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The Study of Thermal Decomposition of Solid Carbonaceous Reducing Agents

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The article presents the research results in thermal decomposition of coal of different ranks: 2B – brown coal; D – long-flame coal; T – noncoking coal; SS – low-caking coal. Experiments to determine the volume and composition of gases generated by heating coal in an inert atmosphere are described. It is determined that the resulting gas phase is mainly composed of hydrogen and carbon monoxide. The temperature ranges are determined for the processes of thermal decomposition of coal. A thermal decomposition process includes two stages: stage I – removing hygroscopic and colloid-bound moisture; stage II – a sharp change in coal weight caused by the released volatiles and other coal-derived gases. The effect of coal thermal decomposition products on solid state reduction of iron from iron ore oxides is analyzed. It is proved that the gases generated by the thermal decomposition of coal are involved in solid-phase reduction of iron from oxides.

Keywords: reducing agent, coal, carbonaceous reducing agent, direct reduced iron, metallized materials.

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Изучение процессов термического разложения твердых углеродистых восстановителей

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Приведены результаты исследований процессов термического разложения углей разных марок: 2Б – бурый уголь; Д – длиннопламенный; Т – тощий; СС – слабоспекающийся. Показаны результаты экспериментов по определению объемов и составов газов, образующихся при нагреве углей в нейтральной атмосфере. Определено, что образующаяся газовая фаза преимущественно состоит из водорода и монооксида углерода. Установлены температурные интервалы процессов термического разложения исследуемых углей. Процесс термического разложения включает в себя две стадии: стадия I – удаление гигроскопической и коллоидносвязанной влаги; стадия II – резкое изменение массы угля, вызванное выделением летучих и продуктов газификации угля. Установлено влияние продуктов термического разложения углей на процессы твердофазного восстановления железа из оксидов железной руды. Показано, что газы, образующиеся при термическом разложении углей, участвуют в процессах твердофазного восстановления железа из оксидов.

Ключевые слова: восстановитель, уголь, углеродистый восстановитель, железо прямого восстановления, металлизированные материалы.

Introduction

Production and utilization of metallized materials has become a promising trend in ferrous metallurgy due to a degradation in the quality of metal scrap, depletion of iron ore deposits, high cost and scarcity of coking coal ranks, environmental law enforcement.

In this article, by metallized materials we mean metallurgical raw materials in which the main phase is represented by metallic iron. Basically, metallized materials are prepared in special metallurgical units via solid-state reduction of iron from its oxides without the use of coke. Solid reduction reactions occur with participation of solid carbon – C and gases – CO and H₂ at temperatures of 680-1200 °C to form a liquid phase [1].

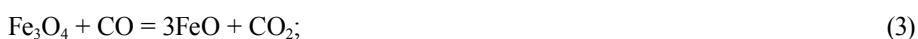
The most common metallization technologies are “Midrex”, “HyL III”. These technologies are implemented in shaft furnaces and retorts using the converted gas as the reducing agent. High consumption of natural gas and complexity of the conversion technology stipulated a development of metallization techniques using more available reducing agents, primarily coal [2, 3].

Discussion

It is believed that the process of solid reduction of iron from its oxides is a topochemical process as a result of which the old crystalline lattice is reduced and a new one is formed. In this process, the iron oxide and the carbon react involving the gas phase which is generated by carbon and can be described by the following gasification reaction:



The process of reduction of iron from its oxides proceeds according to the general law of transformation sequence [4]. At temperatures above 843 K reduction of iron by carbon monoxide proceeds according to the reactions:



Hydrogen is also an active reducing agent in solid-phase reduction of iron from oxides [5]. At temperatures above 843 K reduction of iron by hydrogen proceeds according to the reactions:



The processes of solid-phase reduction of iron from its oxides in reductive roasting of ore-coal charge is greatly influenced by the reducing agent behaviour [6]. Metallization processes using solid carbonaceous reducing agents are associated with thermal decomposition of the carbonaceous component [7]. The solid carbon component in the charge composition is subjected to thermal decomposition to form gaseous products and solid carbon residue [8]. With each particular reducing agent, thermal decomposition process proceeds in different ways [9]. The influence of the physicochemical characteristics of carbon reducing agent on metallization processes has not been fully described and requires elaboration [10, 11].

Materials and methods

Coals of different ranks were used when performing the tests: brown coal of rank 2B; long-flaming coal of rank D; low-caking coal of rank SS; noncoking coal of rank T. The research included studying thermal decomposition of the reducing agent under study and determining the composition of the gas phase generated by thermal decomposition.

The processes of thermal decomposition of coal were studied with the help of thermal analyzer Setaram LabSys Evo. Thermogravimetry methods allow accurate determination of changes in weight loss and heat flow when heating a sample under specified conditions. Data analysis provides a comparative analysis of change in weight loss (TG) and heat flow (HF) of the materials under study depending on temperature. Using thermogravimetric analyzer will also set the kinetic parameters of the solid-state recovery process for mixtures made up of iron ore and various carbonaceous reducing agents.

The composition of the gas phase formed as a result of thermal decomposition of the reducing agents was determined by means of laboratory experimental apparatus shown in Fig. 1.

The experimental procedure was as follows. Samples for the experiments were prepared by crushing the reducing agent and sifting out fractions sized from 0.125 to 0.05. The resulting powder weighing 4g was placed in a ceramic boat and lightly compacted. The boat with the test charge (3) was placed into the center of a quartz tube (2), after which the system was sealed. After that the system inert gas purging was performed for 15 min with atmospheric valve being opened (9). The system pressure was maintained in the range of 5 – 15 mmAq upon readings of U- shaped pressure gauge (6). After cutting-off the feed of the inert gas the furnace was switched on and heated up to 1273 K at a speed of 20 deg / min. During heating the amount of water in the flask was monitored (13). Upon reaching the desired temperature, the sample was heated for 15 minutes until the water flow was stopped, after which the valve was blocked-off (8). The collected gas was cooled to room temperature and displaced into the chromatograph working chamber through the dryer. Analysis of the selected gases was performed by chromatograph LCM – 8D.

The reducing firing of the sample briquettes was carried out in a resistance furnace with a graphite heater. A chemical analysis of the obtained materials was carried out. The metallization ratio was calculated by:

$$H_{\text{met}} = \text{Fe}_{\text{met}} / \text{Fe}_{\text{total}} \times 100, \quad (8)$$

where η – metallization ratio,%, Fe_{met} – content of metallic iron,%, Fe_{total} – total iron content (oxidized and metallic iron)%.

Table 1 shows the resulting physical and chemical characteristics of solid carbonaceous reducing agents under research.

Table 2 shows reference information on physical and chemical properties of the reducing agent used [12, 13].

The tests proved that the process of thermal decomposition of the coal ranks under study goes according to the general principles and includes two stages: stage I – removing absorbent and colloid moisture; stage II – a sharp change in coal weight caused by the release of volatile products of coal gasification (Fig. 2a).

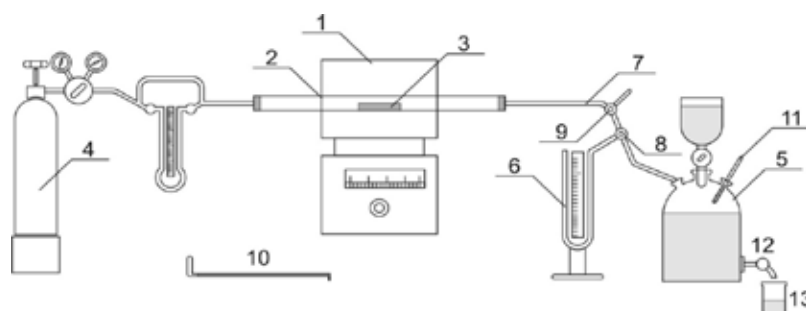


Fig. 1. The experimental unit for gas phase analysis: 1 – a heating furnace; 2 – quartz tube; 3 – ceramic boat with the test charge; 4 – cylinder with inert gas (argon); 5 – gas collector; 6 – U- tube manometer; 8 – shut-off valve; 9 – atmospheric valve; 10 – pusher; 11 – thermometer; 12 – valve; 13 – water collecting flask

Table 1. Physical and chemical characteristics, ash composition and elemental composition of reducing agents

Parameter	Coal grade				Low-sized coke
	2B	D	SS	T	
C _{fix} (fix carbon content), %	49,1	55,6	70,2	76,3	84,4
V ^r (volatile yield in dry ash-free basis), %	42,1	36,0	20,6	9,34	2,1
W ^r (moisture content in as-received basis), %	24,7	10,4	6,7	5,1	1,2
A ^d (ash content in dry basis), %	7,83	5,64	6,41	8,34	12,3
Chemical composition of ash, %:					
Fe ₂ O ₃	10,30	8,17	7,4	16,4	13,12
Al ₂ O ₃	5,40	25,6	16,3	25,0	23,72
CaO	45,30	9,70	2,5	5,38	5,15
P ₂ O ₅	0,20	1,80	0,37	0,75	0,69
SiO ₂	26,90	50,0	46,6	47,9	47,9
S	0,68	0,61	0,02	0,47	0,02
Element composition, %:					
C ^{daf} (carbon content in dry ash-free basis), %:	70,41	72,02	85,30	91,6	96,97
H ^{daf} (hydrogen content in dry ash-free basis), %:	3,88	6,12	4,78	3,20	0,56
N ^{daf} (nitrogen content in dry ash-free basis), %:	0,98	1,74	2,16	1,80	1,42
O ^{daf} (oxygen content in dry ash-free basis), %:	22,58	20,12	6,52	2,3	0,56
S ^{daf} (sulfur content in dry ash-free basis), %:	1,15	0,34	0,14	0,32	0,51

Table 2. Physical and chemical properties of reducing agents

Reducing agent	Density		Porosity, %	Reaction capacity, cm ³ /g×s	Ash melting temperature, K
	actual g/cm ³	apparent g/cm ³			
Coal rank 2B	0,56–1,62	0,31–1,41	38,1–41,2	5,12–5,47	1353–1513
Coal rank D	0,9–1,71	0,91–1,54	14,2–16,1	4,47–4,86	1480–1603
Coal rank T	1,42–1,45	1,26–1,36	11,1–12,0	0,93–1,56	1483–1560
Coal rank SS	1,35–1,54	1,20–1,41	14,1–15,3	0,62–1,08	1513–1653
Law-sized coke	0,95–1,31	0,85–1,21	46,5–531	0,52–1,07	1423–1543

For brown coal, stage II begins at a temperature of 443 K, which is 60 degrees lower than the thermal decomposition of long-flame coal, and 210 degrees lower than the decomposition of noncoking coal. The amount of gaseous products evolved during the thermal decomposition of brown coal is significantly greater than that in the decomposition of long-flame and noncoking coal ranks. Weight loss for brown coal was 90.6%, for long-flame coal it was 84.5%, for noncoking coal it made up 78.3%. The process of thermal decomposition of long-flame coal proceeds less intensively in comparison with other coal ranks under test. Positive thermal effect observed in the studied coals is stipulated by oxidation of carbon and volatiles. Bends of the curves HF demonstrate the complexity of the processes and overlapping endothermic and exothermic effects (Fig. 2b).

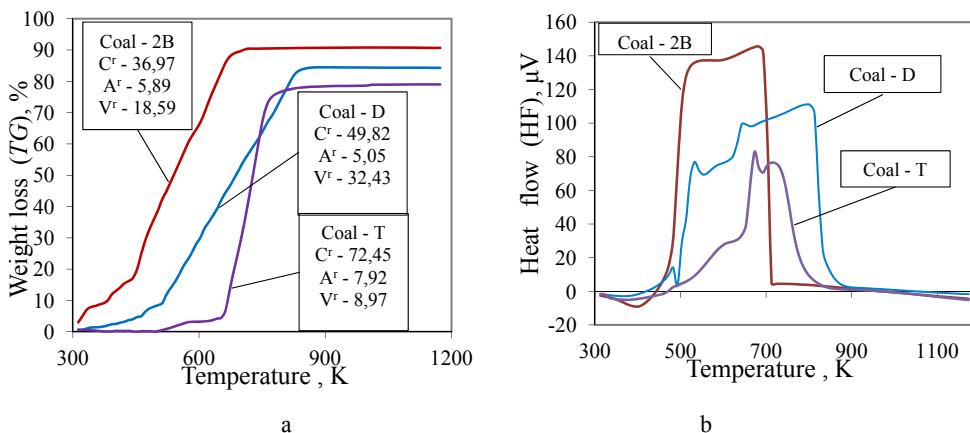


Fig. 2. Thermographic analysis of coals: a – weight loss during heating; b – variation of heat flow during heating

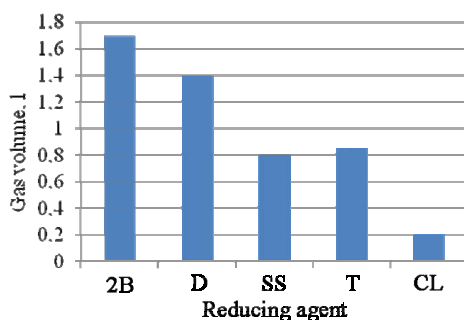


Fig. 3. The volume of the gas phase when heating a reducing agent from group 1 to 1173 K in the argon atmosphere

According to [14] physical state of carbon, in particular, the size and perfection of the graphite crystals, is among the factors that determine the nature of the coal decomposition process. The greater is distortion of carbon reducing agent crystal lattice, the faster is the thermal decomposition process. Distortion of the crystal lattice is observed in young ranks of coal, for example, brown coal; most integral crystal lattice is characteristic for graphite and for the reducing agents used in this research, particularly for low-sized coke.

The experimental study of thermal decomposition processes of different coal ranks determined the amount and composition of the gas phase formed during heating of the reducing agent up to 1173 K in argon atmosphere. Averaged results are shown in Fig. 3 and Table 3.

Gas analysis showed that the coal gas phase contains mostly hydrogen. The greatest amount of H₂ can be found in the gas phase of the brown coal, and the greatest amount of carbon monoxide is found in the gas phase of the low-sized coke. The following gas phase composition is typical for coal ranks under study: H₂ 72 – 75%; CO 9 – 16%; CO₂ 2 – 12%; CH₄ 4 – 7%. Gases of such composition (H₂ + CO = 80 – 91%) are used in the catalytic gas conversion with and Midrex® HyL III® technologies [6]. They also have some influence on the degree of reduction of major elements from oxides in the ore with partial replacement of coke with some rank of coals in ferroalloy production.

To determine the optimal amount of coal of different ranks in charge mixtures a series of experiments were carried out during which the amounts of coal briquettes were changed. The required quantity of coal was determined according to the reaction:



The amount of coal in the charge mixtures was different: $C/C_{\text{stoich}} = 0,8; 0,9; 1; 1,1$ (C – actual carbon content of the mixture; C_{stoich} – stoichiometrically required carbon content). A briquette under test was placed in the graphite crucible and covered with coal (2B – coal rank, fractions from 2 to 10 mm). Then the crucible containing the briquette was subjected to reductive roasting at a temperature of 1373 K for 60 min. The content of Fe_{met} , Fe_{total} of carbon in the resulting materials was determined with the help of chemical analysis. The averaged results of the experiments are presented in Fig. 4.

The experiments showed that increasing the amount of coal in the mixture does not increase the content of metallic iron in the material. As seen in Fig. 4a, the content of reducing agent equal to 90% of stoichiometric requirement is the most advantageous when using long-flame, noncoking and low-caking coals. When brown coal is used it is possible to use an even smaller amount of coal making up 80% of the stoichiometric requirement. Thus, when using brown coal the maximum content of metallic

Table 3. Gas phase composition when heating reducing agents up to 1173 K in the argon atmosphere

Reducing agent	Gas composition, %					
	CO ₂	CO	H ₂	CH ₄	O ₂	N ₂
Coal rank 2B	11,47	6,09	75,59	6,63	0,22	-
Coal rank D	10,73	16,03	66,01	4,86	2,36	-
Coal rank SS	4,84	9,78	77,10	4,24	0,68	3,35
Coal rank T	2,21	13,55	72,67	3,85	0,82	6,89
Low-sized coke	29,52	53,38	11,59	3,96	1,55	-

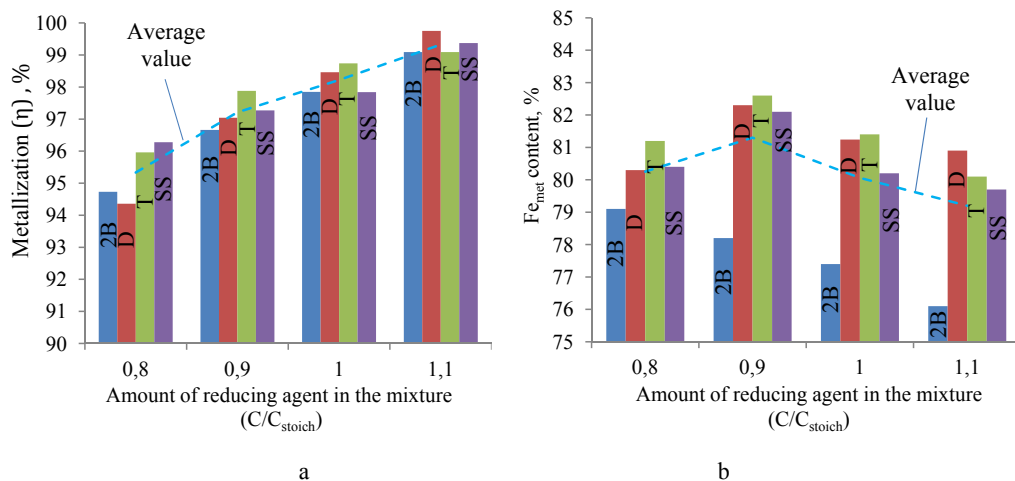


Fig. 4. The effect of the amount of coal in briquettes on the metallization process. Results obtained using: 2B – brown coal; D – long-flame coal; T – noncoking coal; SS – low-caking coal

iron does not exceed 78%. Increasing the coal content in the ore-coal mixture increases the degree of metallization irrespective of the coal rank (Fig. 4b).

Conclusions

The results showed that the process of thermal decomposition of coal has two main stages: stage I – the removing hygroscopic and colloid-bound moisture; stage II – a sharp change in coal weight caused by the released volatiles and other coal-derived gases. Thermal decomposition of younger coal starts at lower temperatures to form more gas phase. The composition of the gas phase formed by the thermal decomposition of coal contains 80-91% of a mixture of hydrogen and carbon monoxide. The experiments also proved that gas phase is involved in the processes of the solid state reduction of iron from oxides using coal. It lets us decrease the amount of reducing agent in the incoming ore-coal mixture.

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