

Improvement of Puffing by the Two-Stage Calcining Method

R. Nishiyama, T. Nakagawa, H. Yamasaki, H. Tanaka

Koa Oil Company, Osaka Research Laboratory

2-1, Takasago Takaishi-shi, Osaka 592, Japan

Introduction

The puffing of coke, irreversible expansion during graphitization, is a significant phenomenon to be prevented in manufacturing artificial graphite electrodes.

This paper presents the results of experiments carried out to determine the puffing behavior of two-stage calcined coke in relation to their structural characteristics and impurity contents.

Experimental

Five types of coke (coke A, B, G, H and I) were used for the experiments. Their properties are shown in Table 1. Coke A was defined as a low sulfur regular-grade needle petroleum coke, and coke B as a fibrous textured premium needle petroleum coke. Coke G, H and I were derived from coal.

The coke samples were calcined in two different ways, the two-stage calcining (Case N) and traditional (Case T) methods. In Case T, the green coke was calcined at a traditional temperature of 1380°C for 30 minutes. In Case N, the green coke was calcined initially at a temperature of 800°C, cooled, then re-calcined at 1380°C for 30 minutes.

Using molded and baked test pieces prepared from the calcined coke, each puffing expansion was measured at temperatures ranging from 100 to 2800°C.

The volatile matter, elemental analysis, ash content, CTE, real density and porosity were determined by the same methods as reported in the previous papers.^{1,2}

Table 1. Properties of Green Cokes

Sample Name	Coke A	Coke B	Coke G	Coke H	Coke I
Volatile Matter (wt%)	8.2	7.6	5.4	5.8	6.6
Elemental Analysis					
C (wt%)	93.5	93.8	94.7	93.7	93.6
H (wt%)	3.4	3.3	3.2	2.9	2.4
N (wt%)	1.6	1.1	0.9	0.9	0.9
S (wt%)	0.48	0.73	0.25	0.32	0.36
Ash (wt%)	0.08	0.05	0.00	0.01	0.07

Interlayer spacings (d₀₀₂) and apparent crystalline sizes (L_c) were determined by the X-ray diffraction method. The texture and structure of the coke were observed by a polarized light microscope and a scanning electron microscope.

Table 2. Properties of Calcined Cokes

Sample Name	Coke A		Coke B		Coke G		Coke H		Coke I	
	N	T	N	T	N	T	N	T	N	T
CTE (x10 ⁻⁶ /°c)	1.5	1.9	1.2	1.6	0.9	1.2	0.9	1.2	—	—
Real Density (g/cm ³)	2.094	2.088	2.095	2.092	2.131	2.129	2.129	2.123	2.122	2.121
Porosity (%)	40.3	35.8	37.0	33.1	52.2	45.8	71.7	59.6	37.3	36.4

* Calcining Method N: New Method, T: Traditional Method

Results and Discussion

The values of the CTE, the real density and the porosity of calcined coke are shown in Table 2. It can be seen that the CTE is lower and porosity is higher in Case N than Case T.

Table 3 shows the results of puffing tests. The expansion of all calcined coke in Case N is lower than in Case T, and the effectiveness of the two-stage calcining method of the puffing improvement is clearly observed.

In order to investigate the cause for this improvement, the characteristics of the calcined coke were examined by means of X-ray analysis, microscopic observation and analysis of sulfur content.

Table 3. Puffing Properties of Test Pieces

Sample Name	Coke A	Coke B	Coke G	Coke H	Coke I
Calcining Method	N	T	N	T	N
Puffing (%ΔL)					
Fe ₂ O ₃ 0%	0.45	0.81	0.04	0.25	0.12
Fe ₂ O ₃ 1%	0.22	0.50	Shrink	0.01	0.07
	0.37	0.84	0.21	0.18	0.43
	1.18	1.42	0.06	0.79	

The doo2 and Lc are shown in Table 4. No significant differences were observed in the doo2 and Lc of cokes calcined in Case N and Case T.

With the polarized light microscope no apparent changes in the coke texture were seen. However, with the scanning electron microscope, more microcracks appeared in coke of Case N than in Case T.

Table 4. Comparison of X-ray Parameter

Sample Name	Coke A		Coke B		Coke G		Coke H	
	N	T	N	T	N	T	N	T
Calcined Coke								
doo2 (Å)	3444	3440	3447	3446	3447	3444	3448	3445
Lc (Å)	38	40	38	40	44	46	46	45
Graphitized Coke								
doo2 (Å)	3366	3366	3365	3364	3362	3360	3359	3358
Lc (Å)	840	880	1000	1000	1000	1000	1000	1000

Pore-size distributions of calcined coke were determined using a mercury porosimeter. An example of the results is shown in Figure 1. It is seen from the figure that the micropores in Case N increase in the range of 1-60 μ diameter. Similar results are obtained in other calcined coke.

It is said that the major reason for puffing is the irreversible structural change of the coke caused by gases emitted from the sulfur and nitrogen compounds and other impurities contained in the coke.^{3,4}

Therefore, the relationship between sulfur content and puffing expansion was studied as shown in Figure 2. Puffing expansion increases as the sulfur content increases. However, with the same sulfur content the expansion of coke in Case N is smaller than those in Case T. Figure 3 shows that as the total pore volume increases the puffing decreases.

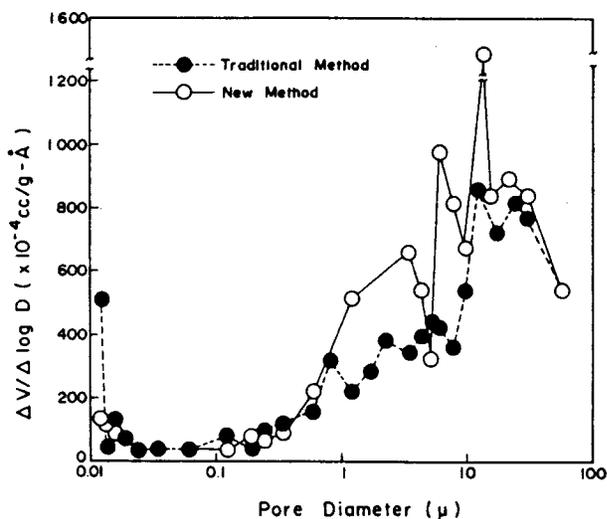


Figure 1. Pore Size Distribution in Calcined Coke B

These facts indicate that the major cause for puffing improvement by the two-stage calcining would be the increase of microcracks and micropores which allows gas to release easily during graphitization. There would be a limit to the degree of puffing reduction by two-stage calcining, since the differences in expansion between coke in Case N and those in

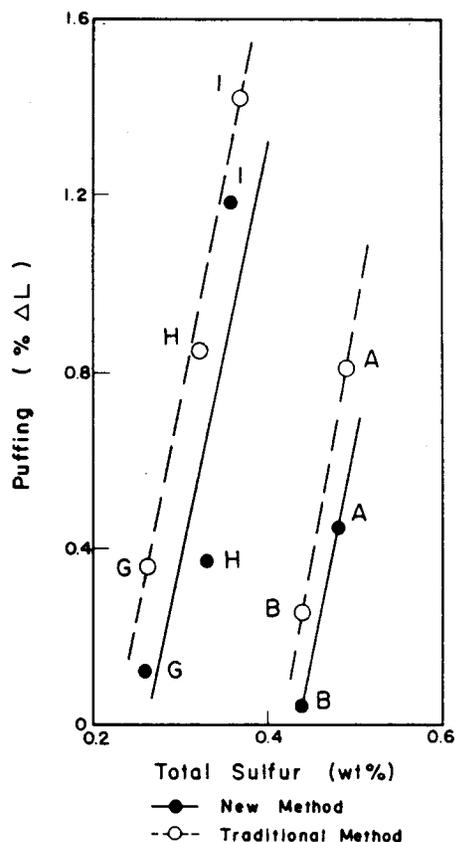


Figure 2. Total sulfur versus puffing

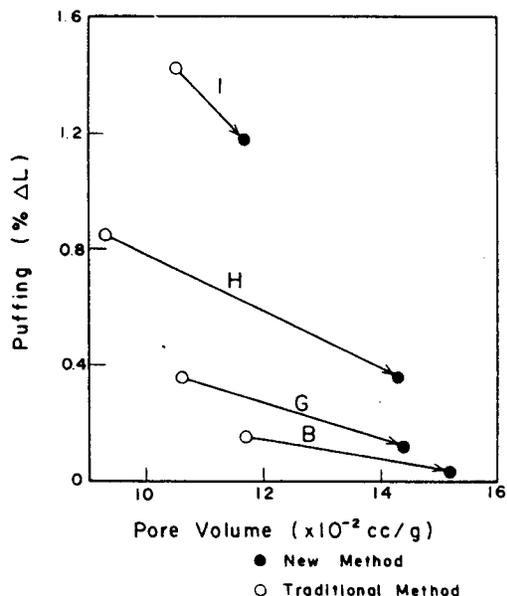


Figure 3. Pore volume versus puffing

Case T are nearly the same as shown in Figure 2. Possibly, calcining conditions would limit the increase of micropores to a definite degree, irrespective of the type of coke.

Conclusions

(1) The two-stage calcining method is effective in improving the puffing behavior of coke as well as the CTE.

(2) The degree of puffing improvement produces almost the same degree of reduction in puffing expansion irrespective the type of coke.

(3) Puffing improvement seems to be caused by the increase of microcracks and micropores developed during two-stage calcining method.

References

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