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# INTERACTION BETWEEN Fe AND $Cl_2$ IN THE BED OF GRAPHITIZED CARBON BLACK

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## Abstract

A possible route to remove Fe catalyst from graphitized carbon black synthesized in Boudouard's reaction is employment of gaseous chlorine in role of carrier. This process was explored by means of DTA method using the equipment designed in the laboratory. Obtained results demonstrate the complexity of processes occurring in systems containing Fe, C and $Cl_2$. Reactions in the system are highly influenced by the geometry of reacting solids. Process of $FeCl_3$ intercalation between graphite layers was observed analyzing DTA curves. The amount of Fe in the raw product of Boudouard's reaction was determined during the process of chlorination. Obtained results indicate that $Cl_2$ stream does not remove all the Fe even at high temperatures and prolonged chlorinating time.

**Keywords:** carbon black, chlorination, intercalation iron catalyst

## Introduction

Graphitized carbon black (CB) is a product of nanocrystaline dispersity. Boudouard's reaction is often used for its synthesis [1]. The reaction occurs on the surface of a catalyst. Among the other known catalysts iron can be used for this purpose. Therefore, the raw product of Boudouard's reaction contains a certain amount of Fe catalyst. This catalyst has an influence on electrical conductivity, magnetic properties, and surface activity of CB [2, 3]. Data concerning the removal of Fe catalyst from the bulk of raw material are scanty [4–6]. Possible use of chlorine for this purpose is worth an investigation, since this gas can be applied as carrier directly after the stage of Boudouard's reaction.

## Materials and methods

Graphitized carbon black (CB) was synthesized:

$$2CO_{(g)} \xleftrightarrow{Fe} C_{(gr)} + CO_{2(g)} \tag{1}$$

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using carbonyl Fe catalyst equipment for synthesis is shown in Fig. 1. Synthesis was executed in quartz tube (1) on 1 g carbonyl Fe catalyst (2) at 460°C. Carbon monoxide was produced in round bottomed flask (4) dehydrating formic acid [1]:

$$HCOOH \xrightarrow{H_3PO_4} CO + H_2O \qquad (2)$$

CO stream was flown through a condenser (7) where it loses the water and bubbled through flasks with KOH solution (9) where traces of formic acid are trapped. Flask with $Ba(OH)_2$ solution (10) served for indication of $CO_2$ produced in the reaction (1).

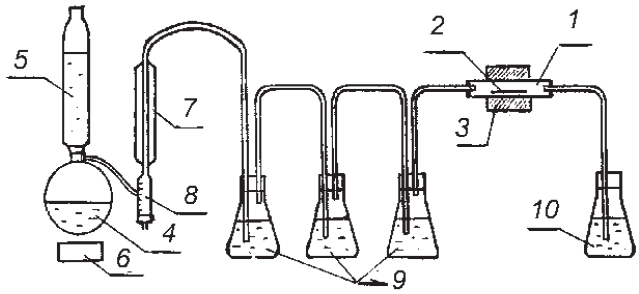


**Fig. 1** Equipment for synthesis of CB. 1 – quartz tube; 2 – ceramic pan with Fe catalyst; 3 – tube furnace SUOL 0,25.1.1/12; 4 – round bottomed flask with $H_3PO_4$; 5 – separatory funnel with HCOOH; 6 – heater; 7 – condenser; 8 – tube for shifting of the condensate; 9 – bubblers; 10 – flask with $BaCl_2$ solution

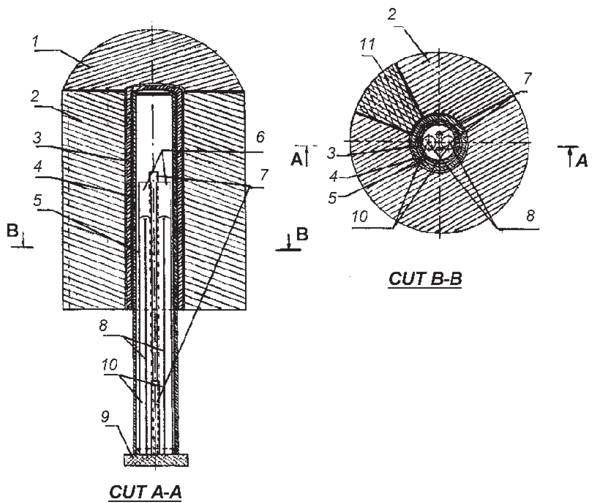


**Fig. 2** Construction of DTA apparatus. 1 – Al cover; 2 – tube furnace SUOL 0,25.1.1/12; 3 – outer quartz tube; 4 – brass foil; 5 – inner quartz tube; 6 – crucibles; 7 – micro pipes for gas support; 8 – thermo-couples (chromel–alumel); 9 – isolating blockage with built-in quartz tubes; 10 – quartz tubes serving as holders; 11 – ceramic sleeve

The necessity to apply equipment designed in the laboratory was conditioned by using of gaseous chlorine that is extremely corrosive agent at higher temperatures. Construction of that DTA apparatus is shown in Fig. 2. Bottoms of crucibles (6) were made of $Al_2O_3$ ceramics that was of high thermal conductivity (~30 W $K^{-1}$ $m^{-1}$). Using this construction chromel–alumel thermo-couples (8) were isolated from corrosive environment in the reaction zone. Thermo-junctions were pressed to bottoms of crucibles for better detection of heat transfer.

Temperature distribution in the reaction zone inside the furnace is uneven. It depends on furnace geometry as well as on winding density. Brass foil in the construction was used for the minimization the influence of uneven heat flow to crucibles. Temperature distribution in the profile of furnace quartz tube was determined using the same set of differential thermo-couple. Temperature in the furnace depends on the clamp voltage. Existing zone of approximately constant temperature is in the middle of tube furnace (Fig. 3). Considering these data, working position of crucibles at altitude of 7 cm was chosen for further experiments. Heating rate in all experiments was maintained 3.5±0.5°C $min^{-1}$. DTA experiments were carried out in the atmosphere of slow chlorine flow (flow rate 50 mL $min^{-1}$) maintained using PEM gas regulating equipment.

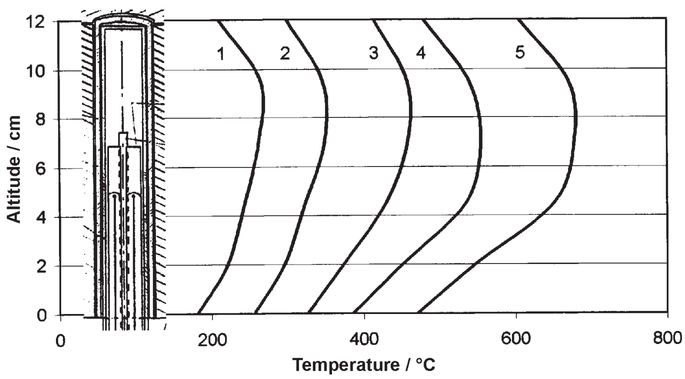


**Fig. 3** Temperature distribution in the profile of quartz tube inside the furnace. Clamp voltages: 1 – 20 V; 2 – 30 V; 3 – 40 V; 4 – 50 V; 5 – 70 V

Fe concentration in the bed of CB was analyzed using two methods. The total amount was determined by means of gravimetric method [7] after burning the analyte. Using the photometric method the concentration of Fe on the surface of small CB crystals was analyzed. Sulfosalicylic acid was chosen as a reagent for photometric Fe determination [8]. To weighed analyte in the beaker was added 10 mL of distilled water and 2 mL of HCl. After 10 min solution was filtered into 50 mL volumetric flask, filter paper carefully washed with distilled water and analyzed according to description.

Fe catalyst particle size distribution was established by means of sedimentation analysis [9]. Obtained data are presented in Fig. 4. Particle size distribution in steel sample was determined using optical microscope AU-26; it was within the range 0.05 to 0.5 mm.

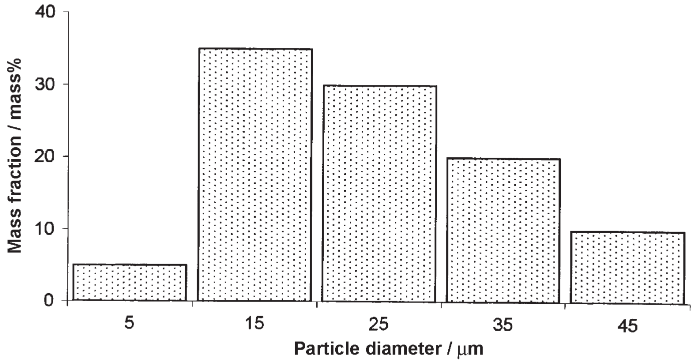


**Fig. 4** Particle size distribution of carbonyl Fe catalyst

## Results and discussion

The system we have investigated consists of three chemical active components: Fe, graphitized CB and gaseous chlorine. It is known that iron pieces without impurities are resistant to corrosive action of gaseous chlorine at room temperature [10]. Fe reactivity grows up significantly at higher temperatures as well as at finer dispersity of the metal. Reaction product $FeCl_3$ is volatile at higher temperatures; its sublimation occurs at 317°C [11]. Graphitized CB is known as a substance that readily adsorbs gaseous chlorine [12]. This adsorption can be amplified by various functional groups attached on the surface of CB. Interaction between reaction products is also possible. For example ferric chloride can dissolve gaseous chlorine and be intercalated between graphite layers [13, 14].

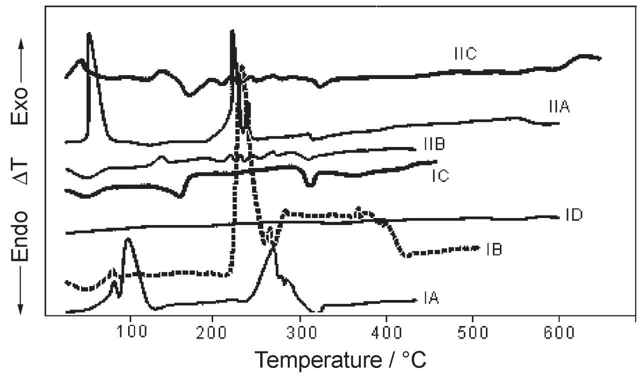


**Fig. 5** DTA curves of analyzed systems in the atmosphere of $Cl_2$. IA – carbonyl Fe; IB – steel; IC – $FeCl_3$; ID – purified CB; IIA – purified CB+carbonyl Fe; IIB – purified CB+$FeCl_3$; IIC – raw product of Boudouard's reaction (Table 1)

Having an objective to ascertain processes occurring in the system pure materials, such as Fe, $FeCl_3$ and graphitized CB were analyzed to start with, in the stream of gaseous chlorine by means of DTA method. Combining these materials into mixtures was made for locating interaction effects between components. Analyzed systems are presented in Table 1.

**Table 1** Systems analyzed by means of DTA

| System | Materials and mixtures | Method of preparation |
|---|---|---|
| I (pure materials) | A. Carbonyl iron | Commercial product; producer P. O. B. M-5168; purissimus |
| | B. Steel | Commercial product; producer VNIISO; sample No. 284-b. Composition (in mass%): Fe – 96.7; Mn – 0.08; Si – 3.05; P – 0.0089; S – 0.0028; Ni – 0.0066; Cu – 0.111 |
| | C. Ferric chloride | Synthesized in laboratory and sublimed in chlorine stream at 400°C |
| | D. CB | In Boudouard's reaction with Fe catalyst synthesized CB heated 45 min in the stream of gaseous chlorine at 540°C. Residual Fe concentration ~1% |
| II (mixtures) | A. CB with carbonyl Fe | Purified CB (with residual Fe concentration ~1%) mixed with carbonyl Fe in ratio 2:1 by mass |
| | B. CB with ferric chloride | Purified CB (with residual Fe concentration ~1%) mixed with $FeCl_3$ in ratio 2.5:1 by mass |
| | C. CB with Fe catalyst | CB synthesized by means of Boudouard's reaction with 37.74 mass% of the Fe catalyst |

DTA curves of these systems in the atmosphere of $Cl_2$ are shown in Fig. 5. In the reaction between carbonyl Fe and chlorine (system IA) at 90 and 265°C two exothermal peaks of unregular shape appear. We assume those peaks indicate the formation of ferric chloride. At 90°C the reaction between Fe and $Cl_2$ begins to occur leading to the formation of $FeCl_3$ and resulting in a high narrow peak on the DTA curve. Such shape of the peak is a sequel of the isolative effect of $FeCl_3$ that covers all the surface of Fe and cuts off the reaction. At higher temperatures chlorine becomes more active; it can permeate through isolative layer of $FeCl_3$ resuming the reaction (peak at 265°C). Later, at ~315°C small endothermal peak of $FeCl_3$ sublimation is obtained. In case when steel is taken to the reaction (system IB) observed processes are specific and different from those in the system with carbonyl Fe. The peak at 90°C is much smaller comparing it with the analogous one in the system IA. This can be explained taking into account different dispersities of these two samples. Later, likewise as in the system IA the reaction stops until 210°C due to the isolative effect of $FeCl_3$. At this higher temperature resumed process differs from that in the system IA. Because of more gross dispersity and impurities steel burning in $Cl_2$ atmosphere stretches up to 420°C and endothermal $FeCl_3$ sublimation peak is disguised by the exothermal plateau of $FeCl_3$ formation. System IC consists of pure $FeCl_3$ synthesized in the laboratory. In the DTA curve of this substance at 50°C an endothermal peak exists. At this temperature it is possible to obtain the desorption of $Cl_2$ from $FeCl_3$ sample [14]. Later, an endothermal peak occurring at 150°C can reflect removal traces of humidity adsorbed by hygroscopic $FeCl_3$. At 310°C an endothermal peak of $FeCl_3$ sublimation is observed. Exploring reactions of graphitized CB with residual Fe concentration ~1% in the atmosphere of $Cl_2$ (curve ID) no peaks in the system are observed. The reason for this is the sample preparation (Table 1). Reactions which could occur are exhausted at the stage of heating of CB in the stream of gaseous chlorine at 540°C.

In the system II (Table 1) containing mixtures peaks reflecting similar and even more complex processes are observed. In the mixture IIA consisting of purified CB and carbonyl Fe exothermal peak of $FeCl_3$ formation appears at 60°C. It is indicative of CB being an active media in the reaction between Fe and $Cl_2$. The similar effect is seen at higher temperatures: in the presence of CB, the second exothermal peak appears at 210°C. Comparing the shape and structure of these peaks with those in the system IA certain differences can be seen. The presence of CB not only decreases reaction temperatures but also has an effect on the process. The first exothermal peak appears more abruptly and its shape is more regular as it is in case with system IA. The process at higher temperatures is more complex: several sharp isolated peaks indicate $FeCl_3$ formation. CB there can act as a mediator adsorbing gaseous chlorine and intercalating $FeCl_3$ produced in the system. Exploring the mixture IIB consisting of purified CB and $FeCl_3$, in DTA curve series of specific small peaks in the range 150 to 300°C are observed. It is known that similar peaks originate in the process of $FeCl_3$ intercalation between graphite layers [15]. DTA curves of mixtures IIA and IIB have small singular peaks at ~320°C where sublimation of $FeCl_3$ occurs.

Mixture IIC consists of raw product of Boudouard's reaction (1), i. e. from carbonyl Fe catalyst which particles are covered with graphitized CB [16]. In the DTA curve of this mixture the peaks can be explained considering the information obtained in previous experiments. At the beginning of the DTA experiment a peak at 60°C is obtained. It is analogous to the similar peak in the system IIA, only its height is smaller. Later, beginning from 150°C, complex series of small peaks are obtained on the DTA curve. These indicate the simultaneous intercalation of $FeCl_3$ between layers of graphitized CB and the removal of moisture adsorbed by the raw product of Boudouard's reaction. In this DTA curve no peaks indicating second step of $FeCl_3$ formation are observed. Small peaks of $FeCl_3$ intercalation cover the corresponding area. Apparently, in Boudouard's reaction dispersed carbonyl Fe catalyst reacts over in one step until the temperature 150°C is reached. Moisture in the raw product of Boudouard's reaction can appear keeping it not isolated in contact with air. At ~320°C small endothermal peak of $FeCl_3$ sublimation is observed.

Obtained results demonstrate the complexity of processes occurring in systems containing Fe, C and $Cl_2$. Together with chemical properties and thermodynamical parameters reactions in the system are influenced by the geometry of reacting solids. Stages of $FeCl_3$ formation are highly exothermal. At the same time this effect can be considerably decreased in systems with highly dispersed Fe. There are some endothermal processes: $FeCl_3$ sublimation and moisture removal. Process of $FeCl_3$ intercalation being slightly expressed thermally is of high positive entropy [17].

Removal of Fe catalyst from the raw product of Boudouard's reaction was carried out in the stream of gaseous chlorine. The chlorination reaction was executed in a quartz tube heated by a tube furnace. $Cl_2$ flow rate was maintained 0.5 L $min^{-1}$. Gravimetric and photometric methods for determination of total and surface Fe concentration were used. Results are presented in Figs 6 and 7. The total amount of Fe in graphitized CB before chlorinating was 37.74 mass%, surface Fe concentration reached 0.08 mass%. This is indicative of almost all Fe catalyst being capsulated by carbon. In the stream of gaseous chlorine after 10 min total Fe amount is doubly reduced. At the same time surface Fe concentration increases considerably. These changes can be explained making the presumption that gaseous chlorine penetrates through the carbon covering and reacts with Fe. The reaction product $FeCl_3$ is sublimed and carried out from the reaction zone. In that way, the total amount of Fe decreases. Surface Fe concentration increases since the sublimation of $FeCl_3$ occurs through the surface of CB covering.

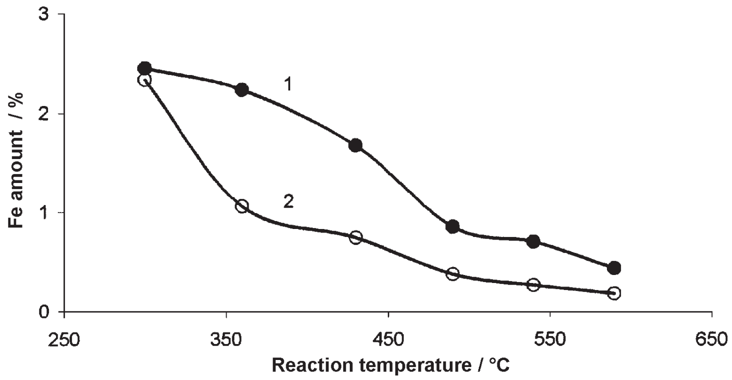


**Fig. 6** Fe amount in graphitized CB at different temperatures of chlorination reaction. Reaction time 45 min. 1 – total Fe; 2 – surface Fe concentration

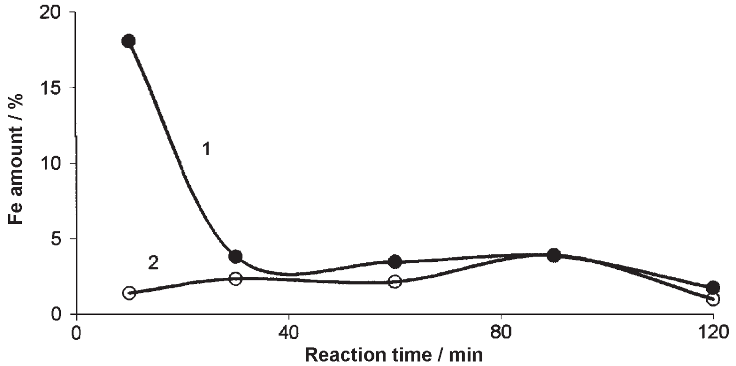


**Fig. 7** Fe amount in graphitized CB at different duration of chlorination reaction. Reaction temperature 450°C. 1 – total Fe; 2 – surface Fe concentration

The reaction temperature exerts more influence upon efficiency of Fe removal in comparison with the reaction time. Results obtained in the experiment indicate that $Cl_2$ stream does not remove all the Fe from CB even at high temperatures and prolonged chlorination. Residual $Cl_2$ concentrations (~1%) are fixed after boiling of CB (processed with 2 h at 590°C) in hydrochloric acid 0.5 h. The intercalation of $FeCl_3$ can be the reason for this [18].

## Conclusions

Interaction between Fe and $Cl_2$ in the bed of graphitized carbon black was investigated. For that purpose the DTA experiment using equipment designed in the laboratory was conducted. Pure materials, such as Fe, graphitized carbon black, $FeCl_3$, and their mixtures were analyzed. Peaks on DTA curves show that processes occurring in the system are complex. Together with chemical properties and thermodynamical parameters reactions are influenced by the geometry of solids. Experiments for removing of Fe from the bed of graphitized carbon black were done. Obtained results indicate that $Cl_2$ stream does not remove all the Fe even at high temperatures and prolonged chlorinating time. The intercalation of $FeCl_3$ can be the reson for this.

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