Puffing Inhibitors for Coal Tar-Based Needle Coke

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Abstract The efficiency of puffing inhibitors was studied systematically using carbon samples from coal tar based needle coke. Puffing could be reduced by the addition of nickel and cobalt oxides.

The bulk density of the electrodes subjected to graphitization was increased by the addition of the above-mentioned oxides, because these oxides have a catalytic ability for carbonization.

The interlayer distances of the needle coke added with effective puffing inhibitors decreased considerably and the minimum points of such distances shifted to lower temperatures. The action of puffing inhibitor is to change the timing of the gas evolution from and the softening of the carbon bodies.

Introduction

The occurrence of irrversible volume expansion (puffing) during graphitization is well known to manufacturers of graphite electrodes. In the case of petroleum coke, the negative aspects of puffing can usually be overcome by the use of low-sulphur needle coke or the addition of a puffing inhibitor, such as iron oxide.

The cause of puffing of petroleum coke is generally considered to be related to the sulphur content and structure of coke. Metal oxides are believed to act as puffing inhibitors through reaction with the sulphur of coke to form sulphides[1].

As reported in the previous papers[2),3)] the puffing of coal tar based needle coke (pitch coke) is not caused by sulphur but is attributed mainly to the nitrogen content and structure of coke. Therefore, puffing inhibitors for petroleum coke are not necessarily effective for pitch coke. E. G. Morris et al., reported that the puffing of pitch coke can be inhibited by the use of chromium oxide[4)]

The objects of the present study are to determine the effective puffing inhibitors for pitch coke and to elucidate the puffing inhibition mechanism.

Results and Discussion

1. Amount of puffing and bulk density (B.D.)

The green test pieces were moulded from a mixture of calcined pitch coke (65%) (Nippon Steel Chemical LPC-U), a binder pitch (34%), and metal oxides (1%) by hot pressing. After baking the test pieces thus moulded (20mm in diameter and 100 mm in length) at 900°C for 6 hours, the amount of puffing and the B.D. were measured. The results of measurement are given in Table I. It will be noted from Table I that puffing is reduced significantly by the addition of chrominum, nickel and cobalt oxides but the B.D. of the sample added with chromium oxide is lower than those of samples added with nickel or cobalt oxides.

One of the important objects of puffing inhibition is to increase the B.D. and to enhance the strength of the electrode. Accordingly, the addition of chromium oxide is not necessary effective for pitch coke from a practical point of view. On the contrary, since the B.D. of the sample subjected to graphitization is increased by the addition of nickel and cobalt oxides, it is reasonable to assume that these oxides are the effective puffing inhibitors for pitch coke.

Table 1. Effect of Additives on Puffing and B.D.

Additive	—	WO_3	Fe_2O_3	NiO	Cr_2O_3	CoO
Puffing %	1.22	1.30	1.07	0.79	0.61	0.95
B.D.	1,439	1,436	1,448	1,521	1,440	1,542

2. T.G.A. curves of green test pieces

In order to obtain more information about the change of B.D. occurring during baking, a thermal gravity analysis of green test pieces was conducted. The curves obtained from this analysis are shown in Fig. 1. It will be noted that the weight loss of the sample added with nickel oxide is smaller than that of the sample added with chromium oxide. This behavior can be well explained by the fact that nickel compounds act as a carbonization catalyst. These results agree with the results reported by other investigators, which suggest that nickel and cobalt compounds have a catalytic ability for carbonization.

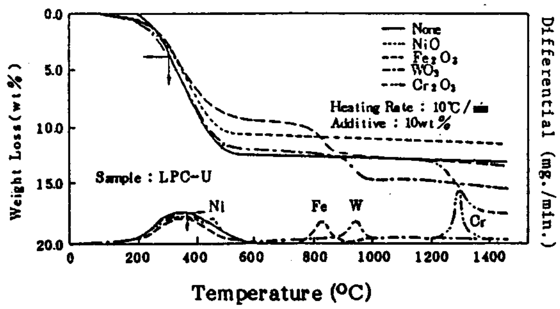

Fig.1 T.G.A. Curves of Green Test Pieces

It was confirmed by measurement that changes in B.D. during baking are affected by the kind of metal oxide added. This indicates that changes in B.D. are dependent upon the catalytic ability of metal oxides for carbonization.

3. State of Metal Oxides at High Temperature

An X-ray diffraction experiment was conducted using a high-temperature X-ray diffractometer to determine how the state of metal oxides is changed at high temperatures at which they act as puffing inhibitors. The results obtained are shown in Table 2. The metal oxides added to the green test pieces were changed to various reduction compounds during heating, and the diffraction patterns could not be observed at high temperatures. This means that the metal compounds melted and crystals ceased to exist at high temperatures.

The molten metal compounds seem to disperse in the carbon bodies. Nickel and cobalt oxides which are effective puffing inhibitors are reduced at relatively low temperatures.

It is essential that puffing inhibitors melt and disperse into the carbon bodies at high temperatures at which puffing occurs.

Table 2. Metal Compounds at High Temperatures

Additives	Compd	1000°C 1400°C 1600°C 1800°C
Fe_2O_3	Fe_3O_4	—
	Fe	—
	FeC	—— 1180
NiO	Ni	—— 1400
Cr_2O_3	Cr_2O_3	—— 1340
	Cr_3C_2	1230 —— 1890
WO_3	WO_3	— 1030
	W	—— 1350
	W_2C	1110 —— 1620
	WC	1160 ——

4. Change of interlayer distances

Changes in interlayer distances during the course of deformation were measured using a high-temperature X-ray diffractometer. It became evident that puffing is an intercrystalline phenomenon as already pointed out by E. Fitzer et al.[5] The results of the present authors' measurement are shown in Fig. 2. Comparing the changes of interlayer distances in artificial graphite with those in needle coke, it will be noted that the C/2 of artificial graphite increases gradually with increasing temperature because of thermal expansion but that of needle coke decreases at about 1,800°C. Especially, the C/2 of the needle coke added with an effective puffing inhibitor decreases sharply and its minimum points shift to lower temperatures. This phenomenon plays an important role in puffing inhibition.

There is no doubt that puffing is caused by the pressure generated by the gas evolution from the carbon bodies which have softened. Accordingly, the action of puffing inhibitors is to change the timing of the gas evolution from and the softening of the carbon bodies.

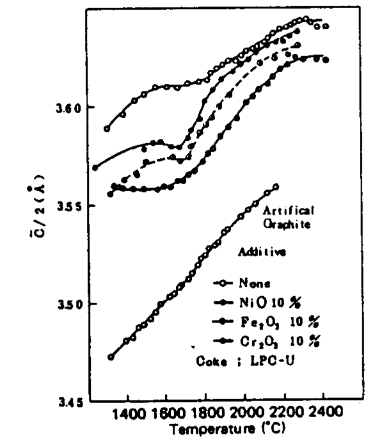

Fig.2 Change of C/2 during Graphitization

Conclusion

Metal compounds which can serve as effective puffing inhibitors should have catalytic abilities for both carbonization and graphitization. The bulk density of the samples is increased by the action of the catalytic ability for carbonization and puffing is reduced by the action of the catalytic ability for graphitization.

Puffing is inhibited because timing of the gas evolution from and the the softening of the carbon bodies is changed by the addition of metal compounds.

Nickel and cobalt oxides are the effective puffing inhibitors for coal tar based needle coke.

References

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