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Studies of the Properties of Coke Plates of VCC and Doncarb Trademarks

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Abstract

The operating experience for anode materials used in the production of fluorine shows that not all plates that meet the requirements of Russian technical specifications TU 48-12-34–95 have the required service life; some of them are destroyed quite quickly during operation. In this regard, we have carried out the studies of coke plates of Russian manufacturers using differential thermal analysis (DTA), X-ray structural analysis (XRD), atomic emission spectroscopy (AES), scanning electron microscopy (SEM), various physical-mechanical and electrical methods. The technical characteristics of the coke plates of two different trademarks: "Doncarb" produced by Doncarb Graphite LLC (Chelyabinsk) and "VCC" produced by the Volzhsky Chemical Complex LLC (Volzhsky) were determined: porosity, ash content, density, compressive strength, electrical resistivity. The technical characteristics described above fully meet the requirements of the Russian technical specifications. It was shown that the content of impurities in Doncarb plates is 0.50 mass %, while that in VCC plates is 0.33 mass %. The porosity of the coke plate materials was carried out. In general, Doncarb samples are characterized by the presence of pores 0.6–12 μm in size, while the presence of larger pores (more than 117 μm) is characteristic of VCC samples. The presence of the turbostratic structure of carbon with the parameters d_{002} = 0.347–0.345 nm was established for the coke plates of both trademarks. Classification of coke plates with respect to their thermal stability was carried out on the basis of the data obtained by means of differential thermal analysis. The use of the obtained data as a supplement to the parameters included in TU 48-12-34–95 allows one to improve the evaluation of the quality of coke plates and to predict their lifetime reliably.

Keywords: coke plates, atomic emission analysis, scanning electron microscopy, differential thermal analysis, X-ray structural analysis

INTRODUCTION

Gaseous fluorine is used in atomic industry to obtain uranium hexafluoride (UF_6), which is applied to separate uranium isotopes. Fluorine production is carried out through the electrolysis of the melt of potassium hydrofluoride $KF \cdot 2HF$; the latter reagent is obtained by the saturation of potassium fluoride melt with gaseous hydrogen fluoride. An industrial electrolyzer is composed of a case with electrode cells located in parallel, the cooling system, carbon anodes, louvered box-shaped cathodes, gas separating bell for the collection of anode gas fluorine [1].

Anode materials most widely used are coke plates (CP) which must meet some requirements [2]:

chemical stability with respect to fluorine and hydrogen fluoride, high mechanical strength during operation, low electric resistance and good electric contact with the copper current carrier.

The operation lifetime and interrepair time of the electrolyzers depend first of all on the quality of CP used to manufacture anodes. Therefore, it is necessary to know the properties and characteristics of CP in order to improve the technical and economic parameters of the fluorine generation process.

The initial raw material for CP production is petroleum or coal pyrolysis low-sulphur coke of a definite fractional composition, and petroleum or coal pitch. The technology of plate manufacture includes pressing of the blanks, their double baking according to special schedules, and intermediate impregnation with pitch in an autoclave [3].

Coke plates are non-uniform in chemical and phase composition, contain at least two kinds of carbonaceous coke entering the interaction with atmospheric oxygen at different temperatures and with different maximal rates [1].

The quality of CP used to manufacture the anodes of fluorine electrolyzers should meet the requirements of TU 48-12-34–95 "Burnt coke plates". These requirements state the following parameters and requirements to CP [4]: apparent density, not less than 1.64 kg/dm^3, compression strength, not less than 58.8 MPa, porosity, not more than 21 %, ash content, not more than 0.6 %, specific resistance, not more than 25–40 $\mu\Omega \cdot m$.

Many authors studied CP. For example, it is stated in [5] that the performance stability of the anodes is determined mainly by the structure and nature of the filler and coke binder. The authors of [6] established that plate destruction occurs in the regions with the lowest and highest temperature (70–80 and 200 °C). The lower part of a CP has a lower temperature. The authors of [7] showed that one of the reasons of CP destruction is the unsatisfactory protection of the zone of contact of the copper current-carrying rod with the CP.

Experience of the industrial performance of anode plates in fluorine production showed that not all anodes meeting the requirements of the TU provide the necessary operation lifetimes. This is the evidence that the parameters controlled by TU 48-12-34–95 are insufficient to evaluate the quality of CP. In this connection, we carried out integrated studies of CP using different chemical, physicochemical, physicomechanical and electric methods.

The goal of the work was to carry out an integrated analysis of the quality of CP manufactured by Russian makers, for the purpose of evaluating the possibility of their use in fluorine production in Russia.

EXPERIMENTAL

Research methods

CP manufactured by LLC Doncarb Grafit (Chelyabinsk), below are referred to as Doncarb, and LLC Volzhskiy Chemical Complex (Volzhskiy), below are referred to as VCC.

Coke plates are made of the materials with a low degree of thermal treatment (coke annealing temperature 1250±50 °C, roasting temperature 1200–1300 °C). Not less than six plates of each trademark were analyzed; each analysis was carried out three times. Ashing was carried out in a corundum crucible in the muffle furnace at a temperature of 815±15 °C for 8 h.

Examination and analyses of CP were carried out using the methods of physical-mechanical, chemical and physicochemical analysis, such as differential thermal analysis (DTA), X-ray structural analysis (XRD), atomic emission spectroscopy (AES), scanning electron microscopy (SEM) according to the procedures described in [8–20]. The compression strength, apparent density, porosity, ash content and specific electric resistance of the CP material were determined using the standard procedures [21–24].

Chemical analysis of initial CP and ash was carried out with the atomic emission spectrometer with inductively coupled plasma iCAP 6200 DUO (Thermo Scientific, USA). The dissolution of samples collected from initial CP and the ash was carried out in the microwave system MARS 6 (CEM, the USA) according to the procedure presented in GOST R 54237 "Solid mineral fuel" [25]. Sample ashing was carried out in a corundum crucible at a temperature of 815±15 °C. The advantages of AES are short analysis time, the possibility of the quantitative determination of a large number of elements in the liquid, solid and gaseous states within a broad concentration range with a high accuracy (up to 10^{-5} %) using a small sample mass [8].

Investigation of pore size distribution in the plate material was carried out with a scanning electron microscope Vega 3 SBH (Tescan, Czechia) with the energy-dispersive attachment X-Act. For each sample, not less than five images were

taken from the outer surface with different magnification; not less than 500 measurements of visible pores were made. Scanning electron microscopy is one of the most widely used methods for diagnostics. The resolution of a scanning electron microscope approaches several nanometres, while magnification is easily varied from ~10 to more than 300 000. In the presence of an attachment for X-ray fluorescence analysis, SEM gives the information on surface topography, chemical composition of the substances and provides visualization of surface nonuniformities within one layer [9, 16, 17].

Thermogravimetric analysis of CP samples was carried out with an SDP Q600 derivatograph (TA, Intertech, the USA), the samples were heated to 900 °C at a rate of 10 °C/min.

The following parameters of oxidizability were used to control the quality of CP materials:

– ΔA, % – mass loss by the sample at the thermogravimetric curve (TG) at the maximum of the curve of differential scanning calorimetry (DSC) of the derivatogram;

– B, % – the ratio of the second intensive extremum to the sum of the intensities of both extrema on the curve of the differential thermogravimetric (DTG) derivatogram;

– ΔT, °C – the difference of the temperatures of the second and the first extrema of the DTG curve of derivatogram.

The parameters B and ΔT allow evaluating the content of graphitized structures or the content of the ordered structural modification, while ΔA parameter allows us to estimate the rate and completeness of the oxidation of CP material

Evaluation of the grade of CP quality was carried out according to the procedure which is used at the Angarsk Electrolysis Chemical Plant, a Public Corporation [19]:

1) quality grade 1 (I rate): $\Delta A \le 55$ %; $B = 0$ %; $\Delta T \le 40$ °C; number of peaks $n = 1, 2$;

2) quality grade 2 (II rate): $\Delta A = 56–65$ %; $B = 51–56$ %; $\Delta T = 41–60$ °C; $n = 2$;

3) quality grade 3 (III rate): $\Delta A = 66–70$ %; $B = 57–60$ %; $\Delta T = 61–70$ °C; $n = 2$;

4) quality grade 4 (IV rate): $\Delta A \ge 71$ %; $B = 61–70$ %; $\Delta T \ge 71$ °C; $n = 3$.

Differential thermal analysis (DTA) is the most widespread method of thermal analysis because of a broad range of information obtained. The method allows establishing the presence or absence of phase transformations, the process nature with time, a shift of one or another effect under external reasons, the temperature of the start and finish of the process [19]. With the help of DTA, it is possible to measure the following values: vitrification, crystallization, melting, sublimation temperatures, and other characteristics.

Investigation of the structure and the input control of CP material were carried out by means of XRD with an ARL X'TRA diffractometer (Thermo Scientific, Switzerland, CuK_α radiation ($\lambda = 0.1541$ nm)). The advantage of this method in comparison with other methods is in the possibility to obtain almost all the data on the structure of the substance with the help of only one tool: X-rays, studying their interaction with the substance under analysis [26]. The interplanar spacing in packets (d_{002}), packet thickness (L_c), the width of the carbon layer (L_a) were determined according to [27], packing density (ρ) was measured as described in [28].

RESULTS AND DISCUSSION

Results of the studies of technical characteristics of Doncarb and VCC CP are presented in Table 1, along with their parameters according to the requirements of TU 48-12-34–95 and certificates of manufacturers (in parentheses). One can see that almost all the considered characteristics of Doncarb and VCC CP correspond to the requirements of TU 48-12-34–95. Exceptions are some parameters of VCC plates for which (according to the data of our analyses) the density is somewhat lower than that required by the TU, while porosity is higher. This may be connected with the use of the modern analytical equipment.

The average values for element content in six plates of each trademark and in ash are presented in Table 2.

It should be noted that the composition of CP is not normalized by the technical requirements, except sulphur (not more than 0.3 mass %) and carbon content (not less than 99 mass %). During ashing, a part of the elements (sulphur and phosphorus) is lost in the form of volatile compounds. According to the data of analysis, scattering of elements content in CP and ash was ±25 %.

The total content of all admixtures in the Doncarb CP does not exceed 0.50 mass %, while in the VCC plates it is not more than 0.33 mass %. The content of the main hazardous admixture – sulphur – in the plates of both grades does not exceed 0.054 mass %, and phosphorus 0.043 mass %. The major impurity in the materials of Doncarb grade is iron, its average content is 0.216 mass %.

TABLE 1

Technical characteristics of CP of Russian manufacturers

CP trademark	Compression strength, MPa, not less than	Density, not less than, g/cm^3	Porosity, not more than, %	Ash content, %, not more than	Specific resistance, μΩ · m, not more than
TU 48-12-34–95	58.8	1.64	21	0.6	25–40
Doncarb	59.9±7.1 (116)	1.64±0.03 (1.75)	18.0±1.1 (13)	0.40±0.05 (0.6)	40.5±0.3 (38.9)
VCC	59.3±6.5 (58.8)	1.61±0.01 (1.64)	24.8±0.1 (21)	0.40±0.05 (0.6)	39.0±1.0 (40)

Note. Values from manufacturers' certificates are shown in parentheses.

TABLE 2

Results of the chemical analysis of coke plates and ash

Element	Content of admixtures in CP, mass %		Content of admixtures in ash[a], mass %	
	Doncarb	VCC	Doncarb	VCC
Al	0.0425	0.0381	0.0463	0.0417
Ba	0.0006	0.0003	0.0006	0.0004
Ca	0.0102	0.0415	0.0120	0.0450
Fe	0.2159	0.0469	0.2122	0.0403
K	0.0418	0.0045	0.0451	0.0040
Mg	0.0037	0.0050	0.0035	0.0034
Mn	0.0026	0.0010	0.0028	0.0011
Na	0.0244	0.0364	0.0210	0.0345
P	0.0145	0.0426	0.0008	0.0104
S	0.0505	0.0538	0.0020	0.0056
Si	0.0839	0.0569	0.0637	0.0594
Sr	0.0008	0.0003	0.0007	0.0005
Ti	0.0026	0.0021	0.0018	0.0016

[a] Composition was calculated for the mass of the sample taken for ashing.

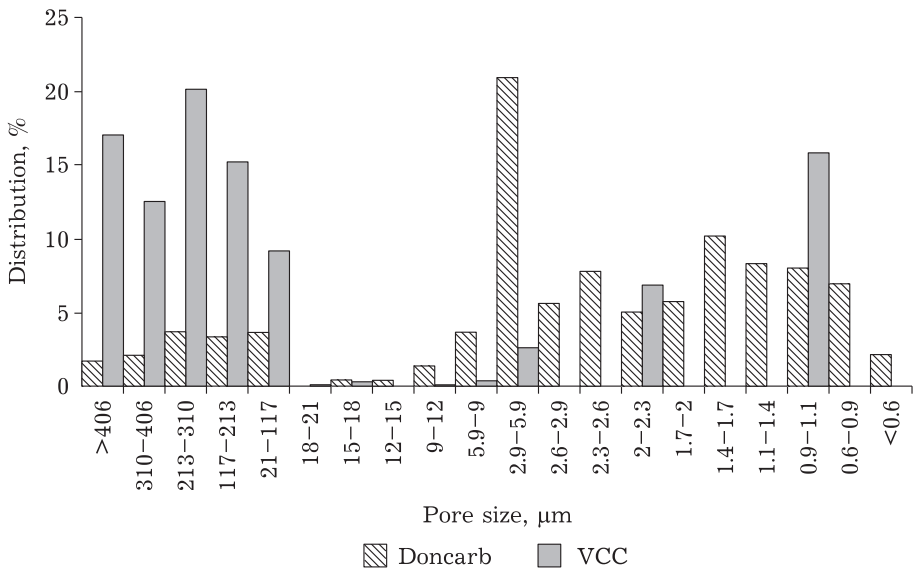

Fig. 1. Pore distribution in the plates of Doncarb and VCC trademarks.

In VCC plates, a more uniform composition of impurities is observed, and there are no clearly distinguished elements. Some nonuniformity of aluminium, calcium, iron, silicon and sulphur content is observed in the samples of different lots of Doncarb CP, while in VCC samples the nonuniformity is manifested for calcium, potassium, magnesium and aluminium.

Results of pore size distribution analysis are presented in Fig. 1.

One can see that the size of the major part of pores in the samples of Doncarb is within the range 0.6–12 μm, 1 % – 12–117 μm and 17 % – 117–406 μm. For the VCC sample, the presence of coarse pores is typical: the size of 65 % pores exceeds 117 μm, about 16 % pores are small: 0.9–1.1 μm.

The results of DTA of CP are shown in Table 3, and some typical examples of the derivatograms are presented in Fig. 2 and 3.

In the examination of the VCC grade plates, mainly double peaks were detected in the DTG curve, so these plates were related to rates II and III. Mass losses in the points of extrema corresponding to peaks 1 and 2 are approximately the same.

A single peak of the curve of derivatogram at a temperature of 630±5 °C is characteristi of the plates of Doncarb grade, *i.e.* the peak appears at a lower temperature in comparison with the VCC CP. This is the evidence that these plates might be obtained at lower temperatures. With respect to quality, the plates relate to ranks I (plates *1–3)* and II because the rate and completeness of oxidation (ΔA) is larger than 55 %.

The diffraction profiles of Doncarb and VCC samples are shown in Fig. 4 and 5. One can see that there are two reflections (002), (10) in the diffraction patterns of both samples at 2θ = 15–50°, characterizing the structure of carbon in CP. The results of XRD and the structural parameters of the CP material are presented in Table 4. One can see that the structure of carbon in both samples corresponds to turbostratic [29], formed during carbonization of amorphous carbon at a temperature up to 1500 °C. Thus, d_{002} for both CP kinds differs only insignificantly from the literature data (d_{002} = 0.344 nm) [30]. The size of packets for both CP samples are close to each other and are equal to L_c = 6.9–7.6 nm, L_a = 14.6–17.5 nm, and their density ~2.2 g/cm^3.

CONCLUSION

The quality of CP used to manufacture the anodes of fluorine electrolyzers produced by the Russian enterprises Doncarb Grafit (marked as Doncarb) and Volzhskiy Chemical Complex (marked as VCC) was investigated. It is demonstrated that the CP of these manufacturers mainly meet the requirements of TU 48-12-34–95 "Burnt coke plates" valid in the Russian Federation. It was established that the chemical compositions of CP are close to each other. The total content of impurities in them does not exceed 0.50 mass %. In general, the con-

TABLE 3

Results of the DT analysis of coke plates

CP trademark	Plate No.	ΔA, %	B, %	ΔT, °C	Peak temperature, °C	Quality class (rate)
Doncarb	1	54.1	0	0	617	I
	2	53.8	0	0	616	I
	3	55.0	0	0	621	I
	4	56.1	0	0	622	II
	5	58.3	0	0	630	II
	6	61.6	0	0	638	II
VCC	1	38.5	0	0	659	I
	2	34.0 84.5	34.8	78	645 723	II
	3	32.7 75.5	36.3	63	650 713	II
	4	3.5 8.4	37.8	50	680 730	II
	5	3.6 7.3	37.8	60	657 717	III
	6	31.4 77.9	37.5	69	649 718	III

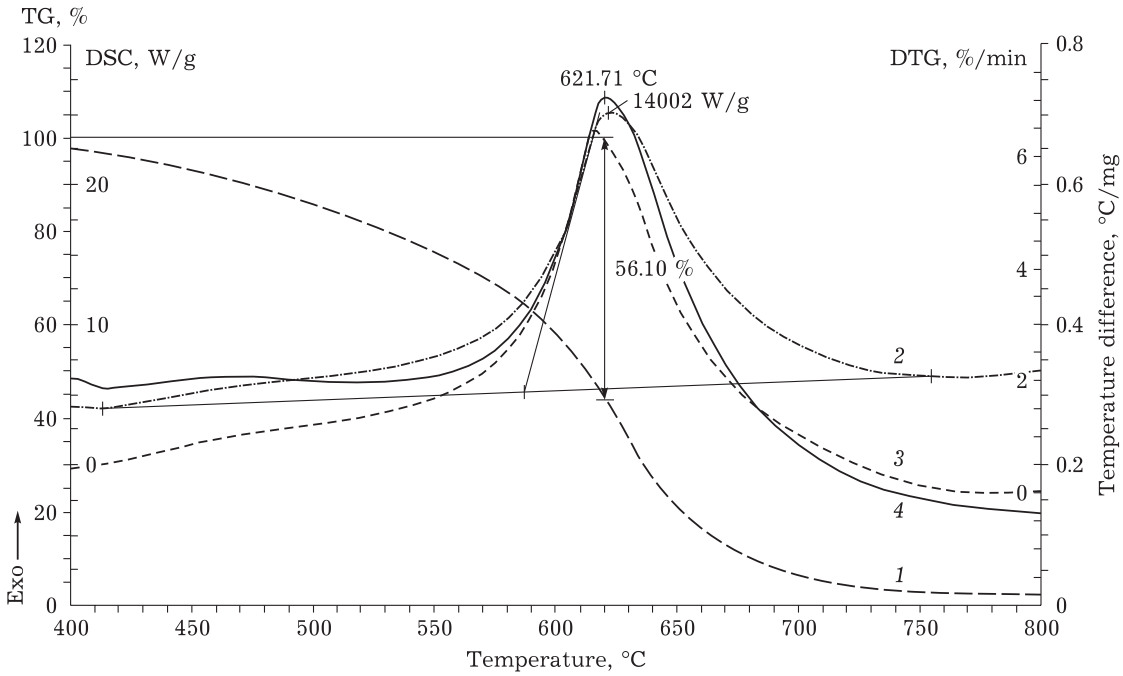

Fig. 2. Derivatogram for Doncarb coke plate No. 4.

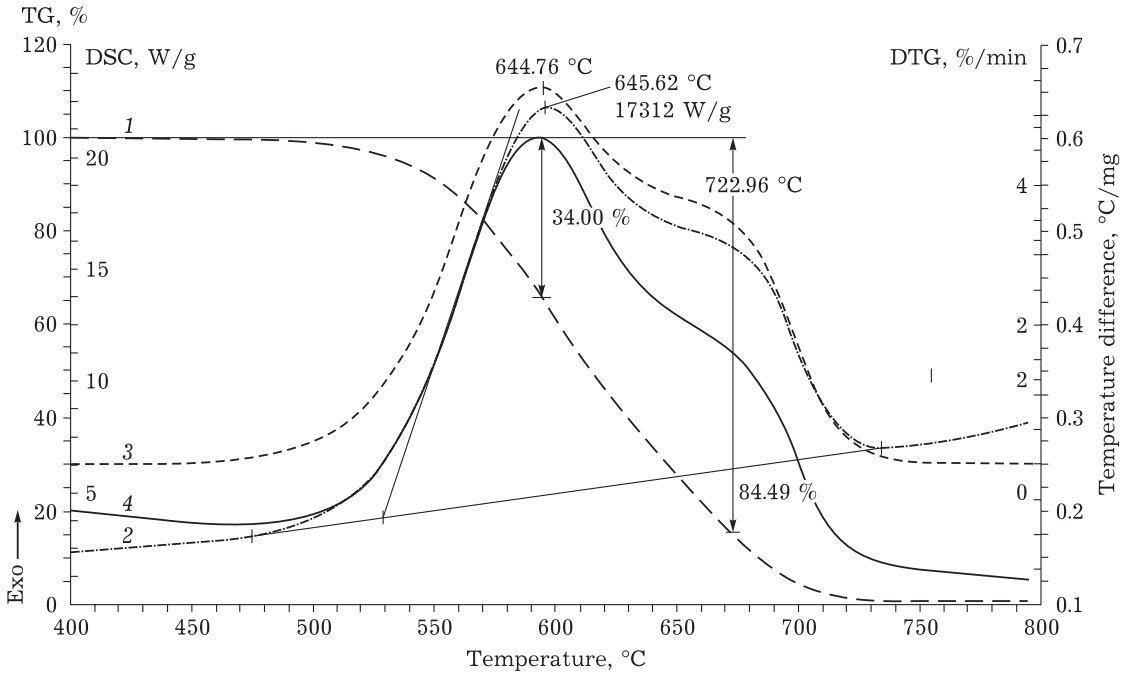

Fig. 3. Derivatogram for VCC coke plate No. 2.

TABLE 4

Results of X-ray structural analysis and structural parameters of coke plates

CP trademark	d_{002}, nm	L_c, nm	L_a, nm	ρ, g/cm^3	Semi-width of (002) reflection, deg	Semi-width of (10) reflection, deg
Doncarb	0.347	6.93	1.62	2.19	2.35	3.72
VCC	0.345	7.61	17.54	2.21	2.14	3.10

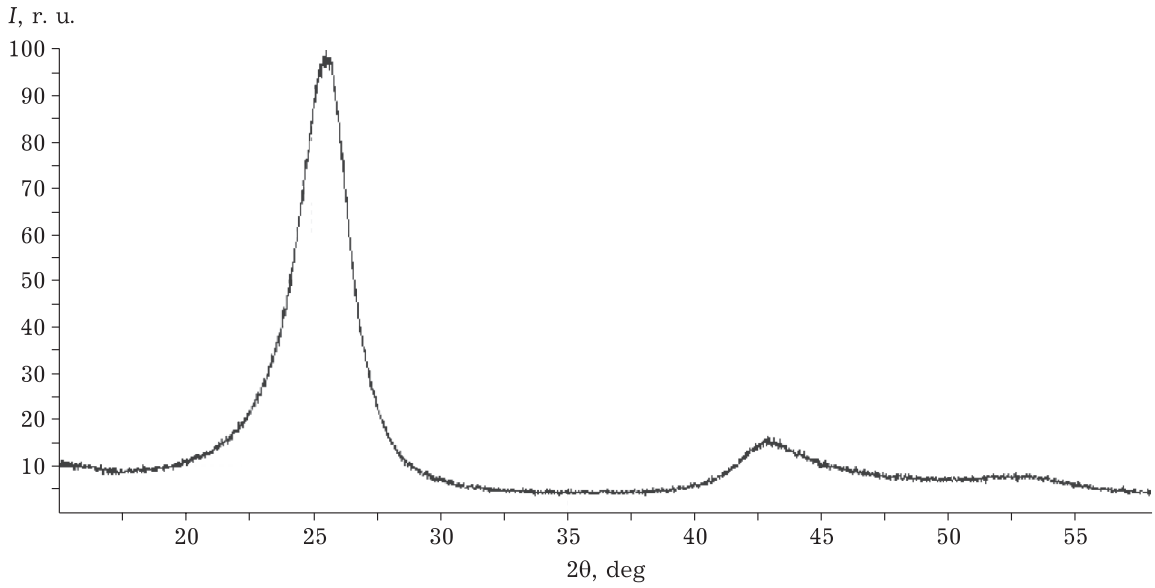

Fig. 4. Diffraction profile of Doncarb sample.

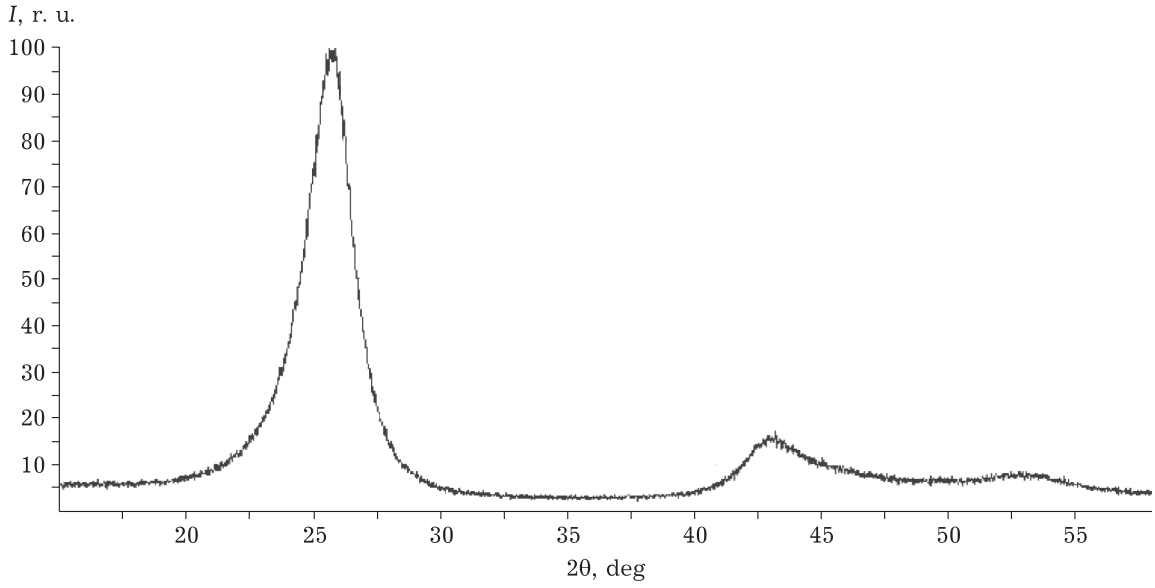

Fig. 5. Diffraction profile of VCC sample.

tent of the major hazardous impurity – sulphur – does not exceed 0.054 mass %, which allows us to assume that CP were manufactured at these enterprises from low-sulphur coke and pitch.

For Doncarb plates, pore size within the range 0.6–12 m is mainly characteristic, while the value is movre than 117 μm for the plates of VCC trademark. According to the results of XRD, the presence of a turbostratic carbon structure with the parameters d_{002} = 0.347–0.345 nm, L_c = 6.9–7.6 nm, L_a = 14.6–17.5 nm in CP was demonstrated, which is the evidence that these plates are suitable for carrying out experimental-industrial tests in fluorine production [18, 19]. As a result of DTA, the quality rates of the plates were determined: three plates of Doncarb trademark and one plate of VCC trademark were related to the I rate, other plates of both trademarks were related to the II and III rates.

In our opinion, coke plates of rates I and II are to be used to manufacture anodes and to further evaluate their performance characteristics under the experimental conditions of fluorine production.

Using the data obtained in the present work and the parameters provided by TU 48-12-34–95, it is possible to provide a reliable evaluation of

the quality of plates and to predict their operation lifetime.

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