NOTES

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Effects of $FeCl_3$ on the Graphitizability of Coal Tar Pitch

Sugio OTANI and Asao OYA
Faculty of Technology, Gunma University, Kiryu, Gunma
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For the purposes of raising the softening points (S.P.) of pitch materials or increasing the yields of cokes, raw pitch materials are conventionally distilled with some additives or by bubbling in an oxidizing gas, such as Cl_2 or air.[1] This manner, though, generally leads to a lowering of the graphitizability of the resulting carbonaceous materials. In an earlier paper,[2] however, it has been reported that the addition of $AlCl_3$ was remarkably effective in raising the S.P. of the residual pitch materials, but that it did not lower their graphitizability. Consequently, $AlCl_3$ is an interesting additive.

In order to clarify the action of $AlCl_3$ and to determine whether $AlCl_3$ is the only kind of additive having such effects, or whether three are some other additives with the same effects, it was thought advisable to investigate the effects of $FeCl_3$, which has a strong resemblance to $AlCl_3$ in character. The experiments described below deal with the effect of the addition of $FeCl_3$ as compared with that of the addition of Fe powder, and with the case of an entire absence of additives.

Experimental and Results

A mixture of 10 g of coal tar pitch and either 1 g of $FeCl_3$ or 0.5 g of Fe powder (under 100 mesh) was distilled with bubbling N_2 gas at desired temperatures below 550°C for 10 minutes. Coal tar pitch without any additives was also distilled as a reference. From the results shown in Fig. 1, it is clear that the S.P. of the residual pitch materials was more effectively raised by the addition of $FeCl_3$ than in the other two cases.

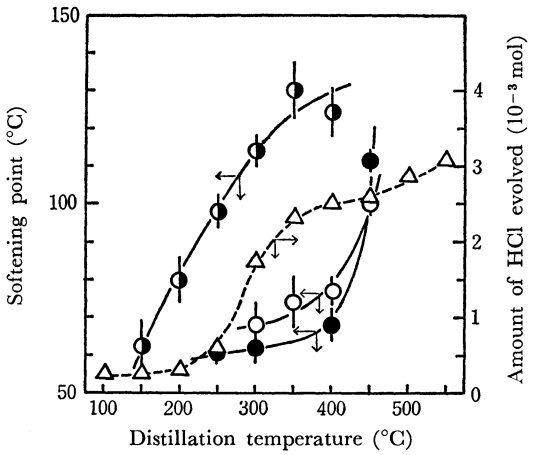

Fig. 1. Changes of softening point and amount of HCl evolved with distillation temperature.
S.P.: —○— no additive, —◑— $FeCl_3$ 10%, —●— Fe 5%, Amount of HCl, —△—

In order to measure the amounts of HCl evolved on heating, the mixture of 10 g of coal tar pitch and 1 g of $FeCl_3$ was heated with bubbling N_2 gas up to 550°C at the rate of 10°C/min, and the HCl thus evolved was absorbed in water and was estimated on the basis of titration with a NaOH solution at 50°C intervals. The evolution of HCl was accelerated at 250—350°C, as is shown in Fig. 1, it corresponded to only 17% of the amount of Cl atoms in $FeCl_3$, even after heating up to 550°C. It is the most characteristic fact that, in spite of the remarkable rise in the S.P. in the distillation temperature range below 250°C, the evolution of HCl in the same range is very small in amount.

In order to estimate the effects of additives on the graphitizability of residues, the following examinations were carried out. First, coal tar pitches were distilled at 550°C for 10 min under the conditions listed in Table 1. The resulting carbonaceous residues were heat-treated at the desired temperatures below 2400°C, and the graphitizability of the resulting carbons was examined by the X-ray diffraction technique.[2] All of the carbonaceous residues which were obtained by bubbling N_2 gas, regardless of the kinds and the amounts of additives, gave graphitizable carbons which show single and symmetrical (002) diffraction patterns upon graphitization. Figure 2 shows the changes in the interlayer spacing d_{002}, and the crystallite thickness, L_c, with

Table 1. Atmospheres of the distillation and the amounts of additives (wt%)

Additive	Atmosphere: N_2	Atmosphere: Cl_2
Fe	3.44	0.69, 1.72, 3.44, 17.21
$FeCl_3$	2, 5, 10, 50	2, 5, 10, 50

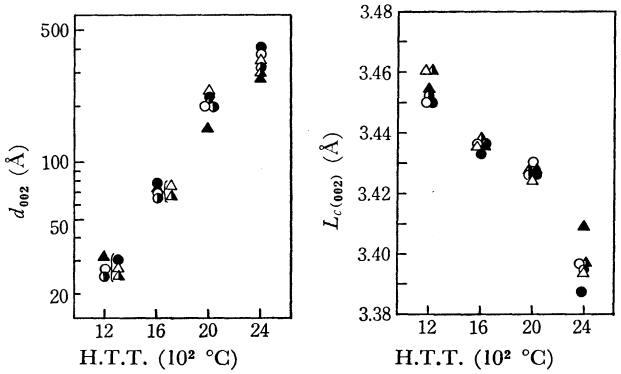

Fig. 2. X-Ray parameters of the residual carbons obtained by the distillation with N_2 gas.
—○—: None, —◑—: $FeCl_3$ 2%, —●—: $FeCl_3$ 5%, —△—: $FeCl_3$ 10%, —▲—: $FeCl_3$ 50%, —▲: Fe 3.44%

1) S. Otani and A. Oya, *Kogyo Kagaku Zasshi*, **73**, 493 (1970).
2) S. Otani and A. Oya, *ibid.*, **73**, 1110 (1970).

the heat-treatment temperature. From the results shown in Fig. 2, it is evident that all the resulting carbons were typically graphitizable. On the other hand, when coal tar pitches were distilled with bubbling Cl_2 gas, all of the resulting carbonaceous residues, regardless of the kinds and the amounts of additives used in this study, gave non-graphitizable carbons which exhibited composite (002) diffraction patterns upon graphitization. It should be pointed out that, when $AlCl_3$ was added in our previous study,[2] the resulting carbonaceous residues gave graphitizable carbons.

Conclusion

The above results show that the addition of $FeCl_3$ is remarkably effective in raising the S.P. of residual pitch without any deterioration of the graphitizability of carbon obtained in the subsequent heating stage. At temperatures below 250°C, the evolution of HCl from the pitch with the addition of $FeCl_3$ is very small in amount in spite of the remarkable rise in the S.P. of the residue. On the other hand, the addition of Fe powder is not effective in raising the S.P. of the residues. Consequently, it seems reasonable to consider that such effects caused by the addition of $FeCl_3$ depend on the action of neither Cl nor Fe, which may be formed by a decomposition of $FeCl_3$ in the distillation stage, but depend on some action of the entire molecule of $FeCl_3$. Such effects of $FeCl_3$ were similar to those of $AlCl_3$ reported previously.[2] Therefore, the effects caused by the addition of $FeCl_3$ or $AlCl_3$ are thought to be due to a certain property, such as the acidic property, which is common to both the reagents.