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Citation	炭素, 2002(203), 113-116 https://doi.org/10.7209/tanso.2002.113
Issue Date	2002-07-25
Doc URL	http://hdl.handle.net/2115/72925
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Graphite Formation at 1150 – 1200°C from Hard-carbon Precursors and Magnetite

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(Received January 10, 2002, Accepted May 5, 2002)

Graphite crystals were formed from a mixture of poly(vinyl pyrrolidone) (PVP) or polyacrylamide (PAA) powder and magnetite powder at 1150–1200°C. The graphite was identified by X ray diffraction and transmission electron microscopy. The carbon yield from PAA at 1200°C was about four times of that from PVP, but PAA needed prolonged heat treatment to transform turbostratic carbon to graphite. The graphite formation with magnetite from hard-carbon precursors (PVP and PAA) required higher temperatures and longer treatment time than with magnetite and soft-carbon precursors, such as poly(vinyl chloride) (PVC) and poly(vinyl alcohol) (PVA). Electron microscopic observations suggested that in addition to a carbide mechanism, a dissolution-precipitation mechanism may also take part in the graphitization of carbon derived from PVP and PAA.

KEYWORDS : Catalytic graphitization, Hard carbon, Organic polymer compounds,
Transmission electron microscopy

1. Introduction

Previously, we reported that graphite crystals are formed from mixtures of metal oxides (Fe_3O_4 , Fe_2O_3 , NiO etc.) or iron powder and powders of organic polymers such as poly(vinyl chloride) (PVC) and poly(vinyl alcohol) (PVA), by heat treatment at 1000–1100°C^{1,2)}. This is a potential process to form pure graphite at low temperatures but the yield of carbon from PVC and PVA is less than 5 mass% at 1000°C. The PVC and PVA are graphitizing carbon (soft carbon) sources, but poly(vinyl pyrrolidone) (PVP), which has been reported to form non-graphitizing carbon (hard carbon)³⁾ also formed graphite crystals at 1200°C by this process²⁾. There is the possibility that polymers reported to be hard-carbon sources give much higher carbon yields. Accordingly the present work further investigated the graphitization of PVP, as well as the graphitization of polyacrylamide (PAA), a potential precursor of graphite.

2. Experimental

Particle size and the degree of polymerization were ca. 50 μm and 90 for PVP, and ca. 1.2 mm and 13000 for PAA. Magnetite (Fe_3O_4) powder was an average of ca. 0.3 μm . In some experiments, ca. 300 μm iron powder was also used. The chemicals used were commercially available as reagents. The powder mixtures in different mass ratios of two starting compounds, for example PVP and Fe_3O_4 , were heated to a temperature between 700 and 1200°C at 500 K h⁻¹ in flowing argon, and kept at the set temperature for 5–20 h. The products were immersed in 5 mol dm⁻³ HCl overnight to dissolve iron which was formed by the reduction of Fe_3O_4 . Carbon residue was examined by X ray diffraction (XRD, Cu K α irradiation), scanning electron microscopy (SEM,

acceleration voltage 2 kV), and transmission electron microscopy (TEM, acceleration voltage 200 kV). Elemental analyses for C, H, and N were also carried out.

3. Results and Discussion

3.1 Carbonization and yield

The carbon yield after 1 h of treatment without Fe_3O_4 is shown as a function of the heat treatment temperature (HTT) in Fig.1. The results of PAA were different from the TG (4 K min⁻¹) curve reported by Dollimore and Heal³⁾; they reported a large mass loss (more than 30%) up to 300°C. The PAA powder used in this work sintered at 300°C and the mass loss was smaller even after 1 h, while above 500°C the loss was much larger than

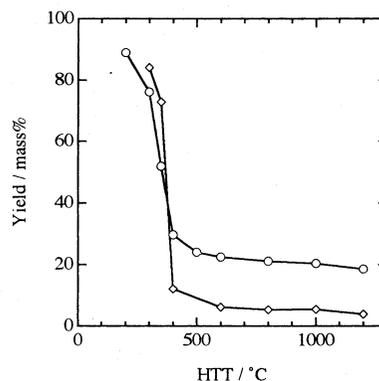


Fig.1 Carbon yields from PVP (\diamond) and PAA (\circ) after 1 h treatment without Fe_3O_4 as a function of heat treatment temperatures (HTT) in Ar. Heating rate was 500 K h⁻¹.

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the reported values. The difference cannot be explained so far. The yields at 1000–1200°C from PVP were similar to those from PVC and PVA, about 5 mass%, while they were about 20 mass% from PAA. Carbons derived from PVP and PAA contained small amounts of nitrogen in addition to hydrogen even when formed at 1200°C : the N/C mole ratios at 1000–1200°C were ca.0.05 for PVP and 0.1–0.05 for PAA. This may be due to the different chemical compositions (N/C in PVP is 1/6, and in PAA it is 1/3) and structure. After the heat treatment with Fe₃O₄, however, the elemental analysis detected no nitrogen in any of the carbon residue after the HCl treatment. This suggests that Fe₃O₄ functions in the decomposition of these polymers even when graphitization does not take place.

Carbonization of PVP was similar to that of PVA, carbonaceous compounds were formed in a liquid phase at around 400°C. With PAA carbonization started at slightly lower *HTT* and pitchlike compounds were formed at around 350°C. The carbon yield around 1000°C suggests that PAA is a useful precursor.

3.2 Graphitization of PVP

By heating a mixture of PVP : Fe₃O₄=70 : 30 (mass%) for 5 h in Ar, products mainly composed of iron and carbon were obtained ; and SEM photographs of the products at 1000 and 1200°C are shown in Fig.2. The products at 1000°C were irregular in shape (Fig.2 (a) and (b)), but those formed at 1200°C were 100–1500 μm diameter spheres (Fig.2 (c)) and carbon particles were embedded in iron (Fig.2 (d)). According to the Fe-C phase diagram⁴⁾, liquid phases form above 1150°C. The shape of the products at 1200°C clearly indicates that they were melted during the heat treatment.

By XRD, the Fe₃O₄ was found to be reduced to α-Fe and Fe₃C at 1000°C, and above 1000°C no Fe₃C peaks and only α-Fe were detected. After the HCl treatment, however, unresolved diffraction peaks were observed at 2θ=40–50° (overlapping with the 100 and 101) up to 1100°C, as shown in Fig.3 , suggesting the presence of iron carbides. At *HTT* ≤ 1100°C, the 100 and 101 lines of carbon are not clearly separated and the 006 line is

indistinguishable, whereas at *HTT* ≥ 1150°C carbon 00*l* lines become very sharp and there is separation between the 100 and 101 lines. Based on precise XRD measurements of the 002 line, *d*₀₀₂ and *L*_c(002) were estimated as a function of *HTT* as shown in Fig.4. Here, the *d*₀₀₂ value was rounded off to four decimal places. The *d*₀₀₂ was less than 0.336 nm even at 800°C, but the 002 line tailed to the lower 2θ side for the samples heated further (up to 1100°C). At *HTT* ≥ 1150°C, the *d*₀₀₂ became 0.3355 nm and graphite of *a*₀=0.2456 nm and *c*₀=0.6710 nm was obtained. In this temperature range *L*_c(002) became larger than 50 nm and well aligned extensive layers of graphite were observed by TEM²⁾. Graphite was formed from the PVP : Fe₃O₄=80 : 20 mixture, and the PVP : Fe₃O₄=90 : 10 mixture

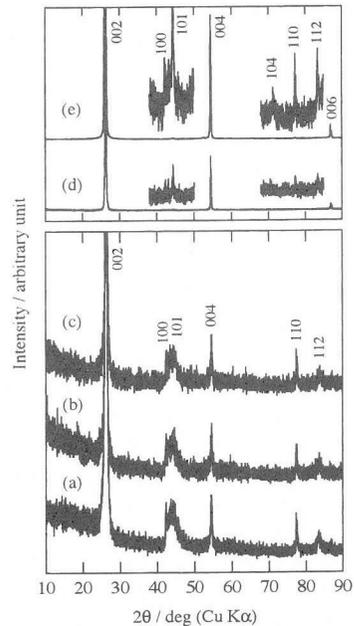


Fig.3 XRD patterns of carbonaceous products obtained from a PVP : Fe₃O₄=70 : 30 mixture by 5 h treatment at (a) 1000°C, (b) 1050°C, (c) 1100°C, (d) 1150°C, and (e) 1200°C. The formed iron was removed by treatment in HCl.

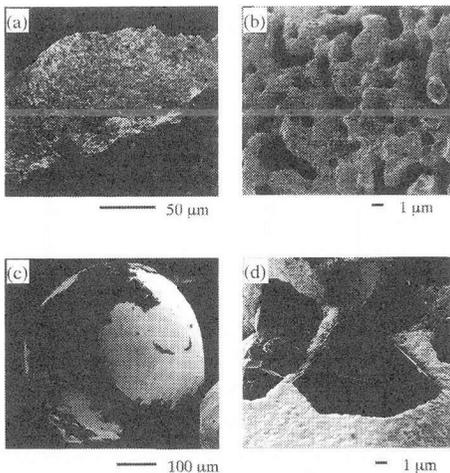


Fig.2 SEM micrographs of the products from the PVP : Fe₃O₄=70 : 30 (mass%) mixture by heating at (a) 1000°C and (c) 1200°C for 5 h in Ar.

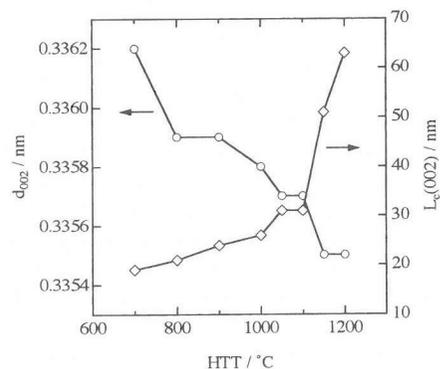


Fig.4 *d*₀₀₂ and *L*_c(002) as a function of *HTT*. Conditions as in Fig.2.

yielded carbon with larger d_{002} in addition to graphite. With PVP : $\text{Fe}_3\text{O}_4 \leq 60 : 40$, no carbon residue was obtained because of low carbon yields.

For mixtures of iron oxides and PVA at $HTT \leq 1100^\circ\text{C}$, it was assumed that graphite was formed through decomposition of iron carbides : fine particles of iron produced by the reduction of iron oxides react with similarly reactive decomposition products of PVA, leading to the formation of iron carbides⁴¹. As described above, however, the graphite formation with PVP is more difficult than with PVC and PVA. In additional experiments, mixtures of PVP and metal iron powder were treated at 1200°C for 5 h. At all the mixing ratios from PVP : $\text{Fe} = 10 : 90$ to $50 : 50$, the 002 diffraction profile of the resultant carbon is a composite with graphite and an additional carbon 002 line with $d_{002} = 0.341 - 342$ nm, while 00 l lines other than 002 were very weak. From the mixture of PVA : $\text{Fe} = 10 : 90$, the heat treatment at 1000°C for 1 h yielded graphite crystals as a single phase ; a non-graphitized part remained for the case of PVA : $\text{Fe} \geq 30 : 70$ ²¹. As the carbon yields of the two polymers are nearly the same, this suggests that the decomposition products from PVP above 400°C , which are pitch-like and fused (**Fig.1**), are not as reactive with iron as those from PVA. It appears that good contact between carbonized PVP and fine iron particles freshly formed by reduction of Fe_3O_4 is an important factor in the graphite formation. In addition, a single graphite phase was obtained when the mixtures melted at 1200°C as shown in **Fig.2** (c), (d), and **Fig.3**, whereas graphitization was not completed at 1000°C as shown in **Fig.2** (a), (b), and **Fig.3**, where the mixtures did not melt. These results suggest that an additional mechanism, a dissolution-precipitation mechanism, may be involved in the graphitization of PVP.

3.3 Graphitization of PAA

The XRD patterns of the reaction products from PAA : $\text{Fe}_3\text{O}_4 = 50 : 50$ at 1000°C for 5 h showed peaks of α -Fe, Fe_3C , and carbon, but at 1200°C the peaks of Fe_3C disappeared while there were γ -Fe peaks. The XRD patterns of the carbon residues after the HCl treatment are shown in **Fig.5**. The unindexed peaks shown by arrows in **Fig.5** (a) could be assigned to Fe_3C . Thus, the product at 1000°C contained iron carbide, similar to PVP, but no carbide peaks were detected in the product at 1200°C . The XRD pattern of the product at 1200°C resembles that of natural graphite (**Fig.5** (b)) and a layered structure is observed (**Fig.5** (c)), but the development of the 00 l lines is not as good as PVP (**Fig.3** (e)). The carbon 002 line in **Fig.5** (b) is apparently symmetric but it is not reproducible. Often the peak was observed as shown in **Fig.6** (b) : d_{002} of the small peak was 0.341–342 nm and that of the main peak was 0.3355 nm, suggesting a two-phase graphitization. The TEM photographs of this sample are shown in **Fig.7**. There were small particles like the one shown in **Fig.7** (a) and they were graphite crystals as shown by the selected area electron diffraction in **Fig.7** (b). Some parts, however, were typical turbostratic carbon, as shown in **Fig.7** (c), consistent with the results by XRD.

Turbostratic carbon did not disappear by decreasing the PAA ratio to 40% (Fe_3O_4 60%) under the same treatment conditions (1200°C , 5 h) as shown in **Fig.6** (a). When PAA : $\text{Fe}_3\text{O}_4 \leq 35 : 65$, no carbon residue was obtained after the HCl treatment.

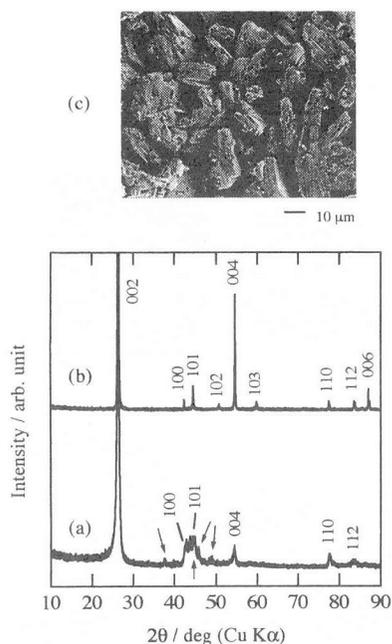


Fig.5 XRD patterns of carbonaceous products obtained from a PAA : $\text{Fe}_3\text{O}_4 = 50 : 50$ mixture by 5 h treatment at (a) 1000°C and (b) 1200°C ; and (c) SEM micrograph of (b). The formed iron was removed by treatment in HCl. Unindexed peaks (arrows) in (a) were assigned to Fe_3C .

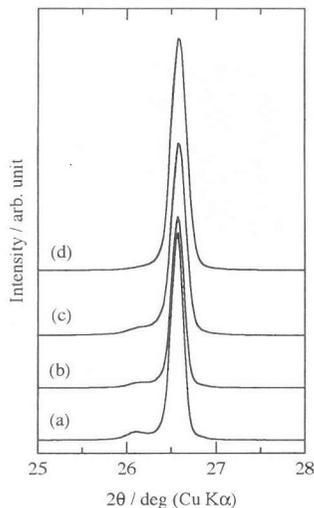


Fig.6 XRD patterns around the carbon 002 peak of the carbonaceous products obtained at 1200°C : (a) PAA : $\text{Fe}_3\text{O}_4 = 40 : 60$, 5 h; (b) PAA : $\text{Fe}_3\text{O}_4 = 50 : 50$, 5 h; (c) PAA : $\text{Fe}_3\text{O}_4 = 50 : 50$, 10 h; and (d) PAA : $\text{Fe}_3\text{O}_4 = 50 : 50$, 20 h. The formed iron was removed by treatment in HCl.

Reductions in the polymer mass ratio was effective to eliminate the second phase for the graphitization of PVA and PVP, but this was not a representative measure of the graphitization of PAA. In the next step, prolonged heat treatment was carried out at 1200°C . By a 10 h treatment, the quality of the product was

much improved as indicated by the XRD pattern in Fig.8, but the carbon 002 peak shown in Fig.6 (c) still occasionally appeared. The carbon 002 peak showed as a definite single line by 20 h of treatment at 1200°C with PAA : Fe₃O₄=50 : 50, as

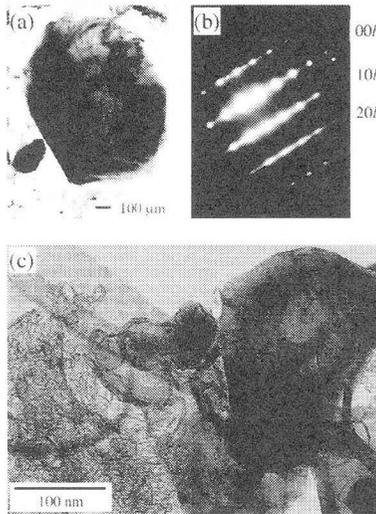


Fig.7 TEM micrograph of a part of (b) in Fig.5 and its SAED pattern, showing the formation of graphite. (c) is a photograph of another part of (b) in Fig.5, showing the formation of turbostratic structure.

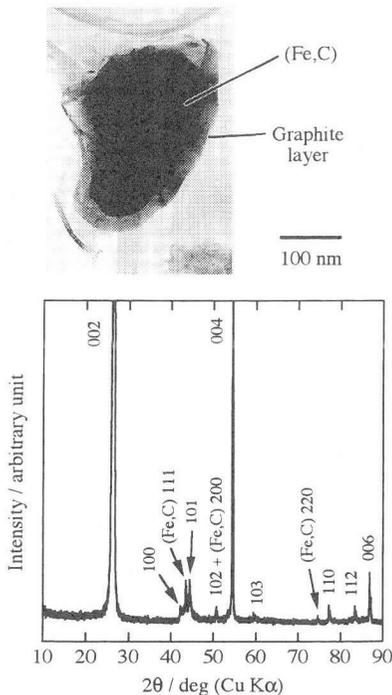


Fig.8 Example of the XRD patterns showing the formation of (Fe, C) austenite phase. The sample was formed under the conditions of (c) in Fig.6.

shown in Fig.6 (d). The yield of graphite from PAA is much higher than that from PVA or PVP, but a higher energy input is required.

As shown in Fig.8, diffraction peaks for γ -Fe, (Fe, C)⁶⁾ occasionally appeared in the carbon residues from PAA, and (Fe, C) particles covered with graphite layers were observed by TEM: the photograph in Fig.8 clearly shows a carbon 002 lattice image. These particles do not dissolve in concentrated hydrochloric acid or even aqua regia. The graphite layers covering the γ -Fe particles suggest that these layers have been formed by the dissolution-precipitation mechanism. Accordingly, as mentioned in 3.2 the dissolution-precipitation mechanism may also take part in the graphitization of the hard carbon produced from PVP and PAA.

4. Conclusions

Graphite crystals are formed from the hard-carbon precursors PVP and PAA, when mixed with magnetite and heat-treated at 1150–1200°C. The carbon yield from PAA at 1200°C is about four times of that from PVP, but PAA requires prolonged heat treatment to eliminate turbostratic carbon. The range of mixing ratios of PVP to Fe₃O₄ which gives graphite is 70 : 30 to 80 : 20. A 5 h treatment at 1200°C yields no carbon residue with PVP ≤ 60%, and two-phase graphitization takes place with PVP = 90%. With PVP = 90%, turbostratic carbon may be eliminated by prolonged heat treatment, analogous to PAA. With PAA : Fe₃O₄ = 50 : 50, a 20 h treatment at 1200°C is needed to eliminate all turbostratic carbon. Mixing ratios with more PAA have not been examined in the present work but these may require longer treatment. Thus, graphite crystal formation with magnetite is possible from the hard-carbon precursors PVP and PAA, but higher *HTT* and longer treatment time are required than with soft-carbon precursors, such as PVC and PVA. Electron microscopic observations indicate that mixtures of PVP and Fe₃O₄ melt during the heat treatment at 1150–1200°C and that γ -Fe, (Fe, C), particles covered with graphite layers are formed from the mixtures of PAA and Fe₃O₄. These suggest that in addition to the carbide mechanism the dissolution-precipitation mechanism may also take part in the graphitization of PVP and PAA.

Acknowledgment

The present work was supported by a Grant-in-Aid for Scientific Research (B) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (No.10044104).

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