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Adjusting properties of electrode pitch with fractions of coal tar

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Регулювання властивостей електродного пеку фракціями кам'яновугільної смоли

Abstract. *The paper presents the investigation results of the organic mass modification of the impregnating pitch of coal tar with low pyrolysis degree. The processes that form the pitch operational properties in the impregnation technology of graphitized electrodes were studied. Specific features of the modifying additive effect on the quality characteristics of the pitch and its group composition were established. Such technological approach makes it possible to intensify the impregnation process of blanks for graphitized electrodes.*
Key words: *impregnating pitch phenolic fraction, modification, group composition, low-pyrolyzed coal tar.*

Анотація. *У роботі представлено результати дослідження модифікації органічної маси імпрегнуючого пеку кам'яновугільної смоли низького ступеня піролізу. Вивчено процеси, що формують експлуатаційні властивості пеку в технології імпрегнування графітованих електродів. Встановлено специфічні особливості впливу модифікуючої добавки на якісні характеристики пеку та його груповий склад. Такий технологічний підхід дає змогу інтенсифікувати процес імпрегнування заготовок для графітованих електродів.*
Ключові слова: *імпрегнуючий пек, фенольна фракція, модифікація, груповий склад, низькопіролізна кам'яновугільна смола.*

1. Introduction

The graphitized electrodes are carbonaceous current-carrying elements for electric arc furnaces. The production of dense electrodes significantly improves their operational conditions and increases the technical and economic parameters of the process. The impregnation of electrode products with organic substances essentially affects the reduction of the total porosity and the redistribution of the pore volume according their equivalent radii.

The processes occurring at the boundary of the solid and liquid phases play an important role in the impregnation process of graphitized electrodes. It has been established [1] that the impregnation volumetric rate, calculated according to Darcy's law, is inversely proportional to the viscosity of the impregnating pitch. The correctness of the macrokinetic impregnation model chosen by the authors was confirmed by experiments [2].

The theory of the impregnating pitch (impregnate) motion in porous media due to capillary absorption is rather widely discussed in the literature [3, 4]. In this connection the purpose of the research was to improve the performance characteristics of the impregnating pitch using a phenolic fraction of low-pyrolyzed coal tar.

The values of fluidity and viscosity of the pitch are directly proportional to the temperature and group composition, and even a small difference in the fractions ratio leads to the significant changes in the impregnate penetration into the pores of the graphitized billet [5].

One of the most important parameters of impregnating pitch properties is α_1-fraction (substances insoluble in quinoline), which affects the rheological properties of the system, and, consequently, its applicability to be an impregnate. Moreover, a significant content of substances insoluble in quinoline (~6 %) causes adsorption of some high-molecular components of the pitch on the billet surface in the form of 1-5 mm layer [6]. This explains the severe restrictions relative to the "mass fraction of insoluble substances in toluene", which are claimed by consumers to the impregnating pitch. The analysis of publications allows to establish general trends and ranges of individual quality indicators of impregnate used for carbonaceous materials impregnation (Table 1).

So for all the variety of quality indicators of impregnating materials, the main one is the low content of substances insoluble in quinoline (2-4 wt %).

A special electrode pitch- impregnate is not produced in Ukraine as a marketable product due to the lack of appropriate technologies. In this regard, it is very important to develop technological methods of high- quality impregnating pitch production, taking into account the instability of the raw materials quality.

The phenolic fraction of the coal tar was used as a modifying additive due to the significant amount of

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phenols, which take part in the formation of complex molecular complexes - azeotropic compounds. A molecular azeotropic complex is a mixture of two or more liquids the composition of which does not change while boiling. It is a good plasticizer which cannot be separated by thermal fractionation.

2. Experimental

Impregnating pitch with 4 wt % of insoluble in quinoline compounds was used as an initial raw material (Table 2).

Peck was heat-treated at 403-413 K, and then the phenolic fraction of coal tar preheated to 333 K (Table 3) was added; after stirring for 30-40 min the mixture was cooled to 293 K.

When choosing the additive to the initial pitch, its operational characteristics, namely the softening temperature ***(T_{soft})*** and flash point ***(T_f)*** were taken into account. The assessment was carried out in accordance with the requirements of PJSC "Ukrainian Graphite". The obtained results were processed by the simplex-lattice planing method [7].

The following stages were used to prepare electrode billets:

Preparation of charge (composition, wt %): calcined petroleum coke 50; calcined oil shale coke 27-30; needle coke 13-20.

Mixing of cokes with a binder pitch: a preheated mixture of cokes is mixed with a pitch melt in a mixer at 393-413 K.

Billets pressing: the blank is pressed through the die carrier and cut at the necessary length.

Billets baking: in a furnace at 1523-1723 K.

Impregnation of billets: in an autoclave for 4-5 h at the temperature of 473 ± 10 K.

Baking of impregnated billets.

Graphitization at 2273-2773 K.

A specific electrical resistivity, bulk density, coefficient of thermal expansion, modulus of elasticity and mechanical tensile strength were determined for the obtained samples according to the standard procedures.

Table 1. Characteristics of industrial indices of impregnating pitch

Raw material	Softening temperature (T_{soft}), K	Ignition temperature (T_{ign}), K	The content of substances insoluble in		Technical indicators, %			Viscosity		Cok yield, %
			toluene, wt %	quinoline, wt %	ash content	volatiles yield	sulphur content	dynamic, mPas	specific	
Impregnating pitch	333-338	≤ 483	≥17	≤ 4.0	≤ 0.3	≤ 68	≤ 0.5	≤ 150	≤ 50	≥ 50

Table 2. Characteristics of the initial coal tar pitch for impregnation

Indicators	Values
Softening temperature, K	338
Volatiles yield, %	64
Ash content, %	0.3
Mass fraction of substances insoluble in: toluene, wt % quinoline, wt %	 24 4

Table 3. Composition of two samples of phenolic fraction of low-pyrolyzed coal tar

Fraction composition	Mass fraction, wt %	
Phenol	21.9	22.1
o-Cresol	8.6	8.8
m-Cresol	11.0	12.0
p-Cresol	7.7	8.0
o-Ethylphenol	0.4	0.7
2,5-Xylenol	2.8	3.0
2,4-Xylenol, 3,5-Xylenol, 3-Ethylphenol	11.0	11.2
2,6-Xylenol	3.0	2.5
2,3-Xylenol	0.9	0.9
2,3,5-; 2,4,5-; 2,4,6-Trimethylphenols	1.5	1.7
α-Naphthol	1.0	0.9
β-Naphthol	0.5	1.0
Unidentified	29.7	27.1

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3. Results and Discussion

The components content (wt %) in the mixtures was varied: pitch - from 94 to 98, FF (phenolic fraction of low-pyrolyzed coal tar) - from 2 to 6 and F (phenol) - the rest. The artificial variables were introduced, as shown in Table 4.

The matrix of the simplex-lattice plan of the second order is shown in Table 5. The matrix contains the code values of pseudofactors X_1 X_2 and X_3.

After the implementation of the plan (Figs. 1 and 2), the following polynomial relationships were established:

$$Y(T_{soft}) = 113.33X_1 + 113.33X_2 + 73.5 – 36X_1X_2 - 24.33X_1X3 + 1.33X_2X_3 \quad (1)$$

$$Y(T_f) = 214.33X_1 + 211.33X_2 + 203.5 - 6X_1X_2 - 0.66X_1X_3 + 8X_2X_3 \quad (2)$$

Based on the obtained models, it can be expected that the phenolic fraction in the amount of 2-6 %, reduces the softening temperature of the impregnating pitch but does not change its flash point. However, with an increase of the additive content in the impregnate up to 8 % or higher we observed significant changes. The process is accompanied by low-molecular, light-boiling components which action can be considered as a positive one until the conditions for the fractions thermochemical transformations are created in the pitch.

The analysis of the obtained modified impregnating pitch showed (Table 6) that the contents of ash, sulfur and moisture of the pitch do not actually change and stay at the required level. After the pitch treatment with 4 and 6 wt % of phenolic fraction the mass fraction of substances insoluble in toluene was 22 and 21 wt %, respectively, and the mass fraction of substances insoluble in quinoline - 3.0 and 2.5 wt %, respectively. The amount of coke residues from the impregnating pitch and the modified one remained virtually unchanged.

Table 4. Pseudocomponents of the system.

Pseudofactors	Content of components in the mixtures, wt %		
	Pitch	FF	F
X1	94	6	0
X_2	98	2	0
X3	94	4	2

Table 5. Conditions and results of the experiments.

Design matrix			Softening temperature (T_{soft}), K			Flash point (T_f), K		
X_1	X_2	X_3	T_{soft1}	T_{soft2}	T_{soft3}	T_{f1}	T_{f2}	T_{f3}
1	0	0	336	336	335	488	487	487
0	1	0	338	338	337	485	483	485
0	0	1	326	327	328	473	478	478
0.5	0.5	0	337	337	336	485	483	485
0.5	0	0.5	330	332	333	482	483	480
0	0.5	0.5	331	332	333	483	482	482
1|3	1|3	1|3	334	334	333	481	483	481

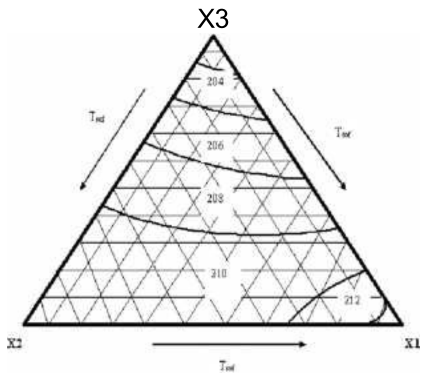

Fig. 1. Mathematical model of the impregnating pitch flash point dependence on FF mass fraction.

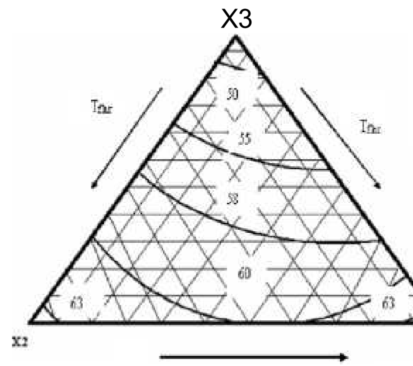

Fig. 2. Mathematical model of the of the impregnating pitch softening temperature dependence on the FF mass fraction.

Table 6. Impregnate quality indices.

Raw material	Coke residue, wt %	Dynamic viscosity at 433 K (Brookfield method), mPas	Technical indices,%			Content of substances insoluble in	
			ash content	volatiles yield	sulphur content	toluene, wt %	quinoline, wt %
Impregnating pitch	53	108	0.1	65	0.5	24	4.0
Impregnating pitch + 4 wt % of phenolic fraction	52	65	0.1	65	0.5	22	3.0
Impregnating pitch + 6 wt % of phenolic fraction	52	60	0.1	66	0.5	21	2.5

Fig. 3. Photos of two electrode billets with a diameter of 400 mm impregnated with a modified pitch.

Table 7. Physico-chemical properties of electrode billets with a diameter of 400 mm impregnated with a modified pitch.

Electrode billets	Indices				
	Modulus of elasticity, MPa	Coefficient of thermal expansion, K^{-1}	Bulk density, g/cm^3	Specific electrical resistance, $Ohmmm^2/m$	Mechanical tensile strength, MPa
Initial	65	$3.2 \cdot 10^{-6}$3	1560	8.0	4.7
Investigated	66	$3.0 \cdot 10^{-6}$	1600	7.5	5.0

To clarify the change in the fractional composition of the impregnating pitch, we additionally estimate the *y*- fraction of the impregnate, which was 37.7 wt % in the initial pitch; 39.0 wt % in the pitch modified with 4 wt % of FF and 40.5 wt % in the pitch modified with 6 wt % of FF. The given and previously obtained data [8] reveal that during modification the phenolic fraction plays the role of an auto-plasticizer. It means that the process is accompanied by the formation of azeotropic complex compounds providing a plastic and highly elastic state the impregnating pitch. This, in turn, promotes a better penetration of the pitch into the billet pores (Fig. 3).

Due to the use of phenolic fraction of low- pyrolyzed coal tar as a modifier, redistribution of the group components of the modified pitch occurs (Table 6), which contributes to a change in the physico-chemical properties of the obtained billets (Table 7). During impregnation with a modified pitch, its sticking on the billet surface was not observed (Fig. 3). Also, due to this technological approach, there is the possibility of repeated application of pitch without significant impairment of the impregnation process, which reduces its consumption during the research.

4. Conclusions

Using the phenolic fraction of the low-pyrolyzed coal tar, the dispersion of a_1-fractions changes, the share of the substances that are insoluble in quinoline and the pitch viscosity decreases, which is in agreement with the literature data. After the destruction of the pitch structure, the mass fractions of ***y-*** and a-fractions have the predominant influence. Thus, the phenolic fraction of coal tar can be used in industrial conditions as a modifier of the electrode pitch-impregnate during its production. The autoplasticization process takes place with the formation of azeotropic complex compounds, which promote the impregnating pitch to be in a plastic and highly elastic state. This, in turn, improves the pitch penetration into the billet pores and facilitates the repeated application of the pitch as the impregnate without a significant impairment of the impregnation process.

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