

PREBAKED ANODE FROM COAL EXTRACT (2) - EFFECTS OF THE PROPERTIES OF HYPERCOAL-COKE ON THE PREFORMANCE OF PREBAKED ANODES

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Abstract

The preparation of prebaked anodes utilizing coal solvent extraction technology is reported. A steaming coal was extracted with methylnaphthalene-based solvent under pressurized nitrogen atmosphere at 653K, and ash-free coal extract (Hypercoal, HPC) was obtained. The HPC was further heat-treated at 633 to 673 K in the presence of the methylnaphthalene solvent to alter the carbonizing properties of HPC. It was found that adjusting the H/C atomic ratio of HPC in the range 0.6-0.65 suppressed excess dilatation ability of the HPC and produced anode-quality coke. The effect of heat treatment temperature of the HPC on the resultant properties of the HPC coke (HPCC) was also investigated. It was confirmed that HPC is a suitable source of anode coke due to the low content of impurities such as sulfur, nickel, vanadium, and good chemical stability.

Introduction

In the prebaked anode industry, it is recognized that the quality of anode coke has continuously declined, namely, higher sulfur and impurities, higher volatile matter content, and lower density, mostly due to the deterioration of crude oil quality. Thus, technologies for alternative sources for anode coke are of great interest.

Kobe Steel, Ltd., have been developing a new non-hydrogenative solvent extraction process for coal with the aim of applying the coal-extract as a binder for the metallurgical coke production. The process and the product (the ash-free coal-extract), is Hypercoal (HPC) [1-4]. A flow diagram of the Hypercoal process and a photo of the Hypercoal pilot plant are shown in Figures 1 and 2, respectively.

Since the content of ash in HPC is usually extremely low, HPC is considered to be a promising candidate for alternative feedstock of anode cokes. In a previous paper, we reported the first attempt to obtain a prebaked anode test specimen using HPC as a feedstock of coke [5]. It was demonstrated that prebaked anodes prepared from HPC coke have various advantages such as extremely low impurities such as sulfur, vanadium and nickel, high apparent density, and low air- and CO₂-reactivity compared to those from anode grade calcined petroleum cokes.

In this study, we have investigated the post treatment of HPC in detail, since the as-prepared HPC does not necessarily exhibit suitable carbonizability for anode coke. The coke produced from the as-prepared HPC is generally too porous for anode manufacture. Thus, it is required to improve the dilatation characteristics of HPC to utilize it as anode coke feedstock.

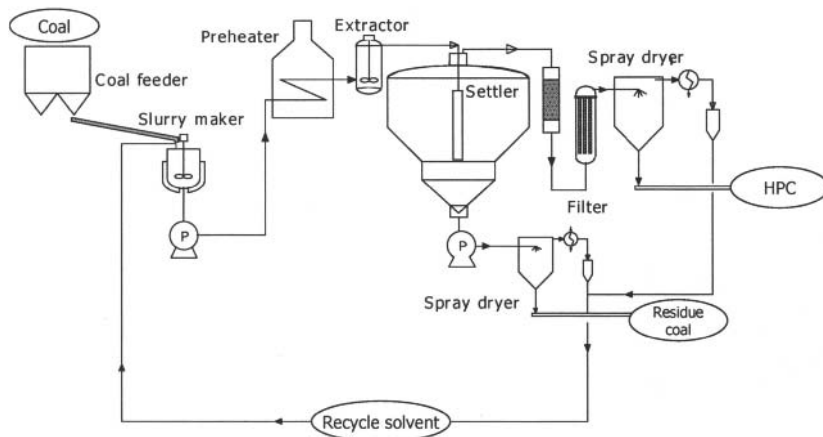


Figure 1. Schematic flow diagram of Hypercoal process

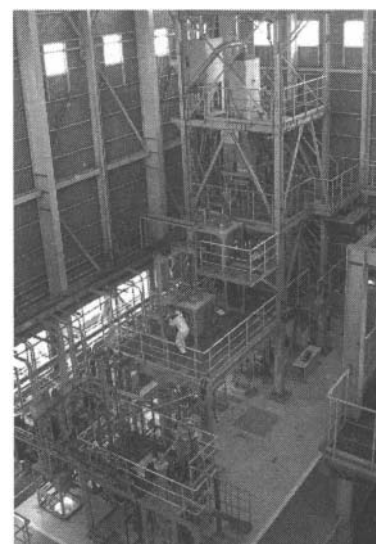


Figure 2. A photo of the Hypercoal pilot plant

Experimental

Materials

Three bituminous coals from Australia were used as the starting material. Proximate and ultimate analyses of the coals and their extract (Hypercoal) are shown in Table I.

Solvent extraction of the coal was carried out under the following conditions:

- solvent, a mixture of 1-methyl and 2-methyl-naphthalenes;
- solvent/ coal ratio (v/v), 4;
- temperature, 673K;
- initial nitrogen pressure, 2MPa;
- duration, 20min.

The coal extract (HPC) was recovered from the extraction slurry by filtering at high temperature and evaporating the solvent from the extract solution. Proximate and ultimate analyses of the extract (Hypercoal) are also shown in Table I. It should be noted that the ash content of the HPC was less than 1 wt%.

For fabrication of anode specimen, a commercially available coal tar pitch was used as the binder. The properties of the pitch are listed in Table II.

Post treatment of Hypercoal

Since the as-prepared HPC possesses extremely high dilatation during carbonization, the HPC was subjected to post heat treatment. Detailed investigation of the post heat treatment for the HPC from Coal A and B was carried out in this study. A 100ml-autoclave was used for the experiment. Twenty grams of HPC and 20 ml of methylnaphthalene solvent were charged into the autoclave, and the content was heat-treated under the prescribed reaction conditions. The heat-treated HPC was recovered by distilling the solvent in vacuum. It was then subjected to elemental analyses and the carbonization test.

Table I. Proximate and ultimate analyses for the coal and HPC

Product	Moisture	Ash	VM C H N S O ^(a)					
	[wt%]	[wt%db]	[wt% daf]	[wt% daf]	[wt% daf]	[wt% daf]	[wt% daf]	[wt% daf]
Coal-A	2.9	12.2	41.3	82.5	5.5	2.0	0.6	9.5
Coal-A HPC	0.0	0.1	41.5	87.8	5.5	2.2	0.6	3.8
Coal-B	2.2	12.4	39.7	84.1	5.7	1.9	0.6	7.7
Coal-B HPC	0.3	0.1	41.2	86.6	5.4	1.9	0.6	5.5
Coal-C	1.8	7.24	40.9	83.6	5.8	1.9	0.7	8.1
Coal-C HPC	0.1	0.06	43.0	85.7	5.5	1.9	0.7	6.2

a) By difference

Coking of HPC and preparation of prebaked anodes

A laboratory scale carbonization test of the post treated HPC was carried out according to the following procedures. An induction heating carbonization furnace was used. Four grams of Hypercoal powder (-1mm) was charged in a quartz tube of 16mmID, and was heated to 1273K at a rate of 3 K/min under inert atmosphere with 0.05kgf/cm² load. The sample was held at 1273K for 30 min. The compressive strength test of the HPC coke tablet was measured to assess the quality of the coke. The carbonization test procedure is shown schematically in Figure 3.

Prebaked anode specimens of rectangular shape of 27mm x 50mm x 120mm were fabricated according to the conventional methods. The crushed HPCC was mixed with the binder pitch of various

amounts (13-17wt% in the paste), and hot-pressed at a pressure of 400 bar at 393K. The pressed green molds were baked at 1373K for 20 hours. HPCC and prebaked anodes were evaluated in terms of the ISO standard test methods for anode cokes and prebaked anodes. A schematic of the prebaked anode preparation from HPCC is shown in Figure 4.

Table II. Properties of the binder pitch used

Properties	Method	Value	Unit
Softening Point	Mettler ISO 5940	113	°C
Insoluble in Quinoline	ISO 6731	8.4	%
Insoluble in Toluene	ISO 6376	27.7	%
Viscosity 433K	ISO 8003	1555	mPas
Density in Water	ISO 6999	1.312	kg/dm ³
Ash content	ISO 8006	0.25	%
S	ISO 12980	0.47	%
Na	"	202	ppm
Ca	"	59	ppm
Si	"	106	ppm
Fe	"	277	ppm
Zn	"	311	ppm
Pb	"	232	ppm

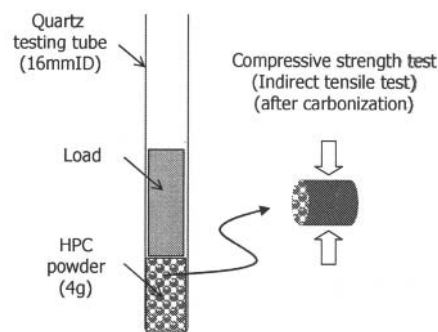


Figure 3. Schematic of carbonization and compressive strength test for HPC.

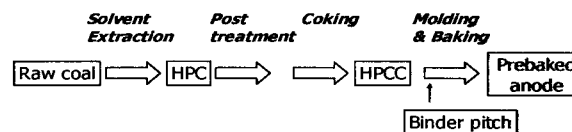


Figure 4. A schematic of prebaked anode preparation from coal.

Results and Discussion

Effects of post heat treatment on the properties of HPC

The change of H/C atomic ratio in the HPC produced from Coal-B during the heat-treatment in methylnaphthalene solvent is shown in Figure 5. It is clear that the H/C ratio of HPC decreases with increasing reaction time. This indicates that a dehydrogenative polymerization reaction of HPC molecules takes

place under the reaction conditions. At higher temperatures, the H/C ratio decreased much faster. A similar reaction behavior was observed for the HPC produced from Coal-A.

The Arrhenius plot of the H/C ratio decrease is shown in Figure 6. The activation energy, E_a of this reaction was calculated to be 172, and 169 kJ/mol for Coal-B and Coal-A HPC, respectively. These values are in good agreement with those reported for polymerization of coal-tar pitch, 150-190kJ/mol [6], and petroleum pitch 200-220kJ/mol [7].

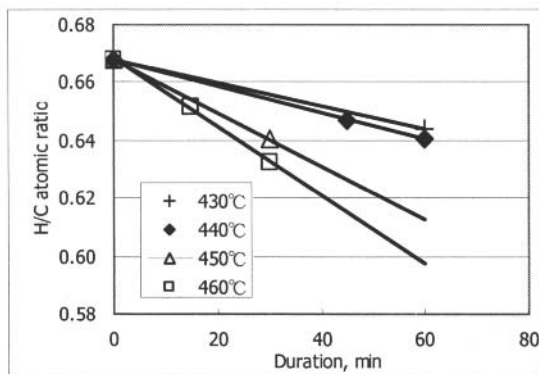


Figure 5. Changes of H/C atomic ratio of Coal-B HPC during the post heat treatment in methylnaphthalene at various temperature.

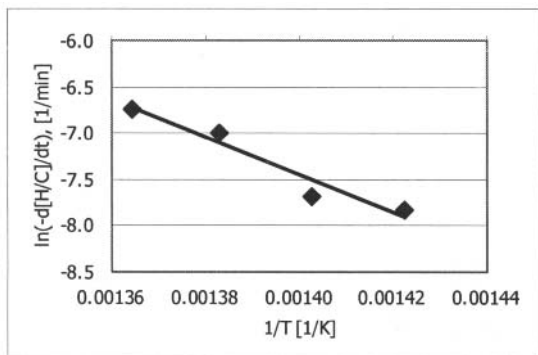


Figure 6. An Arrhenius plot of H/C decreasing rate during the post heat treatment of Coal-B HPC.

The effect of the post heat treatment on the carbonization properties of HPC was assessed in terms of the appearance and the mechanical properties of HPC coke. The compressive strength of the HPC coke was represented as a function of H/C atomic ratio of the heat-treated HPC (before carbonization) in Figure 7. It should be noted that the H/C ratio of the starting HPC was the highest and that the ratio decreases with increasing severity of the heat treatment. As mentioned earlier, HPC with the higher H/C ratio, i.e. as-prepared HPC and HPC obtained from very mild post heat-treatment resulted in coke with poor compressive strength. This appears to be due to excess dilatation ability of HPC: The HPC has expanded too much during the carbonization. On the contrary, with decreasing H/C, the compressive strength of coke increased, and reached a maximum, where the H/C ratio of the HPC was in the range of 0.60-0.65. For HPC with the H/C ratio

smaller than 0.6, the compressive strength of coke again decreased. The solid-state carbonization is the likely reason for poor carbonizability of HPC obtained by excess heat treatment. Figure 8 shows the relationship between the compressive strength and the porosity of HPC coke. The maximum strength was achieved when the porosity of the HPC coke was adjusted to around 40%. No significant difference in the H/C ratio, coke strength, and porosity relationship was observed for the two kind of coals examined. Figure 9 is a polarized light microphotograph of cross section of Coal-A HPC coke. It is a characteristic of HPC coke that a medium to fine mosaic texture is the main component.

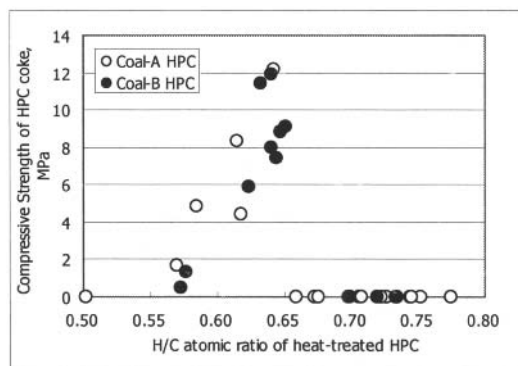


Figure 7. The relationship between the compressive strength of HPC coke and the H/C atomic ratio of the post heat-treated HPC.

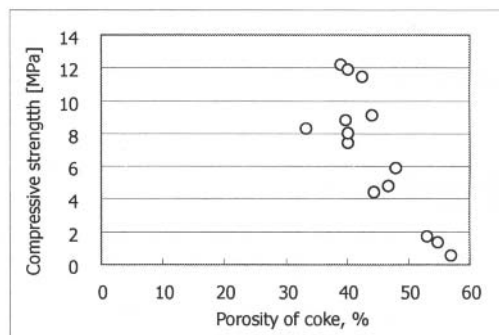


Figure 8. The relationship between the compressive strength and the porosity of the HPC coke.

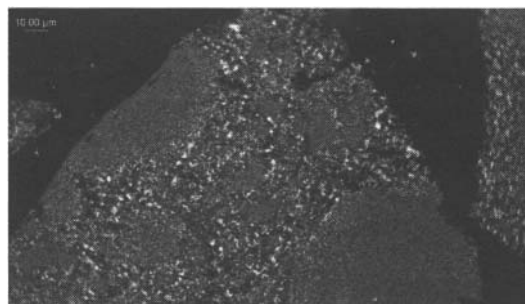


Figure 9. Polarized light microphotographs of polished cross section of coke from Coal-A HPC

Effects of the carbonization temperature on the properties of HPC coke and the prebaked anode

The properties of HPC coke calcined at 1273K (1000°C) and 1573K (1300°C) and a typical petroleum coke (PC) calcined at 1473K are compared in Table III. The content of volatile matter is very similar for HPCC and PC, irrespective of the calcination temperature. The density of the HPCC is substantially lower than PC when the HPC is calcined at 1273K, but are similar at 1573K. The crystallinity of HPC coke may be slightly lower than PC as judged by the X-ray diffraction parameters. The optical texture of HPC and the petroleum coke was quantitatively compared by polarized light microscopic measurement, and is listed in Table IV. The most significant difference is the higher content of fine and/or medium mosaic components in HPC coke, whereas the PC contains coarse mosaic and fibrous texture at a higher amount. This suggests that graphitizability of PC is higher than HPC.

Table III. Properties of HPC coke and Petroleum coke

Source	VM, w %		Density, g/ml		d_{002} , nm		Lc, nm	
	HTT1000	HTT1300	HTT1000	HTT1300	HTT1000	HTT1300	HTT1000	HTT1300
Coal-A HPC	0.26	0.18	1.855	2.031	0.3487	0.3481	23	24
Coal-C HPC	0.31	0.06	1.848	1.997	0.3513	0.3509	15	15
Ref. PC	0.39		2.025		0.3474		25	

PC was calcined at 1473K

Table IV. Optical Texture of HPC coke and Petroleum Coke

Source	Content, %						
	Isotropic	Fine mosaic	Medium mosaic	Coarse mosaic	Fibrous	Leaflet	Inert
Coal-A HPC	0	41	55	4	0	0	0
Coal-C HPC	0	44	47	9	0	0	0
Ref. PC	0	0	15	43	24	19	0

The properties of the prebaked anode prepared from HPC coke prepared with different calcination temperatures were investigated. Table IV compares the results with that of anode from a conventional petroleum coke. As a general tendency, HPC coke calcined at 1273K has a slightly poorer performance for feedstock for prebaked anode, as compared to PC, i.e. lower apparent density, higher electrical resistivity, and higher coefficient of thermal expansion (CTE). However, when the HPC coke was calcined at 1573K, the properties of the anode from HPC coke are almost the same as those from petroleum coke, except the higher CTE.

Table V. Properties of anode specimen prepared from HPC coke and Petroleum coke

Source	Apparent density, g/ml		Resistivity, $\mu\Omega m$		CTE, $10^{-6}/^{\circ}C$	
	HTT1000	HTT1300	HTT1000	HTT1300	HTT1000	HTT1300
Coal-A HPC	1.338	1.380	62.0	53.5	5.08	5.64
Coal-C HPC	1.335	1.306	61.1	71.7	5.25	5.47
Ref. PC	1.365		57.4		4.56	

Conditions for anode specimen preparation
Pitch content in the mold: 17.8 wt%
Molding: 45MPa, 2min; 27mm x 50mm x 120 mm
Calcination: 1000°C

Conclusions

Results of this study can be summarized as follows:

1. A prebaked anode sample for aluminum smelting was successfully prepared from coal by utilizing Hypercoal coke technology.
2. It was demonstrated that the controlling the H/C atomic ratio of HPC to 0.6 -0.65 by post treatment to produce acceptable anode-grade coke, whereas the as-prepared HPC exhibited excess thermal dilatation.
3. The effect of heat treatment temperature of HPC on the properties of the final HPC coke (HPCC) was investigated. It was confirmed that HPC is a quite suitable source of anode coke in terms of coefficient of thermal expansion, electric resistivity, density, and contains a low content of impurities such as sulfur, nickel, vanadium and has good chemical stability.

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