KINETICS OF REDUCTION OF WASTE FAYALITE BY CALCIUM CARBIDE

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Received 25 April 2018
Accepted 28 June 2019

ABSTRACT

Investigations of the slag, obtained from the non-ferrous metals, are of great importance to expand the raw material base for complex utilization, to increase the extraction of useful elements and to protect the environment. The kinetic of reduction of the waste fayalite by calcium carbide was investigated for two ratios of 1:1 and 1:10. Thermogravimetric analysis was carried out. Activation energy was determined, the maximum for the ratio 1:1 was 18.81 kJ/mol, and for ratio 1:10, \(E_a = 21.31\) kJ/mol. The rate constant is also determined and the equations for the two defined temperature ranges were respectively derived. The maximum rate of reactions for the two mixtures is obtained, for the first mixture \(v = 1.7176 \cdot 10^{-3} \text{ mg/min at a temperature } 1221 \text{ K} \), and for the second mixture the maximum rate is \(v = 1.2393 \cdot 10^{-3} \text{ mg/min at } 1230 \text{ K} \).

Keywords: waste fayalite, calcium carbide, kinetics, activation energy, reduction rate.

INTRODUCTION

The fayalite waste from copper slag flotation is located on significant areas and their landfilling is a reason for secondary environmental pollution. The main phase is fayalite \(2\text{FeO} \cdot \text{SiO}_2\), whose content in the dry mass reaches 85 mass % [1].

The preliminarily decopperized molten copper from smelter slags is maintained in a molten state and a solid reducing agent is mixed into the slag to recover iron [2]. Carbonthermic method was adopted to reduce the iron in the form of fayalite in copper slag into metal iron [3, 4]. It was evident that the reduction process of fayalite by carbon could be routed as:

\[
\text{Fe}_2\text{SiO}_4 \text{(or } 2\text{FeO} \cdot \text{SiO}_2) \rightarrow \text{FeO} + 2\text{CaO} \cdot \text{SiO}_2 \rightarrow \text{Fe} \quad (1)
\]

Synthetic fayalite slags were reduced in laboratory experiments at temperatures in the range of 1250 - 1450°C, using either a floating graphite disk or immersed graphite rod by Warczok and Utigard [5]. According to them, the rate of reduction increased with the increasing of temperature. For fayalite, the reduction rate is given by

\[
u(\text{mol } \text{O}/\text{m}^2 \cdot \text{s}) = 5.39 \cdot 10^6 \cdot \exp \left( -29,600/T(K) \right) \quad (2)
\]

The activation energy was found to be 246±29 kJ/mol. The investigation of Jurgen Kunze et al. [6] relates to a method for reducing and/or refining a metal containing slag. According to Deepak Dwivedi [7], the obtained activation energy of iron ore fines, reduced by coal, was higher (124.71 kJ) than the coal + coal dust as a reducing agent (59.75 kJ).

Calcium carbide is used as a reducing and desulfurization agent in the electric furnace smelting and pig iron desulphurization [8 - 12]. There are various models describing kinetics, thermodynamics, and transport processes to predict the sulfur levels in the hot metal throughout a blow of calcium carbide [13 - 15].

The experimental and thermodynamic studies of waste fayalite [16], MgO reduction [17, 18] and chromium containing slag [19] with calcium carbide have been investigated.

At the same time, the exothermic effect of the following reaction can be used:

\[
\text{CaC}_2 + 3(\text{FeO} \cdot \text{SiO}_2) = \text{CaO} \cdot (\text{SiO}_2)_3 + 3\text{Fe} + 2\text{CO} + Q \quad (3)
\]

Fayalite waste is reduced well by a carbon containing reducing agent and the presence of CaO improves the reduction process. Calcium carbide doesn’t affect the
other chemical compositions and is more effective than calcium oxide. These facts are the basis for examining the thermodynamics and the kinetics of waste fayalite reduction by calcium carbide.

The aim of this paper is to investigate kinetics of reduction of waste fayalite by calcium carbide.

### EXPERIMENTAL

**Materials and Apparatus**

The chemical composition of waste fayalite is defined by weight via ICP-OES analysis. The results are shown in Table 1. The main components in the waste composition are Fe-total - 47.96 % and Si - 12.71 %. The phase composition is determined by Tracor Northern (TN) 2000 X-ray microanalyser. The main presented phases are FeSiO$_4$ and Fe$_3$O$_4$.

Two mixtures with waste fayalite and calcium carbide with ratio 1:1 (Mixture 1) and 1:10 (Mixture 2) as briquette were prepared. The thermodynamics of mixtures were studied by EMF (Electromotor Force) method, using galvanic cells with a solid electrolyte ZrO$_2$ (CaO) and reference electrode Ni/NiO. The following galvanic cell was used in this work:

\[
\text{Pt} \quad \text{studied sample} \quad \text{ZrO}_2(\text{CaO}) \quad \text{Ni},\text{NiO} \quad \text{Pt}
\]

The mixtures were investigated also by DTA method (apparatus STA PT1600) within the temperature range 293K - 1473K. The STA PT1600 TG-DTA (STA Simultaneous Thermal Analysis) apparatus was used to perform the DTA analysis. The samples were heated to 1473°C with a heating rate of 10°C/ min.

### RESULTS AND DISCUSSION

**Thermodynamic investigation of briquette obtained from waste fayalite with calcium carbide**

In the initial waste material, the iron is in the form of magnetite and fayalite phases. Theoretically, the reduction process of this waste material with calcium carbide could be carried out by the reaction (4):

\[
7 \text{Fe}_3\text{O}_4 + 2 \text{CaC}_2 + \text{Fe}_2\text{SiO}_4 = 23 \text{FeO} + \text{Ca}_2\text{SiO}_4 + 2 \text{CO} + 2 \text{CO}_2
\]  

(4)

The data for the thermodynamic characteristics: specific heat capacity $C_p$, Enthalpy $H^o_{298}$, and Entropy $S^o_{298}$ were used to calculate the change of the Gibbs energy (4) [20]. An equation for $\Delta G$ of the reaction (4) was deduced.

\[
\Delta G = 231584 - 2299 \cdot T, \text{J/mol} \quad R^2 = 0.9993
\]  

(5)

were $R^2$ is the correlation coefficient.

Equation 5 is based on standard thermodynamic data in the temperature range 298K - 1673K, which explains the high correlation of the obtained equation.

On the basis of stoichiometric calculations for reaction 2, two mixtures in ratios 1:1 and 1:10 between fayalite and calcium carbide as briquettes were prepared [16].

**Electromotor Force (EMF) method results**

The EMF method with solid electrolyte is one of the main methods used in the thermodynamic study of the processes in the metallurgical aggregate. The principle of the method is to create a difference in the partial pressure of oxygen on both sides of a solid electrolyte [21]. On the basis of experimentally measured values of the EMF method in case of non-isothermal heating of the studied briquettes, the Gibbs energy of mixtures 1 and 2 were derived:

Mixture 1

\[
\Delta G_{\text{exp}} = -406150 + 234.54 \cdot T, \text{J/mol}, \quad R^2 = 0.9416
\]  

(6)

Mixture 2

\[
\Delta G_{\text{exp}} = 269021 - 716.45 \cdot T, \text{J/mol}, \quad R^2 = 0.9814, \text{ valid for temperature range 773 - 993K}
\]  

(7)

\[
\Delta G = -586770 + 340.20 \cdot T, \text{J} [22].
\]

\[
\Delta G_{\text{exp}} = -2.10^{-7} + 44887. T - 20,927. T^2, \quad R^2 = 0.8829, \text{ valid for temperature range 1063-1153 K}
\]  

(8)

Processes in mixture 2 (1:10) were described by two equations for Gibbs energy. On the basis of the initial chemical composition, the obtained X-ray analysis and
the correspondence with the thermodynamic equations of the ΔG change, follows:

The equation (7) is valid for the temperature range 773 - 993K. It is related to the reversible reaction $\text{Fe}_2\text{O}_3 \leftrightarrow \text{Fe}_3\text{O}_4$. ΔG data, received for reversible reaction from S.I.Filippov [22], are similar to those obtained from the experimental data of the deduced equation.

Interactions between calcium and silicon oxides, under metallurgical conditions, occur at temperatures above 1000K. The equation (8) for the same mixture 2 describes the formation of a new phase hedenbergite ($\text{CaFeSi}_2\text{O}_6$), which was confirmed by X-Ray analysis, illustrated on Fig. 4.

During the experiments it was established that the presence of calcium carbide decreases the physico-mechanical properties of the studied briquettes, and therefore the reduction process. The strength of the pellets is reduced due to the high hydrophobicity of
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calcium carbide. For this reason, calcium carbide is applied in various processes in the steel metallurgy, but it is injected directly in the metal melt.

Kinetics investigation of briquette obtained from waste fayalite with calcium carbide

To define the kinetic parameters on the TG curves, the following equation was used:

$$\frac{d\alpha}{dt} = A_0 e^{-\frac{E_a}{RT}} (1 - \alpha)^n$$

(9)

where $\alpha$ is the degree of conversion of the initial material, $n$ is the order of reaction; $E_a$ stands for the activating energy. The conversion rate ($\alpha$) is a parameter for the solid state reaction kinetics study:

$$\alpha = \frac{m_0 - m_\tau}{m_0 - m_\infty}$$

(10)

where $m_0$, $m_\tau$, and $m_\infty$ are the initial weight of the sample, the weight of the sample at time $\tau$ and the weight of the sample at the end of the reaction, respectively.
Based on equation (9), methods for calculating the activation energy by differential thermal analysis data have been developed [23]. By integrating the equation (9) at $dT = b \, d\tau$ and acquire the type:

$$
1 - (1 - \alpha)^{1-n} = \frac{A_o}{b} \int_0^T e^{-E/R \cdot T} \, dT
$$

Equation (11) decomposed in asymptotic condition provided that $E \gg R \cdot T$ and $n \neq 1$, are represented with:

$$
ln \frac{1}{(1 - \alpha)_n} = \frac{A_o \cdot R \cdot T}{E \cdot b} e^{-E/R \cdot T}
$$

For a first order reaction, response in the range $0 < \alpha < 0.5$ the equation (12) after logarithm is:

$$
ln \alpha - 2 \, ln \, T = A - \frac{E}{R \cdot T}
$$

In practical reading of the thermogravimetric curves, the magnitude $ln \alpha$ can be replaced by $lnm$, where $m$ is the weight loss of the investigated sample.

$$
ln m - 2 \, ln \, T = A_0 \cdot \frac{E}{R \cdot T}
$$

The rate of the process is calculated by the formula:

$$
\nu = \pm \frac{\Delta m}{\Delta \tau \cdot m_o}, \text{ mg/min}
$$

where $\nu$ is the average rate of the process, as the rate of the chemical reaction is recorded for a given time interval, g/min; $\Delta m$ is the change of sample weight, mg; $\Delta \tau$ - time change, min; $m_o$ - initial weight of sample, mg.

**DTA analysis**

Thermogravimetric analysis was carried out and the results are presented in Figs. 1 and 2. DTA transformations of both mixtures are similar. Two endothermic peaks, weak in intensity - at $T \sim 731K$ and $T \sim 884K$ at a ratio of 1:1 on a derivatogram were observed. The first peak is due to the reaction $\text{Fe}_2\text{O}_3 \leftrightarrow \text{Fe}_3\text{O}_4$, where the second one is due to the fayalite decomposition. This is confirmed by X-Ray analysis presented in Fig. 3. The main phases after heat treatment in mixture 1 are magnetite $\text{Fe}_3\text{O}_4$, hematite $\text{Fe}_2\text{O}_3$, and cristobalite $\text{SiO}_2$.

For the case of mixture 2, where the amount of $\text{CaC}_2$ is higher, the endothermic peaks are with stronger intensity at $T \sim 725K$ and $T \sim 823K$. An exothermal effect at $T \sim 911K$ which corresponds to the formation of calcium silicate reaction chain was noticed in mixture 2 as opposed of mixture 1. This was confirmed by an X-Ray analysis shown in Fig. 4.

This pattern shows that a higher amount of $\text{CaC}_2$ is the result due to the formation of hedenbergite $\text{CaFeSi}_2\text{O}_6$ or calcium silicate $\text{CaSiO}_3$. It is also seen that the lines of hematite are weaker than those with a ratio of 1:1.

The results for the activating energy of the mixtures fayalite/$\text{CaC}_2$ were shown in Table 2. The obtained values of the activation energy ($E_a$), in both mixtures, were similar, and show insignificant differences in both temperature interval. These activation energy values refer to processes occurring in the external diffusion area. This limiting area enables to influence the process by changing the hydrodynamics, i.e. by changing the speed and nature of the gas flow.

The equations for the rate constant of both mixtures are as follows:

<table>
<thead>
<tr>
<th>ratio fayalite/$\text{CaC}_2$</th>
<th>stage</th>
<th>Temperature interval, K</th>
<th>$E_a$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>I</td>
<td>315-863</td>
<td>8.31</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>863-1423</td>
<td>18.81</td>
</tr>
<tr>
<td>1:10</td>
<td>I</td>
<td>317-1060</td>
<td>9.04</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>1060-1424</td>
<td>21.31</td>
</tr>
</tbody>
</table>
At ratio fayalite/CaC$_2$ 1:1,
for the I stage  $\ln K = -0.9822 \cdot T + 5.70$
and for the II stage  $\ln K = -0.3993 \cdot T + 4.95$.

At ratio fayalite/CaC$_2$ 1:10,
for the I stage  $\ln K = -1.1114 \cdot T + 5.78$,
and for the II stage  $\ln K = -0.4632 \cdot T + 5.09$.

In Figs. 5 and 6 the change of the heating rate of the processes in the temperature range is presented.

Two stages were registered - decreasing and increasing of the mass. The increase of the mass started at different temperatures for both mixtures. The higher amount of CaC$_2$ moves this stage to higher temperatures - from 853K (Mixture 1) to 1073K (Mixture 2). The decreasing of the mass is related to the decomposition of Fe$_2$O$_3$ to Fe$_3$O$_4$ on the reversible reaction $3\text{Fe}_2\text{O}_3 \leftrightarrow 2\text{Fe}_3\text{O}_4 + \frac{1}{2} \text{O}_2$. The mass increase was due to the hedenbergite and calcium silicate phase formation, and that decreases the melting temperature.

The maximum reduction rate at a fayalite/CaC$_2$ in 1:1 ratio is $\nu = 1.7176 \cdot 10^{-3}$ mg/min, at a temperature of 1221 K. In the mixture with ratio fayalite/CaC$_2$ 1:10 two stages with clear maximum rate process were observed.

For the first stage, the maximum rate is $\nu = 1.0687 \cdot 10^{-3}$ mg/min at a temperature of 733K, which corresponds to the reduction of ferric to ferrous ions. In the second stage the maximum rate is $\nu = 1.2339 \cdot 10^{-3}$ mg/min at 1230 K.

**CONCLUSIONS**

The activation energy for the two mixtures fayalite/CaC$_2$ (1:1 and 1:10) was determined in the kinetic studies. The rate and the rate constant equation for the two mixtures are also determined. It has been established that processes occur in the diffusion area.

The experimental results show that using calcium carbide, as a reducing agent and as a binder, were unsuccessful. There is a partial regulation of basicity, but low mechanical properties of the raw briquettes and some specifics at work show that calcium carbide is not suitable for briquetting charge material. Calcium carbide could be successfully used when it is directly blown in the metallurgical bath.
REFERENCES

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