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Catalytic graphitization of hardwood acetic acid lignin with nickel acetate

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Abstract Catalytic graphitization of hardwood acetic acid lignin (HAL) with nickel (II) acetate was investigated regarding the production of highly crystalline carbon. Fusibility, one of the unique characteristics of HAL, was preserved with nickel acetate additions up to 0.3% (as the weight of nickel), although the thermal mobility of HAL was depressed by the addition of nickel acetate. An obvious effect of nickel salt as a catalyst on the development of carbon crystallite from HAL was observed for more than 0.2% addition. The development was found to proceed above 850°C. All the resulting carbons had turbostratic structure, and the apparent crystallite size (L_c) was increased with increasing amounts of catalyst, as determined by X-ray diffraction. Thus, highly crystalline carbon was produced from HAL by catalytic graphitization without compromising the fusibility of HAL by adding a small amount of organic nickel salt.

Key words Hardwood acetic acid lignin · Catalytic graphitization · Fusibility · Turbostratic structure · Crystallite size

Introduction

Graphite, a well known highly crystalline carbon, is utilized in many fields (e.g., as electrodes,¹ intercalated compounds,²

electromagnetic shields³). Its moldability seems to be an important property in addition to its fundamental properties for such applications. Therefore, the production of graphite moldings from isolated lignin is attractive for expanding the fields in which lignin can be utilized. We have already shown that both hardwood and softwood acetic acid lignins (HAL and SAL, respectively) were promising sources for functional carbonaceous moldings, as they can be converted to carbon fibers (CFs)^{4,5} and activated carbon fibers (ACFs).^{6,7} Comparing their molding processes, HAL was transformed into fibers more easily than SAL because of its complete fusibility, indicating that HAL is a suitable source for moldings. In this study, graphitization of HAL was attempted to explore further application of HAL as carbonaceous moldings.

In general, the graphitization is carried out by heating at temperatures higher than 2500–3500°C.⁸ Because carbonized wood is classified as nongraphitizing carbon, lignin is also assumed to be such a carbon. Actually, it seems difficult to develop highly graphite texture in lignin completely even when it is heated to 3000°C.⁹ Although the graphitization of carbonized wood has been performed by spark plasma sintering,¹⁰ we attempted lignin graphitization by a catalytic graphitization method that did not require any special apparatus.

Catalytic graphitization is a convenient technique for enhancing the crystallinity of carbon using transition metals or their inorganic compounds, such as iron, cobalt, and nickel, as the catalysts.¹¹ Both graphitizing and nongraphitizing carbons can be transformed to crystalline materials at relatively low temperatures by such a method.^{12,13} The mechanism is not well clarified, but the phenomena have been classified into four types: G, A, T, and Tn effects.¹⁴ G and A components resulting from the corresponding effects are considered to have a graphite structure, whereas the other components occasionally differ from this structure because they have a turbostratic carbon structure that has less ordered hexagonal layers. The latter effects result in the development of carbon crystallites. Such a graphitization method has not had widespread use in the industry because significant amounts of catalyst remain in

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the resulting graphite products. If practical effects appear with a small amount of catalyst, catalytic graphitization can be a viable method. From the point of view of catalytic graphitization of isolated lignin, HAL is a suitable test specimen because of its low ash content (0.1%), whereas the technical lignins contain significant ash, which can complicate the effect of a catalyst.

We investigated the possibility of catalytic graphitization of isolated lignin using a nickel catalyst. The influence of the catalyst charge and the heat treatment temperature on structural changes in lignin during catalytic graphitization were examined by X-ray diffraction (XRD) analysis.

Material and methods

Hardwood acetic acid lignin was isolated from birch (*Betula platyphylla* Sukachev) by atmospheric acetic acid pulping.¹⁵ HAL and nickel (II) acetate $[\text{Ni}(\text{OAc})_2]$ tetrahydrate were dissolved in acetic acid. The $\text{Ni}(\text{OAc})_2/\text{HAL}$ blending ratios were 0.1%–10.0% as the weight of nickel metal. After magnetic stirring for 30 min, the solvent was removed by evaporation; the residue was dried in vacuo for 48 h at 50°C. The blends were ground into a fine powder using a pestle and mortar. The blend was thermostabilized by heating it up to 250°C at a rate of 30°C/h under air atmosphere. The resulting blends were carbonized at 800–1000°C for 1 h under nitrogen flow. The heating rate was 180°C/h.

The structural changes of the resulting carbons after catalytic graphitization were monitored by XRD of the powdered sample with nickel filtered $\text{CuK}\alpha$ radiation (40 kV and 30 mA). Scanning conditions were as follows: step-interval 0.02° and scan speed 2.00°/min. The interplanar spacing (d_{002}) and apparent crystallite size ($L_{c(002)}$) were calculated by the Bragg and Scherrer equations, respectively.¹⁶ Differential thermal analysis (DTA) and thermomechanical analysis (TMA) were carried out on the MAC Science (Yokohama, Japan) thermal analyzer system (model 010).¹⁷

Results and discussion

Blend of HAL and $\text{Ni}(\text{OAc})_2$

The chemical properties of the HAL used in this study were as follows. The number-average molecular mass (M_n) was 1800; and the polydispersity (M_w/M_n , where M_w is the weight-average molecular mass) was 2.7. The contents of the methoxyl, hydroxyl, and acetyl groups were 17.2%, 4.2%, and 8.4%, respectively, based on the original HAL. Both the acetyl group and the polydispersity of HAL contributed to the fusibility.¹⁷ Therefore, HAL could be readily transformed into fibers and sheets¹⁸ by the thermal molding method.

In this study we assumed that catalytic graphitization was conducted after thermal molding the HAL. Accordingly, changes in the thermal mobility of HAL upon the addition

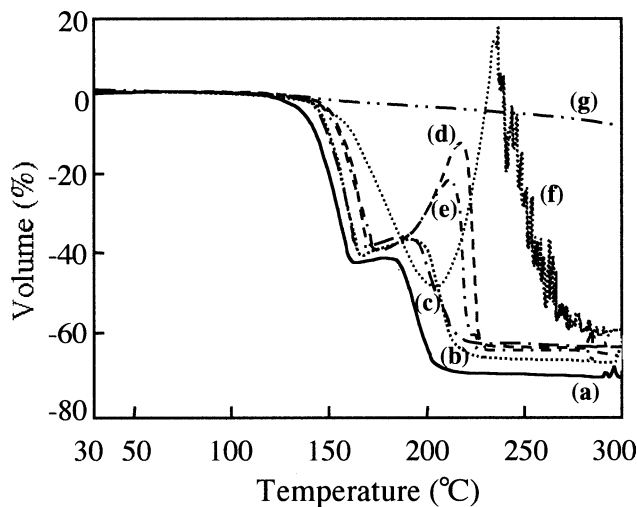


Fig. 1. Thermomechanical analysis (TMA) curves for hardwood acetic acid lignin (HAL) blended with various concentrations of $\text{Ni}(\text{OAc})_2$, a, 0.1%; b, 0.2%; c, 0.3%; d, 0.4%; e, 0.5%; f, 1.0%; g, 5% and 10% (overlapped)

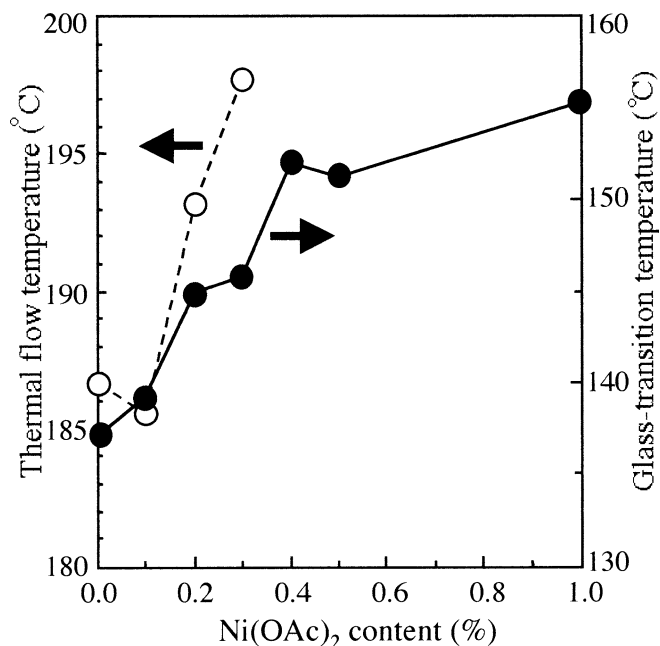


Fig. 2. Influence of $\text{Ni}(\text{OAc})_2$ content on the thermal transition temperature of HAL. Open circles, thermal flow temperature; filled circles, glass-transition temperature

of a catalyst were first investigated by TMA. $\text{Ni}(\text{OAc})_2$ was selected as a candidate catalyst because it dissolved in acetic acid, which was one of the solvents for HAL. It was expected that a homogeneous blend of HAL and the nickel salt would be prepared in the mixture. The TMA curves of the blends are depicted against the charge of the catalyst in Fig. 1. Two clear thermal transitions were observed for the blends with $\text{Ni}(\text{OAc})_2$ up to 0.3% addition. The lower temperature of the transition was the glass-transition temperature (T_g), and the latter was the thermal-flow temperature (softening temperature, or T_s).¹⁷ The T_g and

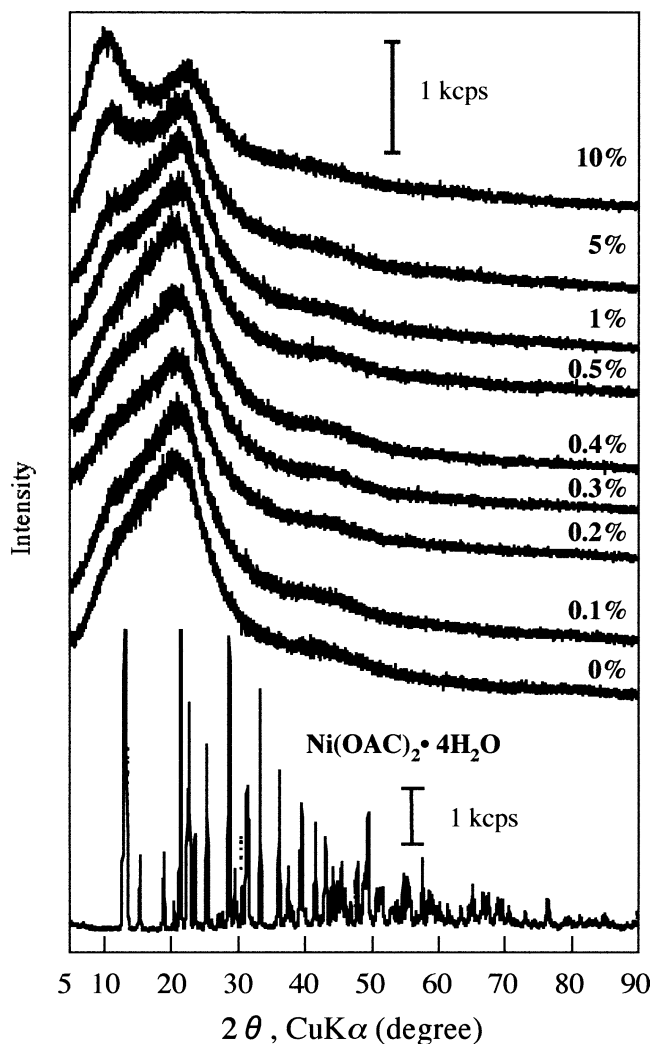


Fig. 3. X-ray diffractograms for HAL blended with various concentration of $\text{Ni}(\text{OAc})_2$, and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$

Ts of HAL- $\text{Ni}(\text{OAc})_2$ blends are shown in Fig. 2. The Tg of HAL was elevated by the addition of nickel. At 1.0% nickel it reached 155°C. When more than 5% nickel was added, the Tg of HAL blends disappeared. These results suggested that the thermal mobility of HAL was depressed by the addition of the nickel salt. The Ts was more sensitive to the charge of the nickel salt than was Tg and increased markedly with increasing charge of the nickel salt. The fusible property of HAL disappeared upon the addition of 0.4% nickel. It is well known that metallic ions chelate to lignin,¹⁹ so HAL was likely to form a complex with $\text{Ni}(\text{OAc})_2$ through the hydroxyl groups and the oxygen of carbonyl groups and ether linkages, leading to depression of the thermal mobility of HAL. The assumption was supported by the XRD results (Fig. 3). When the $\text{Ni}(\text{OAc})_2$ charge increased, a broad diffraction peak at a low angle was increased. The peak was obviously different from the peaks of $\text{Ni}(\text{OAc})_2$ and HAL. These results suggested that a huge ordered structure was formed by the complexation.

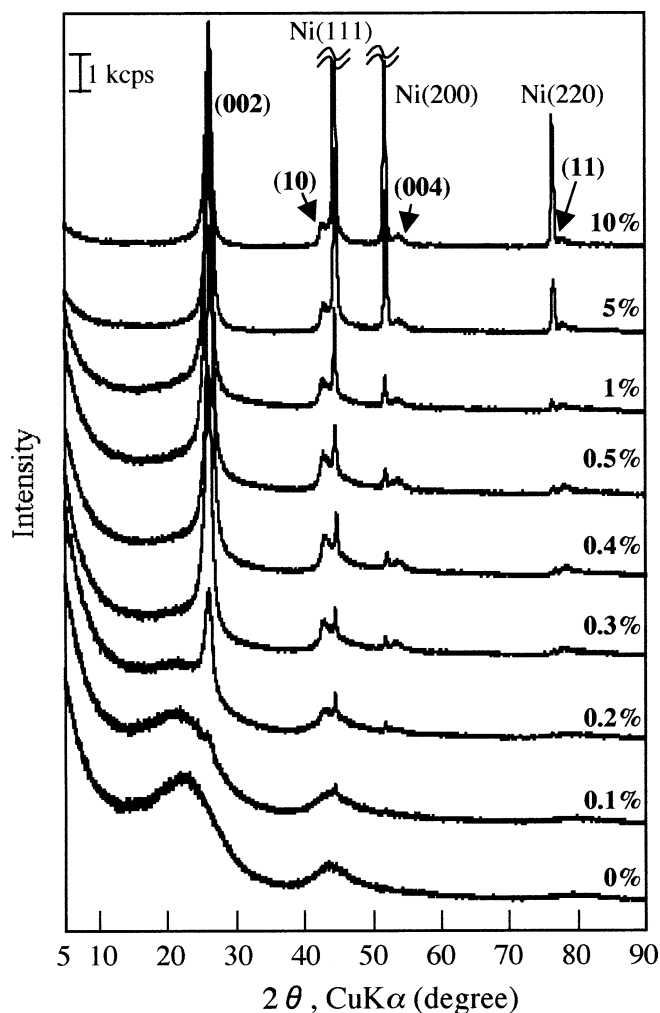


Fig. 4. X-ray diffractograms for blended carbons of HAL and Ni with various charges of $\text{Ni}(\text{OAc})_2$

Influence of nickel concentration on structural change of HAL – nickel carbon

The XRD of the blends carbonized at 1000°C was measured to investigate the effect of catalytic graphitization, as shown in Fig. 4. Strong diffraction peaks for nickel metal were observed as the $\text{Ni}(\text{OAc})_2$ charge increased. This indicates that $\text{Ni}(\text{OAc})_2$ is decomposed by heating at 1000°C and forms nickel crystals in the carbonized HAL.

The diffractogram of the carbonized HAL showed a broad peak at about 22°, implying that HAL carbon has no graphite structure. However, another broad peak was observed at about 44° that approximately corresponds to the (10) diffraction of turbostratic carbon. This indicates that small hexagonal layer units have already formed in the carbonized HAL at 1000°C. Consequently, HAL carbon prepared at 1000°C contained the poorly developed lattice texture of graphite.

After adding 0.2% nickel, a clear peak of the (002) diffraction appeared at 26.0° in the diffractogram of the

Table 1. Influence of nickel concentration on interplanar spacing (d_{002}) and apparent crystallite size ($L_{c(002)}$) of the blended carbons

Nickel concentration (%)	Peak angle 2θ (degrees)	d_{002} (Å)	$L_{c(002)}$ (Å)
0	21.7	—	—
0.01	21.4	—	—
0.05	21.3	—	—
0.1	21.8	—	—
0.2	26.0	3.42	37.3
0.3	26.0	3.42	69.2
0.4	26.0	3.42	69.7
0.5	26.2	3.40	71.8
1.0	26.1	3.41	78.1
5.0	26.3	3.39	88.9
10.0	26.1	3.41	94.4

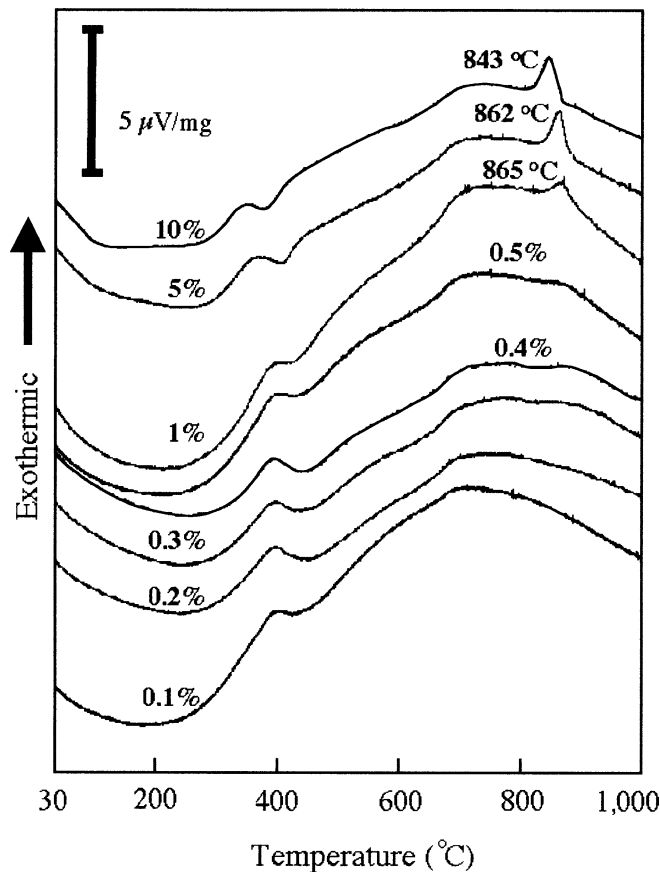
carbonized blend. However, no diffraction peaks [e.g., those assigned to (004) diffraction of graphite] were observed. Table 1 summarizes the 2θ , d_{002} , and $L_{c(002)}$ of the resulting carbons. The (002) angle was slightly lower than that of graphite; the d_{002} of the carbonized blend of HAL and 0.2% nickel (3.42 Å) was larger than that of graphite (3.35 Å). These results suggest that the carbonized blend was classified into turbostratic carbon.

The d_{002} of the carbonized blends showed a tendency to shorten with increasing nickel concentration. The d_{002} of the blend carbon with 5% nickel was 3.39 Å. This value was similar to that of the G-component but a little larger. Although the structure of a certain carbon derived by boron-catalytic graphitization was changed from the A-component to the G-component via the T-component, depending on the boron concentration,²⁰ such transition was not observed for HAL carbons.

The $L_{c(002)}$ of the blend carbons also had a tendency to become longer with increasing nickel. However, even the maximum value at 10% nickel (94.4 Å) was much smaller than that of the G-component. Consequently, the development of carbon crystallite of HAL was performed by the T-effect. The Ni catalyst has G- and T-effects, but the effects depend on the particle size of the catalyst.²¹ In the HAL-nickel blends, it was assumed that $\text{Ni}(\text{OAc})_2$ was dispersed well in HAL because the two materials were homogeneously dissolved in acetic acid. Therefore, nickel metal would also be dispersed well in HAL carbon as fine particles even though the assembly occurred at higher nickel concentrations. This is one of the reasons why the G-effect was not observed with catalytic graphitization of HAL.

Influence of carbonization temperature on the structural change of the blended carbon

The influence of the carbonization temperature on the development of carbon crystallite during catalytic graphitization of HAL was investigated by DTA and XRD. All the DTA curves for blends in the range of 0.1%–10.0% $\text{Ni}(\text{OAc})_2$ (Fig. 5) showed an exothermic peak at about 400°C, followed by a gradual exothermic reaction through 1000°C. This reaction was attributed to the thermal

**Fig. 5.** Differential thermal analysis (DTA) curves for HAL blended with various concentrations of $\text{Ni}(\text{OAc})_2$

decomposition and carbonization of lignin.²² In the case of blends with 1%–10.0% $\text{Ni}(\text{OAc})_2$, another distinguishable peak appeared at around 850°C. The peak shifted to a low temperature with increasing nickel concentration. The exothermic reaction must be caused by the catalytic graphitization.

The XRD of the 10% Ni blends carbonized at several temperatures was measured, as it is easy to detect the effect of catalytic graphitization with high concentrations of catalyst. The formation of nickel crystals was observed for 800°C carbonization, but no graphite peak was detected (Fig. 6). At more than 850°C, the (002) diffraction peak was clearly confirmed. The d_{002} of such carbons was 3.40 Å, suggesting that the carbon was a T-component. On the other hand, the $L_{c(002)}$ was slightly increased from 83.9 Å to 94.4 Å with increasing carbonizing temperature. Consequently, the XRD results reveal that the structural change in HAL carbon from disordered carbon to T-components during catalytic graphitization occurs even at 850°C. The temperature of the structure transition was consistent with the exothermic peak at 843°C with DTA. Hence we can monitor the exothermic reaction resulting from the catalytic graphitization. The reaction might be attributable to structural stabilization from the disordered to the ordered carbon or the remarkable development of hexagonal layers.

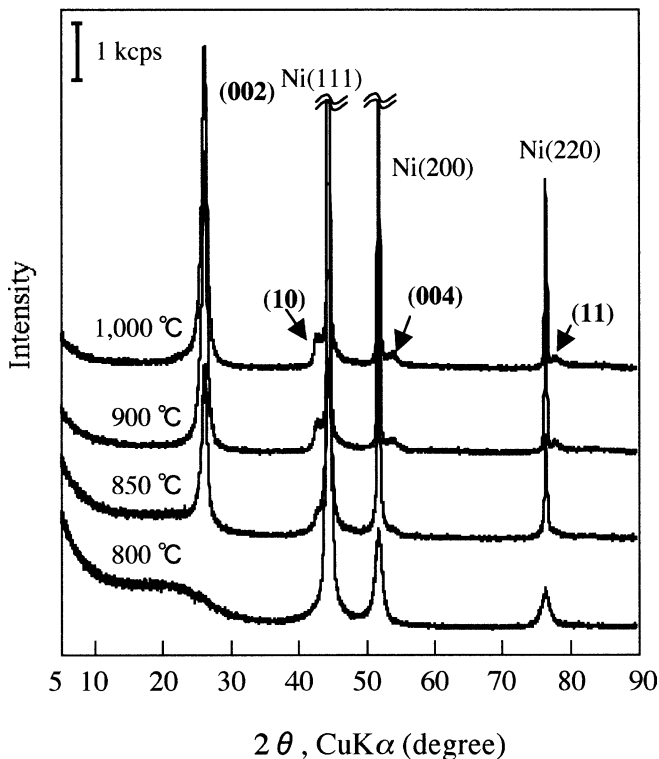


Fig. 6. X-ray diffractograms for HAL blended with 10% Ni(OAc)₂ carbonized at various temperatures

Conclusions

Hardwood acetic acid lignin can be converted to a carbonaceous material with a well-developed, ordered structure by the catalytic graphitization method using Ni(OAc)₂ as the catalyst. Disappointingly, the resulting carbon was classified as a T-component, not a complete graphite structure (A- and G-components). Undoubtedly, the effect of catalytic graphitization was brought about by adding 0.3% catalyst based on the specimen, although the satisfactory effect of catalytic graphitization, in general, was attained in the presence of several percent of catalyst. The appearance of a catalytic effect with a trace of catalyst was mainly due to the good dispersion of catalyst particles in the carbon sources, which resulted from the homogeneous solution of HAL and Ni(OAc)₂. At the present nickel content in HAL, HAL still had fusibility, indicating the possibility of molding HAL into any desired form.

Furthermore, we detected the exothermic peak resulting from catalytic graphitization by DTA. Based on the results, the development of carbon crystallite was found at relatively low carbonization temperatures (e.g., 865°C) for the 1% Ni blend. Thus, HAL can be converted to the carbon with a T-component by adding even a small amount of catalyst at a carbonization temperature of less than 100°C. We are currently investigating catalytic graphitization for HAL moldings.

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