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PREBAKED ANODE FROM COAL EXTRACT (3) – CARBONIZATION PROPERTIES OF HYPERCOAL AND ITS BLENDS WITH BINDER PITCH

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Abstract

The preparation of prebaked anodes from coal using solvent extraction technology was investigated. Several bituminous coals were extracted with methylnaphthalene-based solvent under pressurized nitrogen atmosphere at 653K, and ash-free and high purity coal extract (Hypercoal, HPC) was obtained. It was found that the HPC can be utilized as an additive for binder pitch of anode manufacturing; the HPC improves the coke yield of the pitch and reduces the ash content of the binder. It was also found that a suitable modified HPC was self-sinterable, and was successfully molded and carbonized without binder pitch to result of dense carbon specimen. These results suggest the possibility for coal-based raw materials for prebaked anodes

Introduction

In the prebaked anode industry, it is recognized that the quality of anode coke has continuously deteriorated, 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.

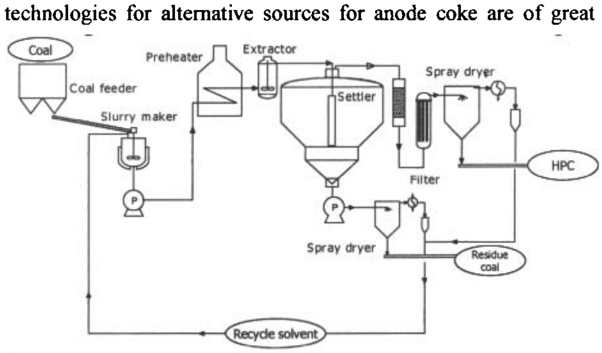


Figure 1. Schematic flow diagram of Hypercoal process.

Kobe Steel, Ltd., have been developing a new non-hydrogenative solvent extraction process for coal aiming to 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 is shown in Figure 1.

Since the content of ash in HPC is extremely low, HPC is a promising candidate for alternative feedstock of anode cokes. In previous papers [5,6], it was demonstrated that prebaked anodes prepared from HPC coke have various advantages such as extremely low impurities of sulfur, vanadium and nickel, high apparent density, and low air- and CO_2-reactivity compared to those from anode grade calcined petroleum cokes.

In this study, new approaches using HPC to manufacture a smelting anode are presented as follow: 1) to use HPC as an additive for binder pitch, and 2) to convert HPC into self-sinterable form and use it as a starting material for the anode. The possibility for binder-less fabrication of carbon block from HPC is presented.

Experimental

Materials

Two types of bituminous coals, Coal-A and Coal-B were used as the starting material of Hypercoal (HPC). Table I shows the coals and their extract (HPC) analysis. Solvent extraction of the coal was carried out under the following conditions: solvent, crude methylnaphthalenes; solvent/ coal ratio (v/v), 4; temperature, 673K; initial nitrogen pressure, 2MPa; duration, 20min. The HPC was recovered from the extraction slurry by filtering at high temperature and evaporating the solvent from the extract solution. It should be noted that the ash content of the HPC was less than 1 wt%.

A commercially available binder pitch for anode production was used as received. The binder pitch analysis is shown in Table I.

Blending experiment of Hypercoal and binder pitch

Blending experiment for the Coal A-HPC and the binder pitch was carried out by using a 1000ml autoclave under the following conditions: temperature, 543 K; HPC to pitch ratio, 0/100, 20/80, 33/67; 100/0 (w/w). The softening temperature (a ring-and-ball method), carbon yield at 823K (evaluated by the heating stage), and the optical texture of the resulted carbon (calcined at 1273K) were evaluated for the blended pitch.

Post treatment of Hypercoal

Due to its inherent characteristics such as relatively low softening temperature and high volumetric expansion during carbonization, the Coal-B HPC was subjected to a post heat treatment to convert into self-sinterable material. The heat treatment was carried out under the following reaction conditions; solvent/coal ratio, 2 (V/V); temperature, 723 K; duration, 20 min; initial nitrogen pressure, 2 MPa. The heat-treated HPC was recovered by distilling the solvent in vacuum. It was then subjected to elemental analyses and the carbonization test. The heat-treated HPC was pulverized (D50 19.5 μm) and was molded into a 50mm O.D. cylinder. Pressing conditions were at room temperature, and the pressure was 1.0 ton/cm^2. No binder material was used. Calcination of the mold was carried out at 1073K in an inert atmosphere, and the rectangular sample of 12mm x 12mm x 60mm specimens were cut from the calcined mold, and were further graphitized at 3073 K.

Table I. Coal and HPC lab analysis

	Proximate Analyses, [%] d.b.			Elemental analyses, [wt%] d.a.f.					Softening
	Ash	Moisture	VM	C	H	N	S	O_{diff}	point [°C][a]
Coal A	2.85	12.2	41.3	82.5	5.5	2.0	0.6	9.5	N.A.[b]
Coal A- HPC	0.04	0.1	41.5	87.8	5.5	2.2	0.6	3.8	324[c]
Coal B	6.08	2.3	36.6	85.7	5.8	2.2	1.0	5.3	N.A.[b]
Coal B-HPC	0.06	0.0	42.6	84.9	5.7	2.0	0.8	6.6	310[c]
Coal B-HPC heat-treated	0.16	0.1	20.1	87.6	4.4	2.2	0.8	5.0	N.D.[c,d]
Binder Pitch	0.14	0.1	41.8	93.1	4.1	1.2	0.4	1.1	97

a Measured by a ring-and-ball method.
b Not analyzed.
c Measured by an optical micorscope equipped with a heating stage
d No softening was detected.

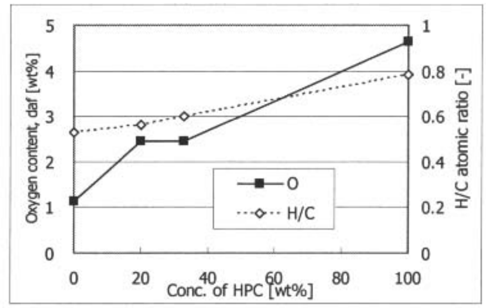
Results and Discussion

Blending of the HPC to the binder pitch

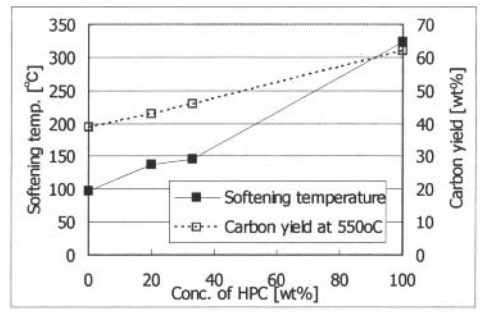
The change of H/C atomic ratio and the oxygen contents in the blended pitch were shown in Figure 2 (a). It is clear that the H/C ratio of HPC increases and the oxygen content increases with increasing concentration of HPC. These are attributable to the higher H/C and oxygen content of the HPC compared to the binder pitch. The physical properties of the blended pitch are shown in Figure 2 (b). The blend of the HPC enhances the carbon yield of the pitch, whereas the softening temperature of the pitch increased with increasing HPC content.

It is also noteworthy that the high sodium content of the binder pitch, namely 200ppm can be reduced by the addition of the HPC, since the sodium content in HPC is typically around 1 ppm [5]

Polarized light microphotographs for the blended pitch after carbonization at 823K were shown in Figure 3. The optical texture of the carbon was almost identical to the binder pitch if compared to the binder pitch coke texture.; Fibrous and coarse mosaic textures were predominant.



(a)



(b)

Figure 2. Changes of oxygen content and H/C atomic ratio (a) and softening temperature and carbon yield (b) in the blended pitch as functions of HPC concentration.

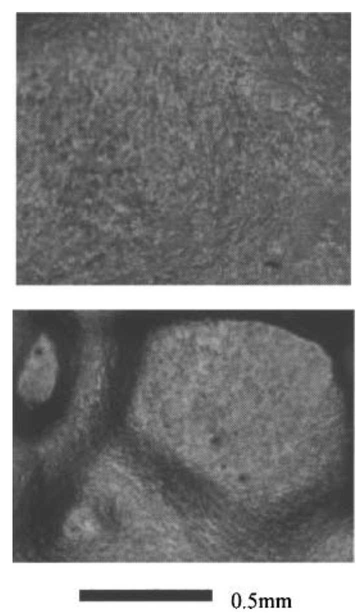


Figure 3. Polarized light microphotographs for the blended pitch after 1273 K carbonization. Top HPC 20wt%; Bottom: HPC 33wt%

Post heat treatment of Hypercoal and binder-less fabrication of anode block

As reported earlier [5,6], the sintering properties of the HPC can be controlled by the post heat treatment. The properties of the heat-treated HPC are listed in Table I. The treated HPC is characterized by its lower VM (volatile matter content) and higher melting temperature compared to the as-prepared HPC. In fact, the heat-treated HPC exhibited no melting behavior upon heating, but was successfully molded without binder, and was baked neither with shape distortion nor breakage. In other words, the HPC can be converted into self-sinterable form by an appropriate post heat treatment.

Table II shows the results of the anode fabrication from the self-sinterable heat treated HPC. The apparent density of the green mold was 1.14 g/cm^3, and it increased to 1.29 g/cm^3 after baking. This low green apparent density value was probably impacted by non optimized process parameters and due to fairly low baking temperature (1073K). As a reference, the properties of the binder-less block after graphitization was also evaluated. The graphitized block exhibited an apparent density at 1.62g/cm^3, and it characterized by low electrical resistivity, high flexural strength, and large hardness. Figure 5 shows the schematic prebaked anode manufacturing process using HPC. The results of this study claim that it may be possible to fabricate anode blocks by a single baking step of the green mold which is prepared by molding the heat treated HPC without binder.

Table II Properties of baked and graphitized block from the heat treated HPC

Apparent density [g/cm^3]		Properties of graphtized carbon block			
As-molded	Baked	Apparent density [g/cm^3]	Electrical resistivity [μΩm]	Flexural strength [MPa]	Shore hardness
1.14	1.29	1.62	22.1	44	77

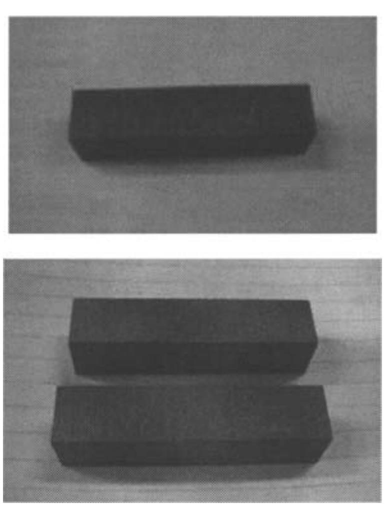


Figure 4. Photographs of the green mold of the heat-treated HPC (Top) and those after graphitization (Bottom).

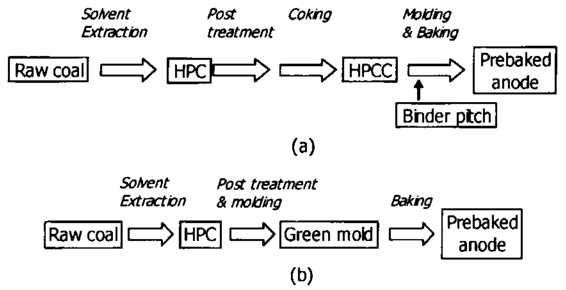


Figure 5. Proposed anode manufacturing process diagram using HPC (a) application of HPC coke (HPCC) and binder pitch; (b) binder-less fabrication process from the self-sinterable HPC

Conclusions

Results of this study can be summarized as follow:

1. Carbonization properties of the blends of binder pitch and the HPC were investigated. It was found that the HPC was compatible with the binder pitch and improves the carbon yield of the binder pitch, whereas the softening temperature of the binder pitch increased with increasing HPC content. It was also pointed out that the HPC should reduce the sodium content in the binder pitch.

2. The HPC can be converted into self-sinterable form by the appropriate post heat treatment. Carbon blocks were successfully obtained by molding and baking the self-sinterable HPC without binder pitch.

3. A binder-less fabrication process for the prebaked anode was proposed based on the HPC technology.

Studies for commercial scale production technologies for the HPC are now in progress at Kobe Steel, Ltd.

Acknowledgments

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