FORMATION OF GRAPHITE AT 1100-1200°C FROM HARD-CARBON PRECURSORS

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Introduction

Previously, we reported that graphite crystals are formed from the mixtures of metal oxide (Fe$_3$O$_4$, Fe$_2$O$_3$, NiO etc.) or metal iron powder and poly(vinyl chloride) (PVC) or poly(vinyl alcohol) (PVA) powder by heat treatment at 1000-1100°C [1,2]. This is an interesting process to form graphite at low temperatures but the yield of carbon from PVC and PVA is about 5% at 1000°C. We surveyed raw materials including polymers, which were reported to give hard carbon, if they also graphitize at these low temperatures. In the present work, the formation of graphite crystals from mixtures of Fe$_3$O$_4$ and poly(vinyl pyrrolidone) (PVP) or polyacrylamide (PAA) at 1000-1200°C is reported.

Experimental

The powder mixtures in different mass ratios of two starting materials, for example Fe$_3$O$_4$ (average size=0.3 µm) and PVP, were heated to a temperature between 1000 and 1200°C, and kept at the temperature for 5-20 h in a flow of Ar. The products were immersed in 5 mol dm$^{-3}$ HCl overnight to dissolve iron which was formed by the reduction of Fe$_3$O$_4$. Carbon residue was examined by XRD, SEM and TEM.

Results and Discussion

By heating the mixture of PVP: Fe$_3$O$_4$ = 70:30 mass% for 5 h in Ar, Fe$_3$O$_4$ was reduced to ($\alpha$-Fe above 1000°C and Fe$_3$C was also formed at 1000°C. The carbon residues after HCl treatment did not contain nitrogen by elemental analysis. XRD patterns of the residue are shown in Fig. 1. When the heat treatment temperature (HTT) was higher than 1100°C, strong and narrow 00$_1$ lines and well split 100 and 101 lines of carbon were observed. The d$_{002}$ at 1150-1200°C was 0.3355 nm, and a$_0$ and c$_0$ were 0.2456 and 0.6710 nm, respectively. These values and morphologies of the residue, shown in Fig. 2, indicate that the products are well crystallized graphite. This is confirmed by lattice fringe image and well-defined electron diffraction spots, as shown in Fig. 3. In Fig. 1, peaks with * were tentatively assigned to rhombohedral phase but there is a possibility of carbidies. When HTT ≤1100°C, higher 001 lines were weak and 002 line tailed to the lower 2θ side. The d$_{002}$, however, was 0.3357-0.3358 nm, being close to that of graphite. With PVP: Fe$_3$O$_4$≤60:30 no carbon residue was obtained because carbon yield was similar to PVA. With PVP: Fe$_3$O$_4$ > 80:20 turbostratic structure was also formed (two-phase graphitization) and the products were not flakes like Fig. 2.

When metal iron powder (average size=300 µm) was used instead of Fe$_3$O$_4$, two-phase graphitization took place similarly. Further, with mixtures of the carbonized PVP powder separately formed at 1200°C and Fe$_3$O$_4$ powder, two-phase graphitization took place likewise. These indicate that good contact between carbonized PVP and iron is necessary before fine iron particles formed by the reduction of Fe$_3$O$_4$ aggregate. PVP is suitable in this respect, since it decomposes through liquid phase. Above results suggest that the mechanism of graphite formation is related to the formation of liquid phase consist of iron and carbon (graphite), which is supposed to occur above 1153°C from a phase diagram.

Carbonization behavior of PM without Fe$_3$O$_4$ was similar to PVP but the yield was about 20% at 1000-1200°C. XRD patterns of the residue from PM: Fe$_3$O$_4$=50:50 after 5 h treatment are shown in Fig. 4. Results are similar to PVP (Fig. 1) but the development of 001 lines at 1200°C is not so good as PVP. Carbon residue did not contain nitrogen. Detailed measurements of 002 line revealed two-phase graphitization, and a single phase was not obtained by increasing the ratio of Fe$_3$O$_4$ as shown in Fig. 5. The residue at 1200°C looked like the one from PVP: Fe$_3$O$_4$ > 80:20 by SEM. To eliminate the second phase, prolonged treatment was carried out at 1200°C. Carbon 002 peak was found to be single line (d$_{002}$=0.3355 nm) after 20 h treatment, as shown in Fig. 6. From this result we can expect a shorter heating time for graphitization. PM is a promising material to produce graphite crystals efficiently at low temperatures.

References

Fig. 1  XRD patterns of the residue from PVP: Fe\textsubscript{3}O\textsubscript{4}=70:30 by 5 h heat treatment.

Fig. 2  SEM photograph of the carbon residue at 1150°C in Fig. 1.

Fig. 3  Selected area electron diffraction pattern and lattice fringe image of the carbon residue at 1200°C in Fig. 1 by TEM.

Fig. 4  XRD patterns of the residue from PAA: Fe\textsubscript{3}O\textsubscript{4}=50:50 by 5 h heat treatment.

Fig. 5  XRD patterns of the residue at 1200°C for 5 h.

Fig. 6  XRD patterns of the residue from PAA: Fe\textsubscript{3}O\textsubscript{4}=50:50 at 1200°C.