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THERMODYNAMIC AND KINETIC INVESTIGATION OF IRON SILICATE REDUCTION WITH DIFFERENT REDUCING AGENTS

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ABSTRACT

The thermodynamics and kinetics of the reduction of iron silicate (fayalite), generated as a result of flotation processes in the production of copper concentrates, were studied. Three reducing agents were used - coke, charcoal, and graphite, in ratios to the stoichiometrically calculated amounts of reducer: 1: 1.5; 1: 2; 1: 2.5. The free Gibbs energy in the temperature range from 973 K to 1040 K was determined experimentally and the corresponding equations for $\Delta G = f(T)$ *were derived. The kinetic parameters were determined using thermogravimetric and differential methods at temperatures up to 1273 K. The results showed that the reduction process using coke went through three stages, and using charcoal - two stages. The reactions that took place were of the first order. Carbonated reduction of iron silicate occurred in the kinetic region. The highest values of the apparent activation energy were obtained as 67.83 kJ mol*$^{-1}$ *when using coke (1257 K), and when using graphite - 60.29 kJ mol*$^{-1}$ *at 1318 K. The lowest values of the activating energy 36 kJ mol*$^{-1}$ *were observed with a charcoal reducer in the temperature range 966-1573 K.*

Keywords: *iron-silicate (fayalite), thermodynamics, kinetics, activation energy.*

INTRODUCTION

One of the products, obtained by the flotation method of enrichment while processing copper concentrates, is iron silicate (fayalite). The material is dispersed as granulometry substance with a high content of iron and silicon dioxide in the form of fayalite, magnetite, quartz, etc. [1]. A small part of fayalite is used in the cement industry and other areas of construction. A significant its quantity is deposited to landfills. In order to expand the areas of application of iron silicate (fayalite) in the field of metallurgy, it is necessary to have a thorough knowledge of the thermodynamic and kinetic features of its reduction.

Ya Luong Liao et al. [2] investigated the carbothermal reduction of iron silicate. The reduction was carried out under conditions of reduction frying at 1423 K for 4 hours. The reduction reaction of fayalite [3] can be expressed by equation (1), and could be obtained by combining equations (2) and (3):

$$Fe_2SiO_4(s) + 2C(s) \rightarrow 2Fe(s) + SiO_2(s) + 2CO(g)$$
$$\Delta G = 354140 - 341.59\ T\ \ (J\ mol^{-1}) \qquad (1)$$

$$2FeO(s) + 2C(s) \rightarrow 2Fe(s)+2CO(g)$$
$$\Delta G = 295808 - 300.44\ T\ \ (J\ mol^{-1}) \qquad (2)$$

$$2FeO(s) + SiO_2(s) \rightarrow Fe_2SiO_4(s)$$
$$\Delta G = -36200 + 21.09\ T\ \ (J\ mol^{-1}) \qquad (3)$$

A. Warczok and T.A. Utigard [4] reduced synthetic fayalite in laboratory conditions in the temperature range 1523 K - 1723 K. They found the activating energy to be $E_a = 246 \pm 29$ kJ mol^{-1}. Jurgen Kunze et al. [5] used as a reducer CaC_2 in quantities ranging from 0.1 % to 1.5 %.

$$4Fe_3O_4(sl) + CaC_2(s) + Fe_2SiO_4(sl) \rightarrow 14FeO(sl) + CaSiO_3(sl) + CO(g) + CO_2(g) \qquad (4)$$

The reaction is exothermic at 1523 K. $\Delta H^{1523\ K.} \rightarrow -11$ kJ mol^{-1} Fe_3O_4.

The proper selection of a reducer and its preparation significantly determines the technical and economic indicators of the production.

The aim of the present work is to investigate the main thermodynamic and kinetic characteristics in the reduction of iron silicate (fayalite) with different reducing agents. We used charcoal with a reactivity at 1323 K - 11.1 mL g^{-1}s^{-1}, and metallurgical coke - 0.57 mL g^{-1}s^{-1}.

Charcoal has a high relative electrical resistance and high reactivity. Coke is widely used in ferrous and non-ferrous metallurgy and foundry [6-7].

EXPERIMENTAL

Materials and equipment

The chemical composition of iron silicate is presented in Table 1. The moisture content is 1.34 %.

The reduction of iron silicate was studied in ratios to the stoichiometrically calculated amounts of reducer: 1: 1.5; 1: 2; 1: 2.5. Briquettes with a diameter of 10 mm and a pressure of P = 1.9 atm were prepared from the mixtures on a hydraulic press.

Thermodynamic phase equilibrium measurement

When studying the thermodynamics of heating of the investigated systems, a galvanic cell with solid electrolyte $ZrO_2(Y_2O_3)$ was used as well as reference electrodes Ni/NiO.

Gibbs free energy data $DG°_T$(NiO)

$Ni + O_2 = 2NiO$ (5)

is according to [8, 9]

$\Delta G^o(NiO) = -233651 + 84.893\ T$, kJ mol^{-1} or

$$lgP_{O_2} = \frac{-12225}{T} + 4.44 \qquad (6)$$

The equation for the reference electrode Ni/NiO is:

$$lg\ P'_{O_2} = -\frac{E.20193}{T} - \frac{12225}{T} + 4.44 \qquad (7)$$

All nine samples were heated up to a temperature of 1040 K, taking into account the recorded changes in electromotive force (EMF). The oxygen partial pressure of the investigated oxide in each sample and temperature was determined. Based on them, the change in Gibbs' free energy was determined. Fig. 1 shows the change of the experimentally obtained values of the Gibbs energy depending on the temperature.

The average value of the dependence $lgPco_2/Pco$ for all samples was 14.69. From the experimental values, the equations of the dependence of $\Delta G = f(T)$ were derived:

$\Delta G = -a + b.T$, J mol^{-1} (8)

The coefficients "a" and "b" are presented in Table 2 for each variant and reducing agent.

The results show that graphite has lower absolute values of free energy compared to the other reducing agents. When using a reducer in a ratio of 1:1.5 to iron silicate, charcoal has the highest values of ΔG. Due to the low amount of the reducer and the relatively low heating temperature, both fuel (oxidation) and gasification processes of carbon and reduction processes cannot

Table 1. Chemical composition of iron silicate, mass %.

Fe_2O_3	FeO	SiO_2	Al_2O_3	CaO	MgO	ZnO	PbO	Cu	MnO
11.26	51. 55	27.18	3.76	2.32	1.19	1.69	0.53	0.47	0.06

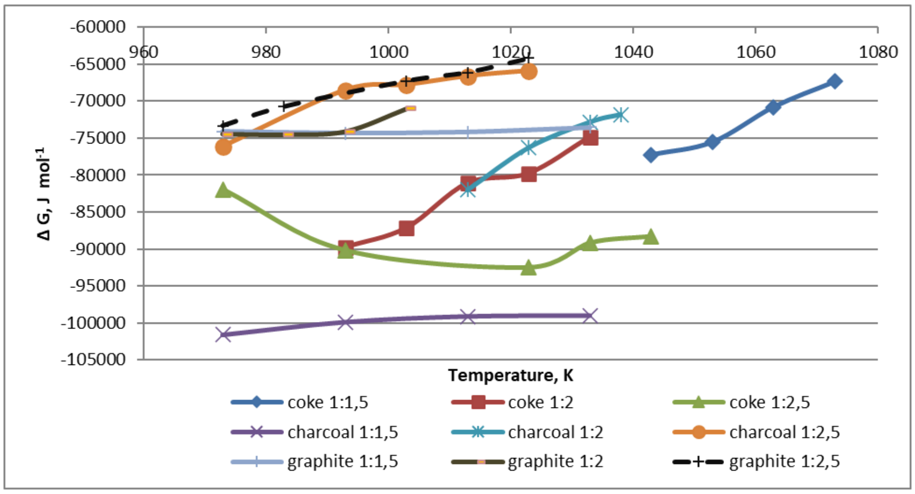

Fig. 1. Comparative graphs for the temperature dependence of ΔG for the investigated reducing agents.

Table 2. Coefficients “a” and “b”, included in equation (8) of $\Delta G = f(T)$.

	coke 1:1.5	coke 1:2	coke 1:2.5	charcoal 1:1.5	charcoal 1:2	charcoal 1:2.5	graphite 1:1.5	graphite 1:2	graphite 1:2.5
a	437665	457970	123974	142575	496403	268147	95348	248201	245022
b	344.92	370.62	34.00	42.54	409.71	198.95	21.05	176.2	176.85

progress well. Only the first degree of reduction of iron oxides takes place, namely

$3Fe_2O_3 + C \rightarrow 2Fe_3O_4 + CO$.

At iron silicate-reducer ratios of 1:2, the reducer is sufficient for both combustion and gasification processes to occur. At these ratios, coke has higher Gibbs energy values. The gasification reaction progresses as well as $Fe_3O_4 \leftrightarrow Fe_2O_3$. In the temperature range 683 - 723 K, CO decomposes into CO_2 and solid carbon, according to the Baudouar reaction, but above 1573 K the reaction proceeds until the complete gasification. The X-ray phase analysis of the products of the three samples showed mainly Fe_3O_4 and small amounts of Fe_2O_3. Fayalite Fe_2SiO_4 is found in all samples, which is completely realistic, as it thermally dissociates at a temperature of 1473 K. From the X-ray phase analysis it can be said that the best ratio of fayalite: reducer is 1:2. At a ratio of 1:1.5, there is a shortage of a reducer. Basically, it burns and is not enough for the reduction. At a ratio of 1:2.5, there is an excess of a reducer, which burns and creates an additional oxidizing atmosphere.

Kinetics

A thermogravimetric apparatus STA PT1600 TG-DTA/DSC (STA Simultaneous Thermal Analysis) - LINSEIS Messgeräte GmbH, Germany was used in the experiments.

In general [10], the gasification rate for a heterogeneous reaction can be described as:

$$r = \frac{dx}{dt} k(T) f(x) \tag{9}$$

$$k(T) = A\, exp\left(-\frac{E_a}{R\,T}\right) \tag{10}$$

where A is the pre-exponential factor; E_a is the activation energy; and R is the universal gas constant, $R = 8.314$ J K^{-1} mol^{-1}. Here, *f(x)* is the gasification mechanism function and x denotes carbon conversion.

Ratios of iron silicate to the reducing agent: 1:2 were used to study the kinetics. The initial weight of the samples was as follows: sample 1 - 23 mg, sample 2 - 22.9 mg; sample 3 - 23 mg. The investigations was performed in the temperature range 293 K - 1573 K, the heating rate was 283 K min^{-1}, the samples are powder with a particle size of not more than 0.5 mm, in a static air-gas environment, in stabilized corundum crucibles; the temperature was measured with thermocouple type S (Pt10%/Pt-Rh). The obtained derivatograms are presented in Fig. 2 to Fig. 4.

Differential scanning calorimetry (DSC) detects changes in temperature and heat flow during thermal transitions of material by placing sample material in a furnace. On the DSC curve of sample 1 containing iron silicate and coke (Fig. 2), three exothermic peaks were observed. One of them was at a temperature of ~ 613 K, the second at ~ 712 K (the enthalpy of formation was 217 J g^{-1}), and the third one at ~ 901 K (the enthalpy of formation was 1311 J g^{-1}). The first effect corresponds to the oxidation of magnetite to magnetite hematite or maghemite [11]. In the range from 649 K to 720 K, coke is burned with the release of CO_2, which creates an additional oxidizing atmosphere in the reaction space. The third exothermic effect characterizes the transition of γ-Fe_2O_3 to α-Fe_2O_3 in the temperature range 783 K - 1023 K. The increase in the mass of the sample after this temperature, Fig. 2 thermogravimetry (TG) curve shows the partial dissociation of fayalite to hematite and of hematite to magnetite. This explanation is confirmed by the X-ray phase analysis, according to which the final product contains Fe_2O_3, Fe_3O_4, Fe_2SiO_4, and free SiO_2. At 1573 K, the beginning of a melting process in the sample was observed.

The reactions that take place in the temperature intervals are of first order, because in the temperature range 607 K - 720 K, n = 0.67, and in the temperature range 723 K - 1123 K, n = 0.93 (n- a degree indicator

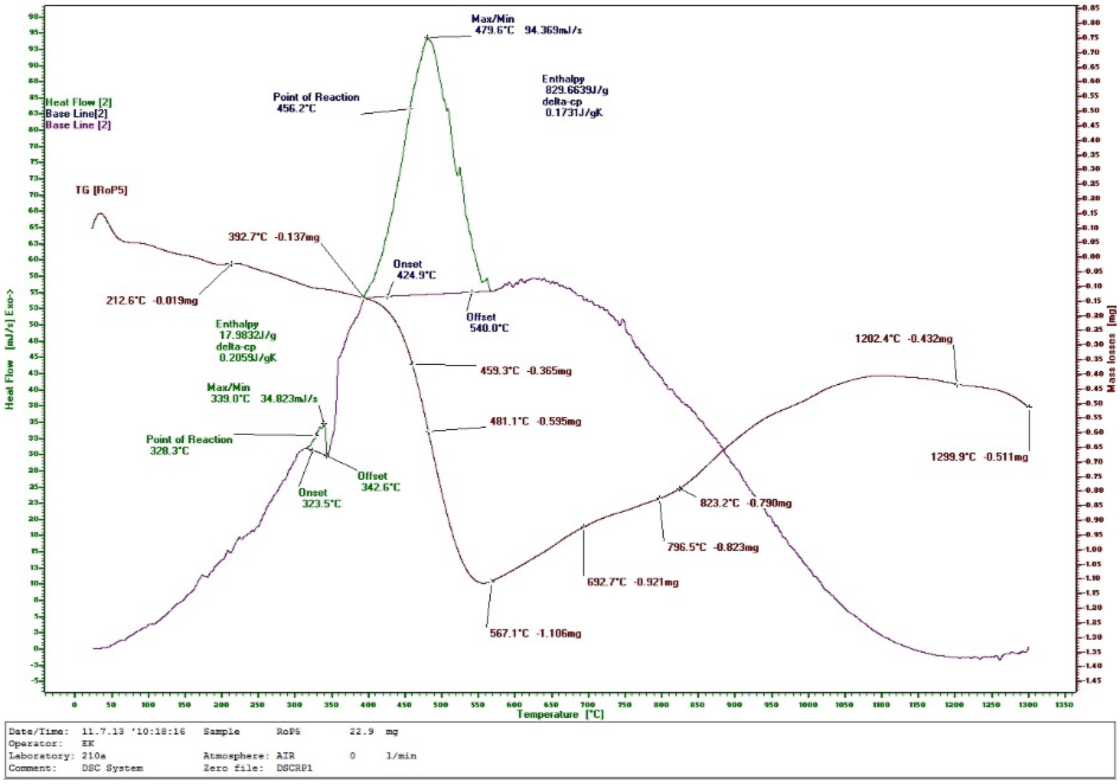

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Fig. 2. Thermogravimetry and differential scanning calorimetry (TG-DSC) curves of sample containing iron silicate and coke.

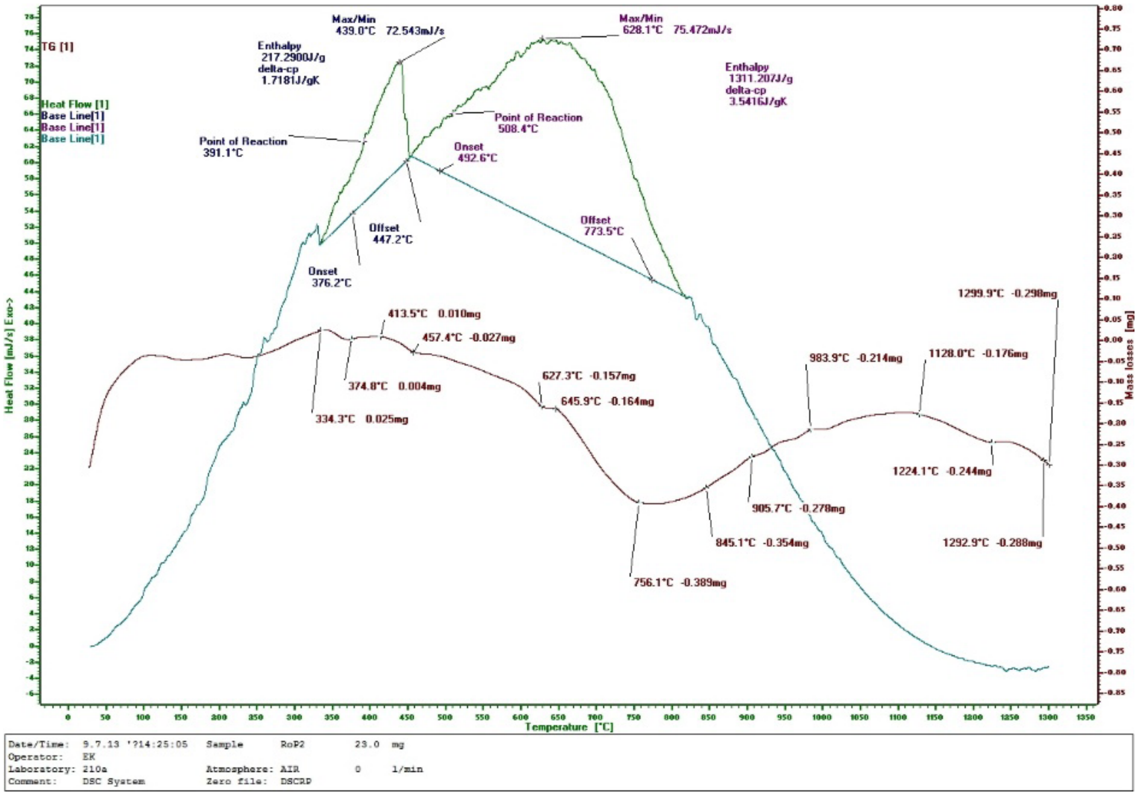

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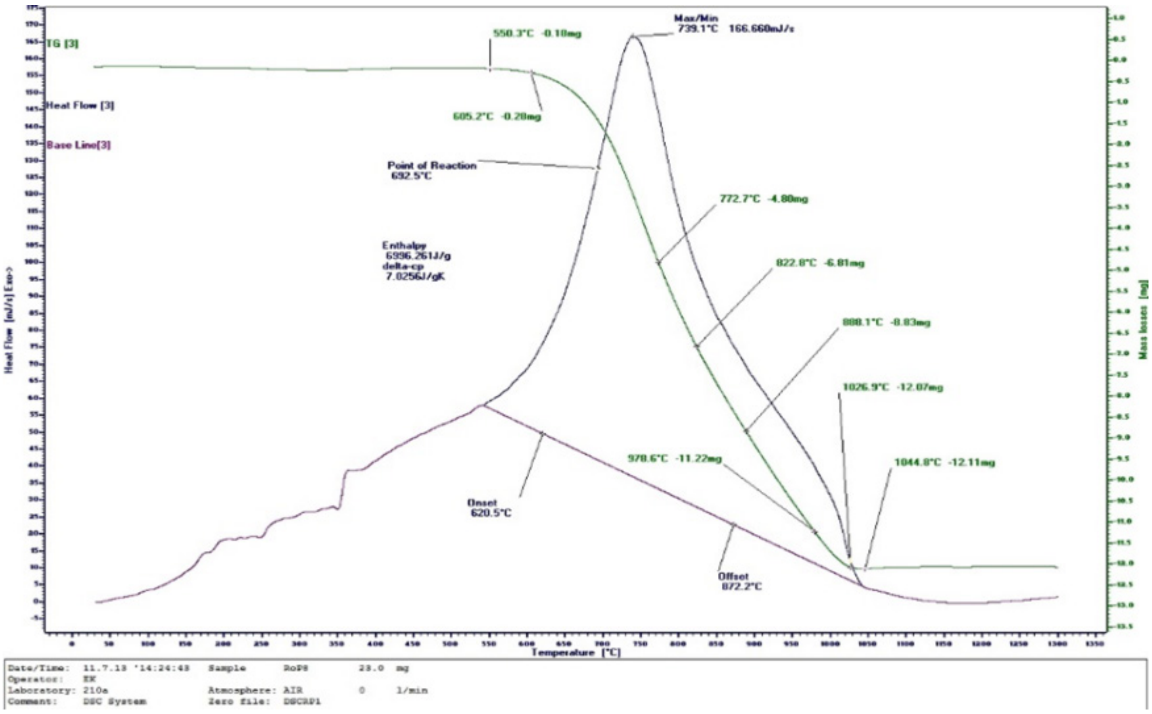
Fig. 3. Thermogravimetry and differential scanning calorimetry (TG-DSC) curves of sample containing iron silicate and charcoal.



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Comment: DSC System Zero file: DSCRP1

Fig. 4. Thermogravimetry and differential scanning calorimetry (TG-DSC) curves of sample containing iron silicate and graphite.

derived experimentally).

$\ln K = \ln A - B / R.T$

$\ln K_1 = 1743/T - 5.81 \quad R^2 = 0.9610$

$E_a = 33313$ J mol^{-1} (1401 K – 1573 K)

$\ln K_2 = 3549/T - 9.71 \quad R^2 = 0.9992$

$E_a = 67832$ J mol^{-1} (1029 K – 1257 K)

$\ln K_3 = 2352/T - 4.22 \quad R^2 = 0.9412$

$E_a = 44954$ J mol^{-1} (648 K – 900 K)

The calculated values of the activation energy showed that the processes took place in the kinetic region.

In sample 2 containing iron silicate and charcoal, two exothermic effects were observed as seen in Fig 3. The first one was in the temperature range 597 K - 616 K and it reflected the oxidation of magnetite to γ-Fe_2O_3 (enthalpy of formation was 18 J g^{-1}). According to Gorshkov [11], this transition is in the temperature range 548 K - 648 K. The second exothermic effect is in the temperature range 703 K - 813 K, associated with the combustion of carbon in charcoal (enthalpy of formation was 830 J g^{-1}). The beginning of the reaction is at a temperature of 729 K. In this sample, there was an increase in mass, analogous to sample 1. X-ray phase analysis of the product again shows the presence of Fe_2O_3, Fe_3O_4, Fe_2SiO_4, and free SiO_2. The reactions that occur in the temperature range 607 K – 687 K (n = 1.02) and 703 K - 813 K (n = 1.34) are of the first order.

$\ln K_1 = 1883/T - 7.93$

$R^2 = 0.9856 \quad E_a = 35990$ J mol^{-1} (966 K – 1573 K)

$\ln K_2 = 1464/T - 4.13$

$R^2 = 0.9499 \quad E_a = 27981$ J mol^{-1} (486 K – 840 K)

The calculated values of the activation energy for the two temperature intervals showed that the processes took place in the kinetic region.

In sample 3 iron silicate-graphite, shown in Fig. 4, there was an alternation of weak in intensity exothermic and endothermic effects associated with phase changes γ-$Fe_2O_3 \leftrightarrow \alpha$-$Fe_2O_3$ without change in the mass of the sample. In the temperature range from 898 K to 1145 K, with an enthalpy of formation of 6996 J g^{-1}, the intensive combustion of graphite takes place. The beginning of the reaction is at 966 K. The mass loss at 1046 K is 20.86 % and reaches 52.48 % at 1300 K, and beyond this temperature no change in mass is reported, which is due

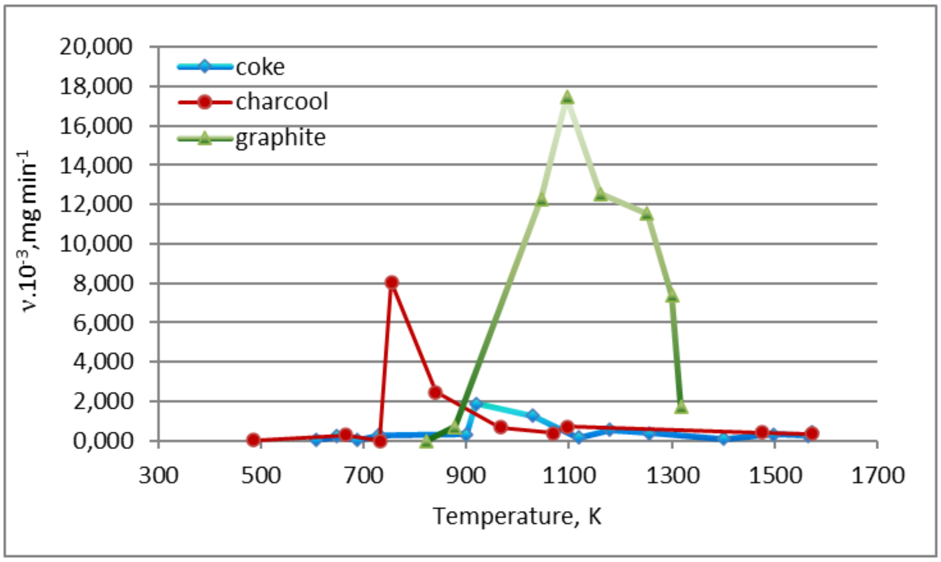

Fig. 5. Relative rate of the ongoing processes as a function of temperature.

to phase transformations. X-ray phase analysis shows mainly hematite and free SiO_2. The reactions that take place in sample 3 in the temperature range 898 K - 1145 K are of the first order n = 1.08.

$\ln K = 3354/T - 2.46$

$R^2 = 0.9192$ $E_a = 60292$ J mol^{-1} (823 K – 1318 K).

Fig. 5 shows a comparison of the rates of the ongoing processes using the three types of reducing agents.

It has been established that the processes with the use of a coke reducer agents take place at the lowest rate. With a charcoal reducer, the rate is the highest at T = 754 K, while with a graphite reducer - T = 1096 K, showing the burning rate of graphite. The rate of the reduction of iron silicate is controlled by the Boudoir reaction.

CONCLUSIONS

The Gibbs energy of the nine samples of iron silicate (fayalite) and the reducing agents - coke, charcoal, and graphite was determined. The results of thermodynamic studies show that coke is the most suitable reducer at a ratio of 1:2.

The reduction kinetics of mixtures of iron silicate and reducing agent were studied at a ratio of 1:2. The rate constant of the processes occurring in the three samples was determined and the activating energy was calculated. It was found that in all three reducers, the reactions were of the first order and took place in the kinetic region.

The total rate of the reduction when using coke changes slightly, despite the fact that several processes take place - oxidation, dissociation, phase transformations, and others. The highest speed was achieved with a graphite reducer. X-ray phase analysis with a graphite reducer showed the presence of only hematite and free cristobalite.

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