EFFECT OF ADDITION OF Sm_2O_3 AND Nd_2O_3 ON THE GRAPHITIZATION OF PHENOLFORMALDEHYDE-RESIN CARBON BEADS

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Introduction

An effect of addition of rare earth elements on graphitization of non-graphitizing carbon is interesting, but is not known well. We investigated an effect of some rare earth elements on graphitization of non-graphitizing carbon and found samarium oxide gave a remarkable influence on the graphitization [1]. There is also interest in graphite microsphere, but few report on formation of graphite microsphere from non-graphitizing carbon beads.

This paper describes a structural and morphological change with HTT of phenolformaldehyde-resin carbon beads with samarium oxide or neodymium oxide addition in comparison with that of non-added beads.

Experimental

Phenolformaldehyde-resin beads with average particle size of 30.9 μm (PF-resin bead, Nippon Carbon Co.) were used as a starting material. The beads were heat-treated at 900°C for carbonization (PF-9 beads). Then Sm_2O_3 or Nd_2O_3 was added to the PF-9 beads. Sm content of the mixed powder was about 5at% against carbon. After calcination at 1000°C, the PF-9 beads were heat-treated at 1500, 1800, 2000, 2200 and 2500°C for 1 hour in Ar gas (PF-Sm or PF-Nd beads). The PF-Sm or PF-Nd beads were investigated by XRD analysis and SEM observation. Polarized microscopic observation was also carried on the polished section of the PF-Sm and PF-Nd beads heat-treated at 2500°C. Heat-treated PF-beads were oxidized at 800°C in air and investigated by SEM-EDX observation.

Results and Discussion

1. Structural change

Figure 1 shows an effect of heat treatment on XRD profiles of the PF-9 beads along with that of the PF beads. The PF-9 beads showed broad 002, 10 and 11 graphite peaks which were characteristic for non-graphitizing type carbon up to 1800°C. Above 2000°C, a sharp 002 peak is observed. Figure 2 shows an effect of heat treatment on XRD profiles of the PF-Sm beads along with those of the mixed powder and Sm_2O_3 powder. The PF-Sm beads showed strong Sm_2O_3 peaks at 1500°C, while they showed a strong and sharp graphite 002 peak above 1700°C with small 004, 101, 100, 110, 112 and

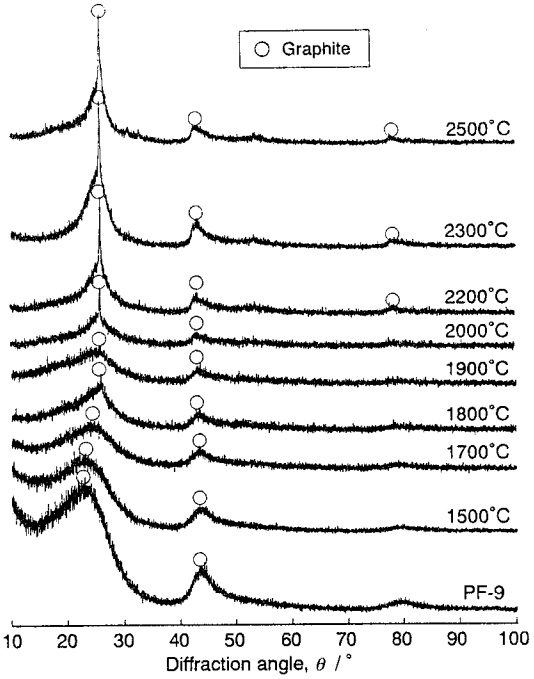

Fig. 1. Effect of HTT on XRD profiles of the PF-9 beads.

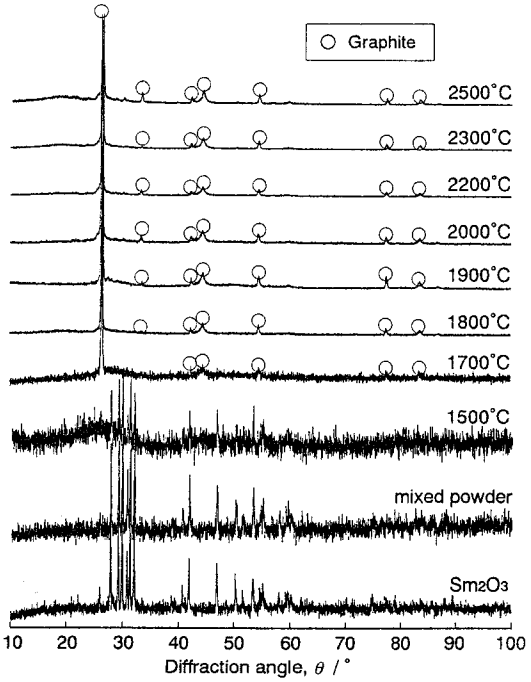

Fig. 2. Effect of HTT on XRD profiles of the PF-Sm beads.

006 graphite peaks. This result suggests that three dimensional structural ordering occurred above 1700°C and that Sm_2O_3 addition gave remarkable influence on a structural change of the PF-9 beads. On the other hand, in the case of the PF-Nd beads, peaks of neodymium carbides were found with a sharp 002 peak above 1700°C.

Figure 3 shows a HTT dependence of d(002) of the heat-treated PF-9, PF-Sm and PF-Nd beads. The d(002) spacing of the PF-9 beads remained about 3.43 Å even after heat treatment at 2500°C. That of the PF-Sm or PF-Nd beads was 3.356-3.358 Å above 1700°C. Figure 4 shows a HTT dependence of crystallite size of the PF-9, PF-Sm and PF-Nd beads. The Lc(002) of the PF-9 beads was below 500 Å, while that of the PF-Sm or PF-Nd beads was larger than 500 Å.

2. Morphological change

The PF and PF-9 beads showed almost perfect spherical shape. The PF-9 beads maintained a spherical shape after heat treatment even at 2500°C. Some small particles of about 1μm in size appeared on a surface of the beads above 1800°C. The PF-Sm and PF-Nd beads also kept a spherical shape up to 1700°C and coexistence of the additive powder was observed up to 1700°C in the case of the PF-Sm beads and up to 2500°C in the case of the PF-Nd beads. On the other hand, the PF-Sm beads heat-treated above 1800°C did not maintained a spherical shape.

The oxidized PF-Sm or PF-Nd beads was spherical shape of about 5μm in diameter, and Sm or Nd and O peaks were observed as strong peaks by EDX. This suggests that the additive existed all over the inside of the particles.

3. Textural change

From polarized microscopic observation, it was known that the PF-9 and heat-treated PF-9 beads showed an optical isotropy, while the PF-Sm or PF-Nd beads showed an optical anisotropy and several grains were found in each bead of the PF-Sm or PF-Nd. These results mean that graphite structure was formed by addition of the additive and each graphite grains grew inside of the beads had its own orientation.

Conclusions

By addition of Sm_2O_3 or Nd_2O_3 phenolform-aldehyde-resin carbon beads changed into graphitic structure with heat treatment above 1700°C, while the carbon beads without additive remained non-graphitizing type carbon. The shape of the beads was also changed with heat treatment by addition of Sm_2O_3,

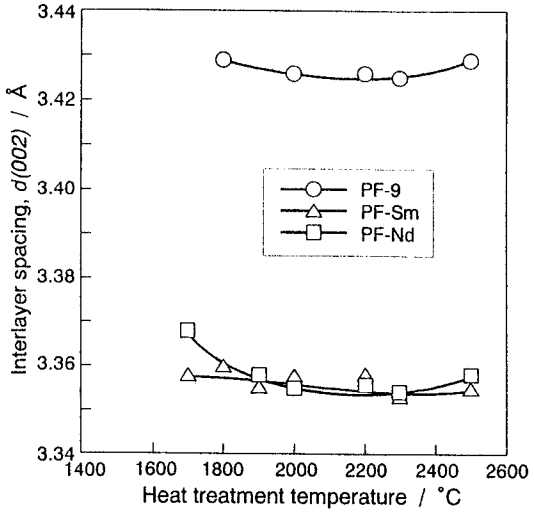

Fig. 3. HTT dependence of d(002)-spacing of the PF-9, PF-Sm and PF-Nd beads.

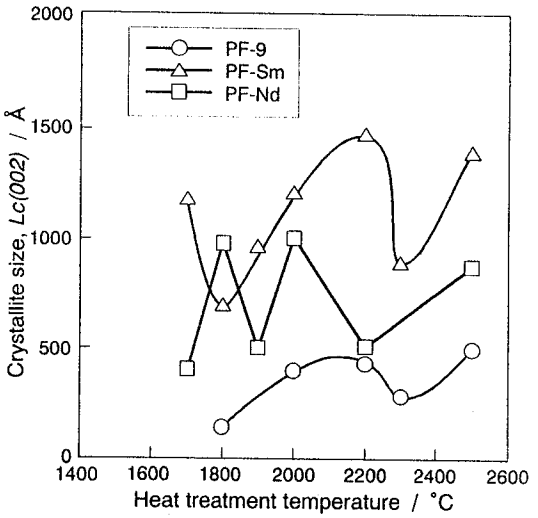

Fig. 4. HTT dependence of Lc(002) of the PF-9, PF-Sm and PF-Nd beads.

while that unchanged in the case of the beads without additive and the beads with Nd_2O_3 addition.

Growth of graphite grains with its own orientation was observed all the inside of the beads with Sm_2O_3 or Nd_2O_3.

Acknowledgments

Part of this work was supported by grant-in-aid for scientific research (C)(No.08650787), the ministry of education, science, sport and culture of Japan.

References

1. K. Kobayashi et. al., Proc. of "Carbon 96", (1996), pp.242-243.