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# The use of coal in a solid phase reduction of iron oxide

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**Abstract**. The results of the research process of producing metalized products by solid-phase reduction of iron using solid carbonaceous reducing agents. Thermodynamic modeling was carried out on the model of the unit the Fe-C-O and system with iron ore and coal. As a result of modeling the thermodynamic boundary reducing, oxidizing, and transition areas and the value of the ratio of carbon and oxygen in the system. Simulation of real systems carried out with the gas phase obtained in the pyrolys of coal. The simulation results allow to determine the optimal cost of coal required for complete reduction of iron ore from a given composition. The kinetics of the processes of solid-phase reduction of iron using coal of various technological brands.

## Introduction.

Promising raw material for the production of high-quality steel is a so called direct reduced iron, which is obtained by outside the blast furnace redistribution of iron-containing materials. Production technology metalized products developed and improved with 60s pro-nineteenth century, and to date the volume of production of DRI reached 76 million tons per year. In Russia and in the world DRI generally prepared using as reducing agent of the converted gas. Granular iron ore is fed into the shaft type furnace, where temperatures not exceeding the melting temperature materials, reduction of iron oxides occurs. The use of natural gas leads to a rise in the cost of iron and limits the development of these technologies in areas where natural gas is scarce. Reducing the consumption of natural gas is possible when replacing coal. Currently, up to 8 % of the world's iron produced by direct reduction is carried out with the use of coal. There are various technological proposals for the use of coal metalized products; there is no single technology, which received wide commercial distribution.

Processes solid reduction of iron oxide with iron ore as a solid carbonaceous reductant coal are not unambiguous assessment, due to multi-component system, and the occurrence of simultaneous reduction reactions involving solid carbon and gaseous products. Keep in mind that in the process of solid reduction reactions simultaneously develop both direct and indirect reduction of iron oxide ores as-is useful [1].

1. Actual job is to research and develop energy-efficient technology of complex processing of iron-ore and coal to produce metalized materials suitable for use in steelmaking critical applications [2].

In conducting research as iron-containing materials used iron ore (iron ore deposit Tashtagolsky) and iron ore concentrate produced by ore beneficiation. As solid carbonaceous reducing agents used nut coke and coals of different technological marks (lignite brand – B2; long-flame coal brand – D;

Coal weakly caking brand – SS; coal skinny mark – MOT). The compositions of the materials used and reducing technical analysis are shown in Tables 1–3.

**Table 1.** The phase composition of the starting iron ore.

| | |
|---|---|
| Lot Of: | hematite ($Fe_2O_3$) |
| Attendant: | magnetite ($FeO{\cdot}Fe_2O_3$), goethite ($\alpha$–FeOOH), quartz ($SiO_2$), kaolinite ($Al_4[Si_4O_{10}](OH)_8$) |
| Lil Bit: | iron chloride, feldspar |

**Table 2**. The chemical composition of iron-containing materials.

| The chemical composition of the iron ore, % mass | | | | | | | |
|---|---|---|---|---|---|---|---|
| $Fe_{overall.}$ | $SiO_2$ | $Al_2O_3$ | $P_2O_5$ | CaO | MgO | S | moisture |
| 52.3 | 19.15 | 3.31 | 0.072 | 0.94 | 0.76 | 0.42 | 5.78 |
| Chemical composition of iron ore concentrate, % mass | | | | | | | |
| 61.2 | 7.92 | 2.41 | 0.02 | 1.96 | 2.31 | 0.41 | 6.27 |

**Table 3.** Technical Analysis reducing.

| Reducing agent | Characteristic | | | |
|---|---|---|---|---|
| | The content [C] in the working masses,% | $A^d$ (ash),% | $V^{daf}$ (volatile),% | $W^r$ (moisture),% |
| Coal –B2 | 49.1 | 7.83 | 46.7 | 24.7 |
| Coal – D | 55.6 | 5.64 | 43.5 | 10.4 |
| Coal – SS | 70.2 | 6.41 | 24.3 | 6.7 |
| Coal – TO | 76.3 | 8.34 | 15.2 | 5.1 |
| Coke | 84.4 | 12.3 | 1.3 | 1.2 |

The studies included thermodynamic modeling of solid-phase reduction of iron oxide iron ores using software system "Terra", developed at the Moscow State Technical University. N.E. Bauman [3].

The process of reduction of iron oxides, iron ore according to the principle Baykova takes place in steps:

$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$ at $T \geq 843$ K.

The use of coal as reducing processes associated with the development of the direct and indirect restoration. Direct reduction of iron oxide with solid carbon is in accordance with the reactions:

$3Fe_2O_3 + C = 2Fe_3O_4 + \{CO\} - 129{,}07$ MJ; (1)

$Fe_3O_4 + C = 3FeO + \{CO\} - 187{,}28$ MJ; (2)

$FeO + C = Fe + \{CO\} - 152{,}67$ MJ. (3)

According to [1] in the presence of a solid carbonaceous reducing the interaction between carbon and iron oxides is carried out with the assistance of the gas phase which is recovered by a carbon gasification reaction:

$CO_2 + C = 2CO - 166{,}32$ MJ. (4)

The thermal decomposition of coal is accompanied by the formation of gaseous products that are involved in the reduction of iron oxides according to reactions:

$3Fe_2O_3 + \{CO\} = 2Fe_3O_4 + \{CO_2\} + 37{,}25$ MJ; (5)

$Fe_3O_4 + \{CO\} = 3FeO + \{CO_2\} - 20{,}96$ MJ; (6)

$FeO + \{CO\} = Fe + \{CO_2\} + 13{,}65$ MJ; (7)

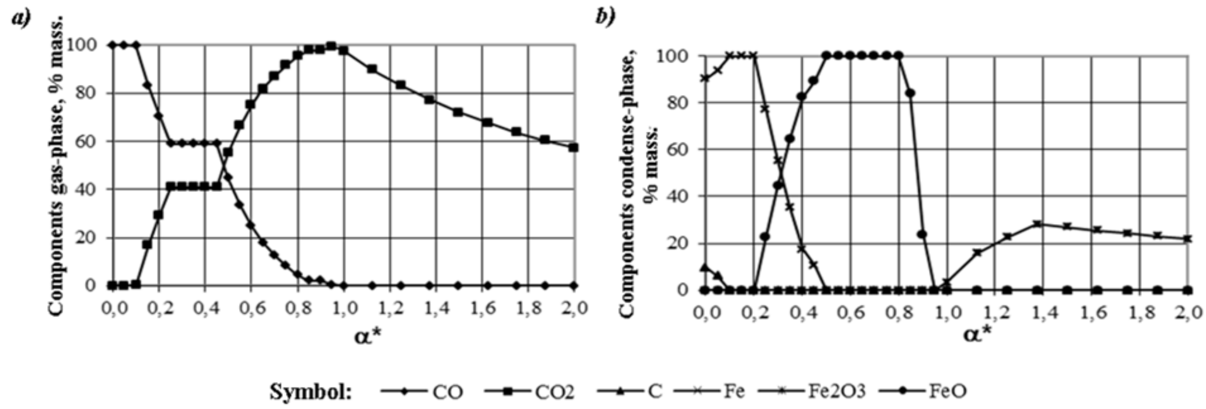
$3Fe_2O_3 + H_2 = 2Fe_3O_4 + \{H_2O\} - 4{,}2$ MJ; (8)

$Fe_3O_4 + H_2 = 3FeO + \{H_2O\} - 62{,}41$ MJ; (9)

$FeO + H_2 = Fe + \{H_2O\} - 27{,}80$ MJ. (10)

2. Thermodynamic modeling includes research on the model of the elementary system and study the recovery of iron ore from the oxides of iron ore using coal of various technological brands.

Model systems elemental composition element wise Fe-C-O, formed by setting the composition of the starting mixture in a 1 mol $Fe_2O_3$ oxide and the number of moles of carbon and oxygen, respectively are varied parameters n and m ($Fe_2O_3$+nC+mO). In the simulation process is carried out the following tasks: determination of the temperature and the amount of carbon to ensure full recovery of iron; determining the optimum values of the index a* (measure a*=m/n – number ratio of oxygen to carbon in the system). Figures 1 shows the dependence of the absolute content of the gas components (a) and the condensed phase (b) of the parameter a*.




a – the composition of the gas phase depending on the values of a*;
b – the components of the condensed phase, depending on the value of a*

**Figures 1.** Thermodynamic modeling in the Fe-C-O.

The analysis of the calculation results showed the presence of three areas. Restorative region exists for values of a* < 0,2. The transition region is characterized by a decrease in the concentration of the reduced iron to extinction and increasing the FeO content in the condensed phase. Oxidative area begins at a* = 0,5, when in the condensed phase completely disappears iron. When a* = 0,95 in the gas phase completely disappears from, and in a condensed FeO. Thus, as a result of research of redox conditions in the system Fe-CO reducing identified boundaries, transitional and oxidizing areas and corresponding values a*. The best conditions for iron reduction corresponds to the value of the index a < 0,2 [4].

Thermodynamic modeling of solid-phase reduction of iron oxide ore using coal of various grades of technology was carried out taking into account the element, reducing carbon oxide compounds (Table 4, 5) and the composition of the gas produced by heating the reducing agents (Table 6) [5 – 7].

**Table 4.** The elemental composition of reducing.

| Reducing agent | Elemental analysis for fuel mass, % | | | | |
|---|---|---|---|---|---|
| | $C^{daf}$ | $H^{daf}$ | $N^{daf}$ | $O^{daf}$ | $S^{daf}$ |
| Coal – 2B | 70.41 | 3.88 | 0.98 | 22.58 | 1.15 |
| Coal – D | 72.02 | 6.12 | 1.74 | 20.12 | 0.34 |
| Coal – SS | 85.30 | 4.78 | 2.16 | 6.52 | 0.14 |
| Coal – TO | 90.79 | 3.96 | 2.93 | 2.16 | 0.31 |
| Coke | 96.97 | 0.56 | 1.42 | 0.56 | 0.51 |

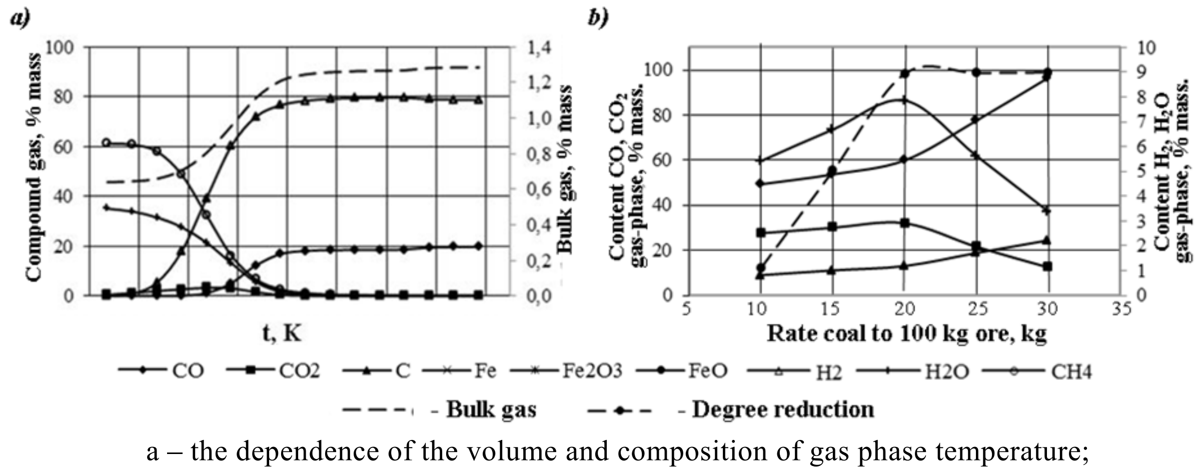
**Table 5.** The oxide composition of the ash reducing, %.

| Reducing agent | $Fe_2O_3$ | $Al_2O_3$ | CaO | MgO | $P_2O_5$ | $SiO_2$ | S |
|---|---|---|---|---|---|---|---|
| Coal – 2B | 10.30 | 5.40 | 45.30 | 5.90 | 0.20 | 26.90 | 0.68 |
| Coal – D | 8.17 | 25.60 | 9.70 | 3.70 | 1.80 | 50.00 | 0.61 |
| Coal – SS | 17.46 | 26.55 | 1.2 | 1.58 | 0.5 | 51.1 | 0.02 |
| Coal – TO | 16.4 | 25.01 | 5.38 | 1.66 | - | 45.2 | 0.06 |
| Coke | 13.12 | 23.72 | 5.15 | 1.76 | 0.69 | 47.9 | 0.02 |

**Table 6.** Composition of reducing gas when heated to 1173 K.

| Reducing agent | The gas composition, % | | | | | |
|---|---|---|---|---|---|---|
| | $CO_2$ | CO | $H_2$ | $CH_4$ | $O_2$ | $N_2$ |
| Coal – 2B | 10.21 | 5.42 | 44.30 | 5.90 | 0.20 | - |
| Coal – D | 8.17 | 25.60 | 50.24 | 3.70 | 1.80 | - |
| Coal – SS | 3.54 | 7.15 | 56.35 | 3.1 | 0.5 | 2.45 |
| Coal – TO | 1.35 | 8.26 | 67.3 | 2.35 | 0.5 | 4.2 |
| Coke | 13.12 | 23.72 | 5.15 | 1.76 | 0.69 | - |

The results of process simulation solid reduced iron using coal as a reductant possible to determine the dependence of the degree of reduction of iron and the gas phase flow of coal from each processing mark. Figures 2 shows the dependence of the volume and composition of the gas phase formed as a result of the evolution of volatile components by heating long-flame coal. The degree of recovery and composition of the gas phase from the flow of long-flame coal in the reduction of 100 kg of ore are shown in Figures 2b.




a – the dependence of the volume and composition of gas phase temperature;
b – the degree of recovery and gas phase composition of long-flame coal consumption in the reduction of 100 kg of ore

**Figures 2.** Thermodynamic modeling of solid-phase reduction of iron oxides long-flame coal.

3. The study included high temperature laboratory experiments. The resulting simulation reducing cost values corresponding to the highest degree of reduction, were used in the manufacture of ore-coal compositions. Pre components subjected to crushing and desired fractions followed by classifying, then in predetermined proportions of ore and reducing agent composition were averaged and subjected to briquetting. These briquettes were placed in a graphite crucible and covered with a lid. The crucible with braces injected into the hot zone resistance furnace heated to a temperature of the experiment and kept at isothermal holding time. For the experiments was chosen isothermal holding temperature 1173 K at the holding time of 90 min. In the resulting experiments metalized materials by chemical analysis

determined the content $Fe_{total}$, $Fe_{met}$, by calculation determines the degree of metallization – $\varphi_{met}$, according to the formula:

$\varphi_{met} = Fe_{met}/Fe_{total} \cdot 100$,

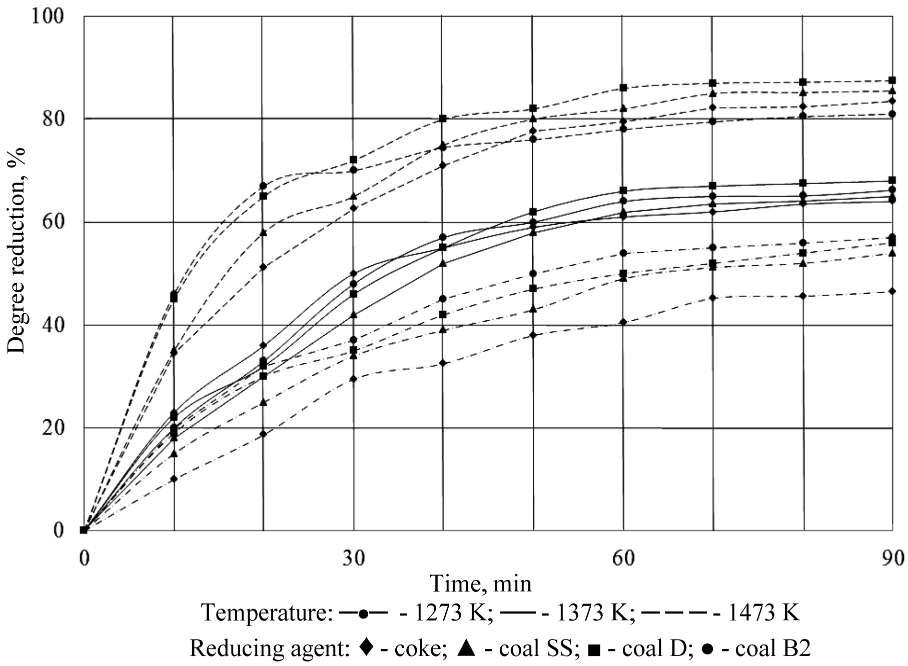
where $Fe_{met}$ – metallic iron content,%;

$Fe_{total}$ – total iron content (amount of oxidized and metallic iron) %.

The highest degree of metallization (close to 97 %) was obtained by applying the ore-coal briquettes, which corresponds to an amount of reducing agent, the resulting thermodynamic modeling (Figure 2b).

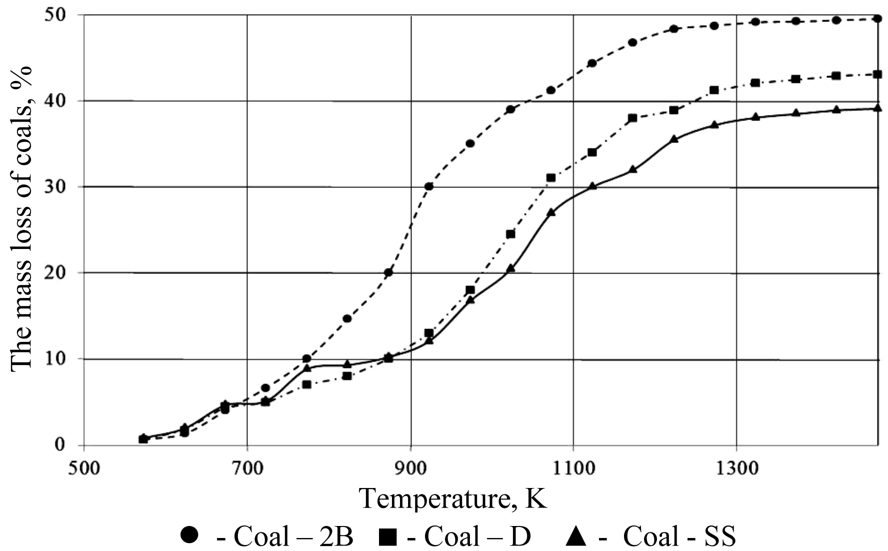
Influence of physico-chemical properties of the carbonaceous reducing processes was studied by solid state reduction of kinetic studies [8]. Experiments were performed using a batch weighing method in a resistance furnace at temperatures 1273, 1373, 1473 K, and the isothermal hold duration 90 min. The calculation of the degree of recovery in the construction of the kinetic curves was carried out taking into account the loss of mass of sample corrected for moisture content in a mixture of volatile and fly away. The criterion considered 100% recovery linkage weight loss corresponding to the total carbon monoxide formation reactions – 1, 2, 3. The experimental results obtained by using as a reducing coke nut, caking, long-flame coal and lignite with different isothermal soak temperatures are shown in Figure 3.

From these dependences that after 60 minutes of isothermal heating at a temperature of 1473 K have the greatest degree of reduction in briquette made up using as a reducing long-flame coal. The resulting material contains $Fe_{met}$ – 83%, with $\varphi_{met}$ – 96 %. As a result, the isothermal hold at a temperature of 1373 K for 60 min. the greatest degree of recovery in briquettes made up using as a reducing agent of brown coal. The resulting material contains $Fe_{met}$ – 67 %, with $\varphi_{met}$ – 97 %. As a result, the isothermal hold at 1273 K for 60 minutes in the highest degree of reduction observed for briquettes made up using as reducing lignite. The resulting material contains $Fe_{met}$ – 50 %, with $\varphi_{met}$ – 97 %. Fig. 3 shows that the intensity of the processes of solid-phase reduction of iron oxides, iron ore depends not only on the material composition used in iron and carbon components, but also on their physical and chemical properties.




**Figures 3.** Dependence of the degree of reduction of the isothermal holding time.

Study of the processes of thermal decomposition was carried out by reducing periodic weighing sample placed in a resistance furnace at a constant heating furnace from 300 to 1200 K. The experiments used a fraction of the corresponding coal used in the manufacture of ore-coal briquettes. To create conditions of oxygen deficiency in the furnace supplied with a neutral gas, argon flow rate of 50 ml/min. Weight loss of sample recorded at intervals of 50 K. The processed results of the experiments are shown in Figures 4.




**Figures 4.** Dependence of the mass loss of coals of different technological brands of temperature.

From the figure it is shown that thermal decomposition process different grades of coal proceeds differently. Thermal decomposition of brown coal begins at temperatures lower than the thermal decomposition of the stone. Amount of gaseous products evolved during the thermal decomposition of brown coal, significantly more than the expansion of long-flame and caking. The process of thermal decomposition of coal caking occurs less intense compared to other brands of coal under consideration [9].

**Conclusions**.

As a result of the research, a thermodynamic model of the process of obtaining the metalized products by solid-phase reduction of iron oxides from iron ore using coal as a reductant. Application of the model allows to determine the optimal cost of coal of different brands in the preparation process of metalized products with a given composition and degree of metallization. In the course of the research also obtained data on the influence of physical and chemical properties of different carbonaceous reducing agents on the intensity of the recovery processes. The data obtained can be used in the development of co-processing techniques iron ore and coal in order to obtain high quality metalized materials.

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