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RESEARCH OF POLYMERIC ADDITIVE INFLUENCE OF ORGANIC COMPOSITION ON THERMOCHEMICAL CONVERSION OF CARBON MASSES

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Abstract. The influence of polymeric additives on properties of carbon masses of self calcinating electrodes in their carbonization process has been investigated. It has been found that polymeric additive intensifies the interaction of carbon filler with an electrode pitch – the binding agent – that is represented with high quality on thermographic characteristics of laboratory masses. The mechanism of components interaction with a modifier has been formulated.

Key words: carbon mass, thermoanthracite, coal pitch, wetting angle, filler, binding agent, carbonization, polymeric additive.

1. Introduction

Ukraine is one of the CIS countries, where the world production of coal-graphite goods equals to about 2.5 million ton per year, from which about 65 % are electrodes for steel production, ferro-alloys, corundum, fibrous structure and others [1].

The specific consumption of electrodes which consists of evaporation, erosion (in the arc area), oxidation and destruction of its working surface in the candle area is the major characteristic of electric furnace steelmaking.

The forming of electrode properties complex is characterized by the set of factors and, first of all, by the properties of initial raw material components, and by the processes of their joint interaction at different stages of carbonization. Physico-chemical processes in the “filler-binder” system condition operational characteristics of the final item [2].

Carbon masses, used for the production of electrodes, anodes, graphite blocks and other products are the mixtures of hard carbon fillers (thermoanthracite, graphite, various cokes and others) with the binding agent – pitch.

Requirements to the raw material properties and to the coal pitches in particular are always conditioned by

basic functions which they fulfill in carbon mass. On the whole the influence of the electrode pitch on the process is more effective when it possesses a high adhesion and sintering ability, low ash content and yield of volatile components, optimum content of substances insoluble in toluene and quinoline, as well as ability to give a high coke.

In this connection the development of technological approaches capable of taking into account the instability of coal resin quality to provide the obtaining of electrode pitches with the promoted operational properties is very actual.

It should be noted that basic directions in area of pitch production are: i) obtaining of the binding agents of stable quality with the narrow changeable interval of indexes; ii) obtaining of rather wide gamut of pitches taking into account the technological features of different electrodes production.

To our opinion, the second direction is the decision of constantly arising problems because it gives the possibility to provide users by the pitch of necessary quality.

2. Experimental

Research of dominant partner of binding agent was carried out using thermal analysis and method of wetting angle determination. The wetting angle between a pitch and thermoanthracite was determined by the method of mapping the megascopic image of the drop on a screen.

The complex thermal analysis was carried out using the D-1500 derivatograph produced by the “MOM” firm in the argon atmosphere within the temperature range of 293–1073 K with the heating rate 278 K/min. The alumina served as a standard.

3. Results and Discussion

Aspiration for improving operational properties of electrode pitch in relation to carbon materials which

characterize its quality in the best way, explained the variety of yielding pitch additives of organic origin [3-5].

It is assumed in work [6] that at modification of raw A (main substance) by the by-product B (modifying additive) some reasons of component A pyrolysis intensification are marked:

- substance B, reacting with A, improves the solubility and the softening temperature of the latter or its derivatives due to moving of hydrogen atoms or hydrocarbon group from B to A;

- substance B participates in the formation of pitch liquid phase, which is formed by A. Furthermore the molecules in main substance form a liquid-crystal phase with difficulty that results in the formation of the stratified structure on the basis of molecules consisting the liquid crystals. At the same time the mass transfer processes are accelerated;

- substance B in the mass transfer reactions serves as the catalyst, providing the growth of permolecular formations of the pitch unequigranular system of the pitch;

- association of permolecular compounds in clusters grows steadily due to interaction of additive B and the modified substance A that promotes anisotropy and predetermines the development of intermediate products structure.

The authors of work [7] note that the small quantity of additive within the limits of 5–15 % furthermore can provoke the system to the substantial changes of

microstructure of the coke residue. So, using different organic additives and methods of their preparation, the cokes with different anisotropy of structure (5–200 mcm) were obtained.

These data find their confirmation in work [8], where additive contribution of additives is shown in forming main properties of coke residue and the substantial role of “dominant partner” effect is underlined.

As carbonization of carbon masses is a complex thermochemical process accompanied by the group of parallel-consecutive reactions, it was necessary to study the mechanism of polymeric additive influence (Table 1), both on the binding agent (Table 2) and on the filler (Table 3).

3.1. The method of “lying drop”

Using the method of “lying drop” [9] it is possible to fix such physical phenomenon, as wetting angle. However, for achievement of the set purpose the method was updated. Modernization consisted of introduction of polymeric additive in the quality of “pseudo” layer locating on the border-line of interface in the “filler-binding agent” system.

The results of thermal interaction between a drop of investigated binding agent with a filler surface are represented in Fig.1.

Table 1

Composition of polymeric additive

Acetophene	Dimethyl-naphthalene	Acenaphthene	Fluorene	Diphenylene-oxide	α -Methyl-naphthalene	Resin
% (mass parts)						
0.21	6.00	17.51	21.00	21.00	0.89	the rest

Table 2

Indexes of binding agent properties

Material	Substances insoluble in		Yield of volatile substances, %	Ash, %
	quinoline, %	toluene, %		
Electrode pitch	7	26.7	61	0.15
GOST 10200-83	≤ 8	25–31	58–62	≤ 0.3

Table 3

Indexes of filler properties

Material	Sulphur, %	Moisture, %	Yield of volatile substances, %	Ash, %
Thermoanthracite	1.0	0.2	0.3	3.6
GOST 4794-97	≤ 1.9	≤ 0.3	≤ 0.5	≤ 5.0

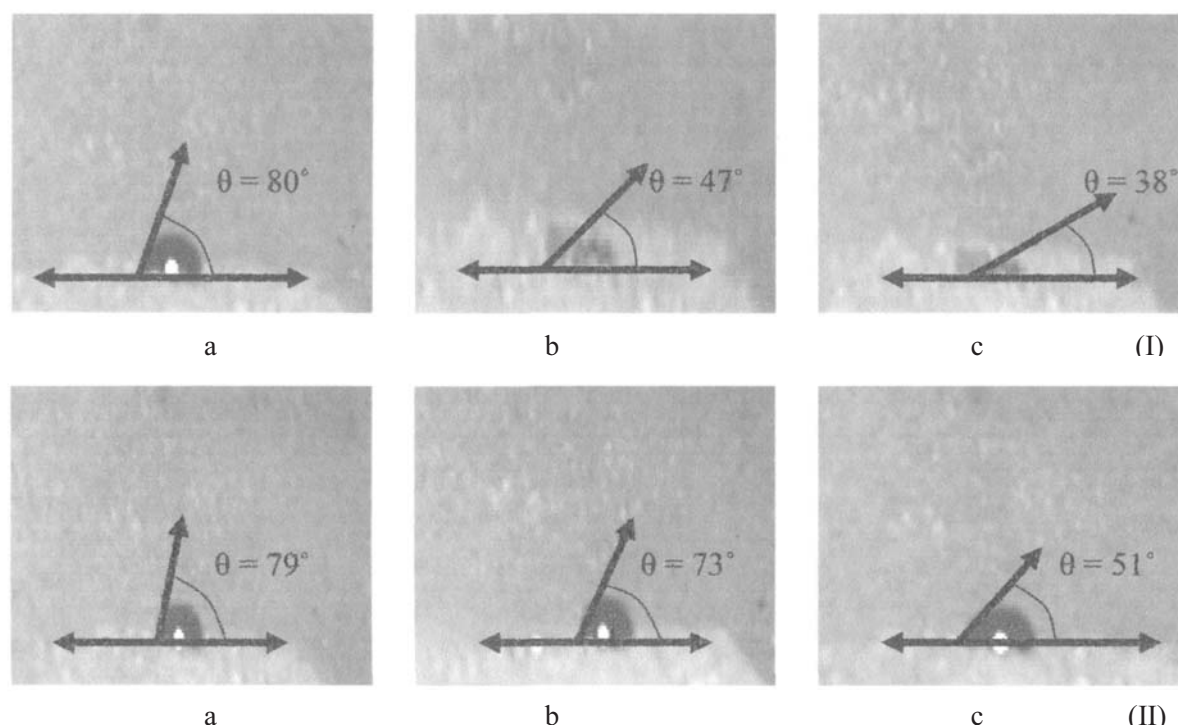


Fig. 1. Character of thermal interaction of pitch drop with hard surface of thermoanthracite (I) and thermoanthracite with additive (II) at the stove working area temperatures (K): 373 (a), 413 (b), 726 (c)

Resulting from the obtained values of wetting angles in relation to the modified surface of thermoanthracite, one can say that polymeric additive changes the character of khemosorption processes, interactions with the binding agent and more probably all it will be revealed while forming the electrode structure.

3.2. Thermal analysis

Such an influence is more evidently reflected on thermochemical conversions of the binding agent in the carbonization process of carbon mass for self-calcinating electrodes (Fig. 2).

One can see on the DTA curve (b) presenting pitch composition with modified filler (4 %) the period of carbon mass staying in the plastic state increases from 503–528°K to 493–533 K compared with initial carbon mass (a), and the additive amount of 6 % (c) causes the displacement

of this period at 488 K. The fact of increase of the period of carbon mass staying in the plastic state when confronted with the less losses of weight testifies to the stabilization of forming fragments of initial pitch structure. Such a supposition is confirmed by the DTA curve.

On the first stage until the temperature of the beginning of destruction determined by the DTA curve, the mass loss with additives is less, than that of initial carbon mass, and rate of loss is lower. On the second stage of conversion the loss mass rate of experimental carbon mass is higher compared with the initial sample. On the third and fourth stages the rate decreases again, although the mass loss on these stages predominates a little bit.

Such a supposition is based on the results of derivatograph analysis. The analysis of initial and experimental carbon masses thermograms was conducted according to the methodic [10]. The results are given in Table 4.

Table 4

Thermographical characteristics of carbon mass carbonization

Samples	Temperature interval, K				Rate of mass loss at the temperature interval, %				Mass loss, %
	I	II	III	IV	I	II	III	IV	
Initial	503–528	528–733	733–823	823–1000	6.20	42.50	33.00	20.10	43.50
Modified by additive (4 %)	493–533	493–738	738–823	823–1000	5.50	36.00	34.50	22.70	43.05
Modified by additive (6 %)	488–533	488–743	743–833	833–1000	6.00	40.20	38.20	23.90	43.18

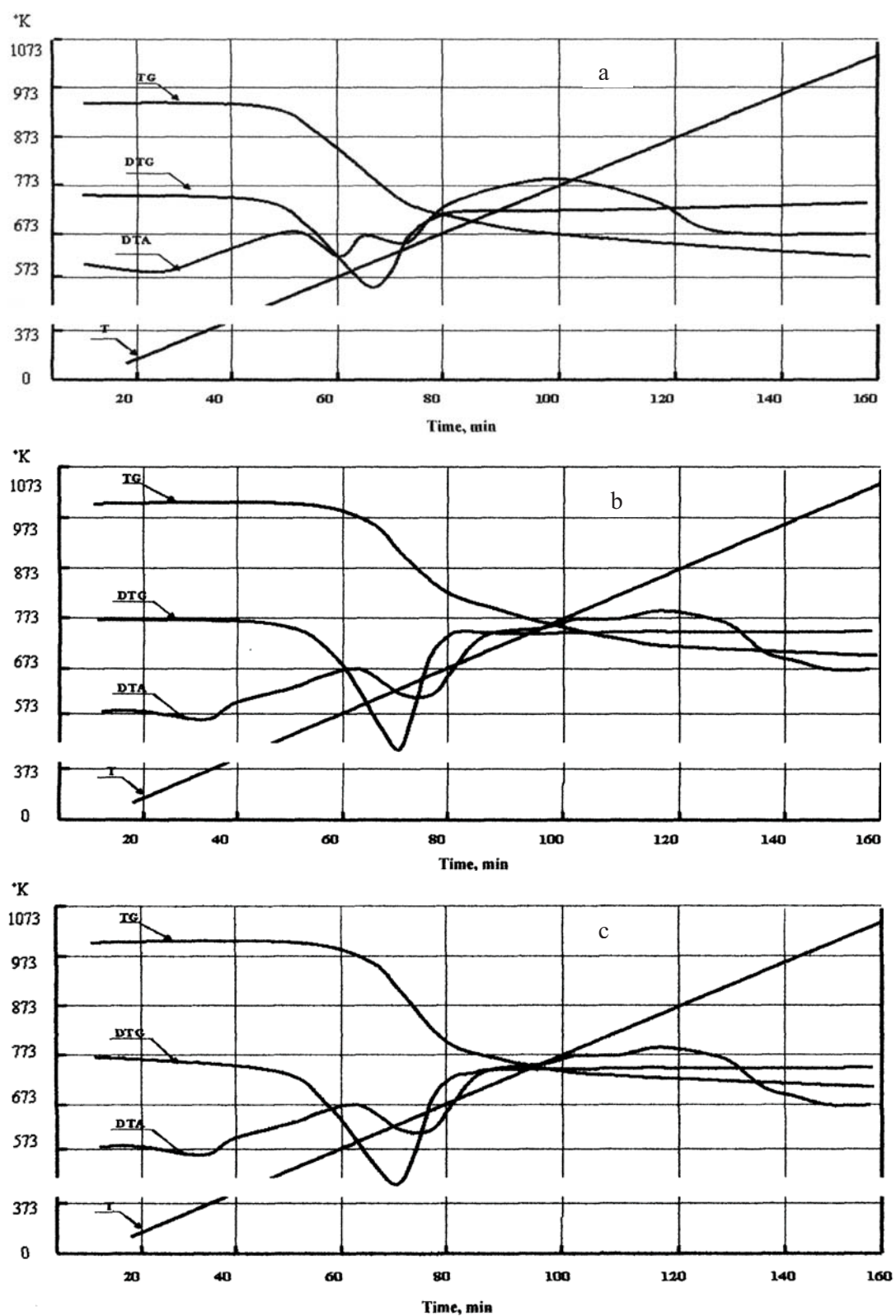


Fig. 2. Thermograms of carbon mass (a) and masses modified by polymeric additive: 4 % (b), 6 % (c)

Estimating the results of the research on modification of filler solid surface, one can state, that a new surface appears on the contiguous areas of carbon material and additive, that changes liophilno-liophobny properties of the filler. On the one hand it results in the temperature decrease of positive wetting angle, and on the other hand – at temperatures higher than 473 K the modified filler is the strong catalyst of thermochemical conversions of the binding agent.

4. Conclusions

Thus, on the basis of the carried out experiments the mechanism of comodifying additive carbonization with a pitch and carbon mass in the process of the thermal heating can be represented in two ways.

On the one hand, the additive before the transition of pitch to the viscidly-fluid state facilitates the process of its macromolecules attraction and extends the temperature interval of mesophase origin. On the other hand due to adhesion forces the additive is disposed and fixed on the surface of pitch macromolecules. The forming gas-vapor products of pitch are forced to pass through the film. Obviously, a nascent adsorption layer from a polymeric mixture is in some way a barrier or filter, because it traps gas-vapor products and partly dissolves them. Further the additive interacts with permolecular compounds, penetrating into the depth of the pitch. Thus the yield of pitch liquid mass increases and the viscosity decreases. If the above-mentioned mechanism is to be examined in the “binding agent–filler” system, then this effect will be going on until the establishment of the equilibrium between the surface of solid carbon material and the binding agent, that in its turn should intensify wetting, adsorption and adhesion, increasing the yield of the coke residue and the baking properties of electrode pitch of the binding agent.

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ДОСЛІДЖЕННЯ ВПЛИВУ ПОЛІМЕРНОЇ ДОБАВКИ ОРГАНІЧНОГО СКЛАДУ НА ТЕРМОХІМІЧНІ ПЕРЕТВОРЕННЯ ВУГЛЕЦЕВИХ МАС

Анотація: Досліджено вплив полімерної добавки на властивості вуглецевих мас самовипалювальних електродів в процесі їх карбонізації. Виявлено, що полімерна добавка інтенсифікує взаємодію вуглецевого наповнювача з електродним пеком – зв'язуючим, що якісно відображається на термографічних характеристиках дослідних мас. Сформульовано механізм взаємодії компонентів вуглецевої маси з модифікатором.

Ключові слова: вуглецева маса, термоантрацит, кам'яновугільний пек, крайовий кут змочування, наповнювач, зв'язуюче, карбонізація, полімерна добавка.