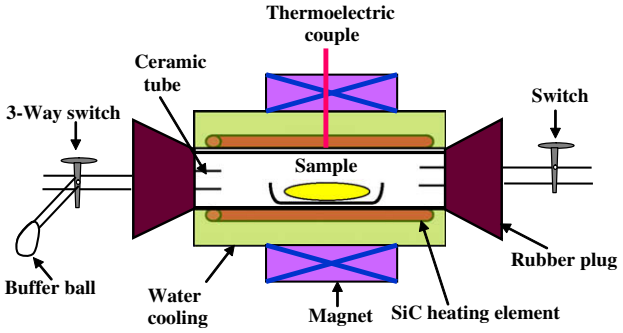

Fig. 1 – Sketch of the experimental configuration.

2.2. Characterization methods

Structural changes of the graphitized resin were characterized by X-ray diffraction (XRD, D8, Advance, Bruker AXS, Germany) with Cu K_α radiation (λ = 1.54178 Å), using silicon as a standard. The operating power was 35 kV and 40 mA. Step scanning was used with an interval of 0.004° (2θ). The 2θ value was obtained from the (0 0 2) diffraction peaks. The interlayer spacing (d_{002}) was calculated using the Bragg equation [29]. The microstructural features were characterized using a high-resolution transmission electronic microscope (HRTEM, JEM 3010. JEOL, Japan).

3. Results and discussion

3.1. XRD studies

The effect of the Fe–Ni content on the graphitization of phenolic resin was first investigated in the absence of a magnetic field. Fig. 2 shows the XRD patterns of the phenolic resin without (curves a and b) and with Fe–Ni (curves c and d) after carbonization at 800 °C and heat treatment at 1200 °C. The (0 0 2) peak shifts toward a higher θ value (decreases in d_{002}) with increases in the Fe–Ni content, as shown in Fig. 2 (curves c and d). The highest degree of graphitization, with a d_{002} of 0.3358 nm, was achieved with 5 wt.% Fe–5 wt.% Ni content. In the absence of Fe–Ni, very little of the resin was graphitized after 1200 °C heat treatment, as seen in Fig. 2 (curves a and b) no matter a magnetic field was applied (curve a) or not applied (curve b). We noted the work by Pol et al. [26] where the graphitization of carbon filaments could be greatly improved in a strong magnetic field (5T). In a weak magnetic field (45 mT), however, the effect of magnetic field on the graphitization is insignificant in the absence of Fe–Ni as shown in curves a and b. The interlayer spacing (d_{002}) and full-width at half maximum (FWHM) are listed in Table 1.

Table 1 – Microstructure parameters of the graphitized resin.

Sample	HTT (°C)	MF[a] (mT)	Cont.[b] (wt.%)	d_{002} (nm)	FWHM (°)
a	1200	45	0	–	–
b	1200	0	0	–	–
c	1200	0	2	0.3360	0.785
d	1200	0	5	0.3358	0.305
e	800	0	5	0.3363	0.598
f	800	45	5	0.3360	0.461
g	1000	0	5	0.3364	0.535
h	1000	45	5	0.3360	0.427
i	1200	0	5	0.3358	0.305
j	1200	45	5	0.3355	0.103

a MF: magnetic field.
b Cont. (wt.%): the contents of Fe:Ni is 1:1.