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REDUCTION MECHANISM OF OXIDIZED IRON-SCRAP BRIQUETTE CONTAINING PULVERIZED COKE DURING HEATING

Reijiro Takahashi, Xinghe Zhang, Jun-ichiro Yagi

Institute for advanced Materials Processing, Tohoku University
2-1-1 Katahira, Aoba-ku, Sendai, 980-8577, JAPAN
Tel: +81-22-217-5173, Fax: +81-22-217-5211
E-mail: reijiro@iamp.tohoku.ac.jp

ABSTRACT

Reaction rates for the reduction of iron oxide, the gasification of coke and the thermal decomposition of the binder in oxidized iron-scrap briquettes containing pulverized coke were measured under the conditions of elevating and fixed temperatures in the nitrogen atmosphere. The reaction rates were obtained by examining the various factors affecting the reaction mechanism. The weight change of the briquette calculated by the rate equations agreed well with experimental values. The rate equations can therefore be applied to the mathematical simulation model of a moving bed process into which oxidized iron-scrap is charged as a burden material.

1. INTRODUCTION

The briquette of oxidized iron-scrap containing coke breeze is attracting much attention as a new ironmaking raw material for enhancing reduction of iron oxide and for effective use of ironmaking resources. This paper deals with reaction rates of oxidized iron-scrap briquette containing pulverized coke in nitrogen atmosphere for applying to the mathematical model of a moving bed reactor for scrap melting.

Many researchers had reported on the reaction mechanism and kinetics of the iron oxide pellet containing carbon.[(1)~(7)] However, these papers did not examine in the view point of application to the mathematical model of scrap-melting furnace for the recycling of oxidized iron-scrap.

The reaction rates for the reduction of iron oxide, the gasification of coke and thermal decomposition of the binder of a briquette are individually measured under the conditions of elevating and fixed temperatures in nitrogen atmosphere. Weight decrease of the briquette containing coke during reaction is caused by the weight changes of carbon due to the gasification of coke and of oxygen due to the reduction of oxidized iron-scrap simultaneously. Two reaction rates are obtained separately by the method of the measurements including both the weight change of briquette and gas volume change caused by the reaction.

The rate equations and rate constants for the reduction of iron oxide, the gasification of coke and the thermal decomposition of binder are determined by examining the various factors affecting experimental values.

2. EXPERIMENTS

2.1 Samples

Three kinds of briquette (see Table 1) were prepared by the mixture of reduced iron, coke breeze and mill scale with a binder composed of syrup, slaked lime and starch. The briquette obtained was 3200 kgm^{-3} in density, approximately 0.070 kg in average weight and 40 mm in major axis of oval shape. Amount of coke breeze added was changed from 7 to 20 mass%.

The briquettes before experiment were dried at 373K in nitrogen atmosphere. The sample after drying was used to the experiment for thermal decomposition of binder. Furthermore, the sample subjected to thermal decomposition at 673K in nitrogen atmosphere was used to the reduction experiment at fixed temperature.

Table 1. Chemical composition of briquettes (mass %)

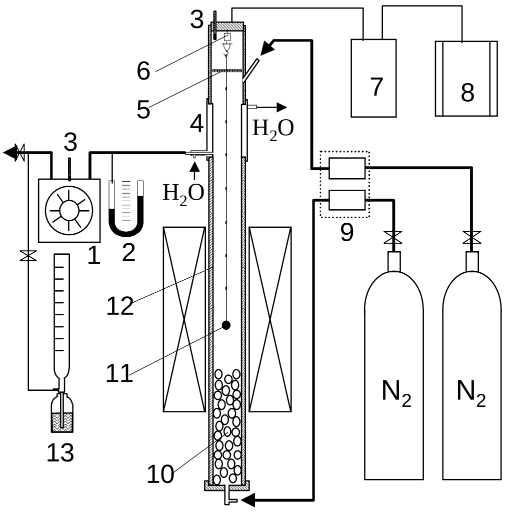
	T.Fe	M.Fe	Fe^{2+}	Fe^{3+}	O	C	C/O
B1	70.0	17.1	43.5	9.4	16.4	7.4	0.60
B2	67.0	17.7	42.3	7.0	15.1	11.2	0.99
B3	55.9	11.8	33.6	10.5	14.1	20.3	1.92

1) C/O: Molar ratio of carbon and oxygen
2) O=0.222FeO+0.429(T.Fe-M.Fe-0.778FeO)

2.2 Experimental method

Experimental apparatus are shown in **Fig. 1**. Reaction tube made of alumina is 52 mm in inner diameter. Alumina sphere of 8 mm in diameter is packed in the bottom of the tube for heating of nitrogen gas. Weight change during reaction is measured by load cell having 200 g in maximum load. To remove the effects of temperature and moisture on the output signal from load cell, following devices is adopted in the constitution of apparatus. There are water jacket between high and low temperature parts, introduction of nitrogen from the top and setting of the thermal shield of radiative heat from the high temperature zone.

Nitrogen gas is introduced from the bottom of reaction tube through mass flow controller. The change of gas volume caused by the reaction is measured by gas meter of accumulating type having 5 ml in minimum scale.



1.Gas meter
2.Manometer
3.Thermometer
4.Water jacket
5.Thermal shield
6.Load cell
7.Strain meter
8.Recorder
9.Mass flow controller
10.Alumina balls
11.Briquette sample
12.Reaction tube
13.Soap film flow meter

Fig. 1 Experimental apparatus for the reaction of briquette sample.

2.3 Evaluation of weight change

Weight decrease of briquette during the reaction of briquette including pulverized coke is caused by both gasification of coke and reduction of oxidized iron-scrap. Two reactions were separated by the measurements of both weight change of briquette and gas volume change caused by the reaction as follows.

Reduction of iron oxide by solid carbon is expressed by Eq.(1).

$$Fe_nO_m + xC = nFe + (2x - m)CO + (m - x)CO_2 \quad (1)$$

Where, $n = 1,\ 2,\ 3$; $m = 1,\ 3,\ 4$; $x = (0.5 \sim 1)m$

In Eq.(1), molar number of CO and CO_2 gases generated by the reaction is equal to molar number of consumed carbon. Therefore, volume change of generated gas only depends on the gasification reaction of solid carbon. Weight decrease of carbon is determined by the following equation.

$$\Delta w_C = \frac{12}{22.4} v_r \quad (2)$$

On the other hand, weight decrease of oxygen is obtained from the difference between total weight decrease of briquette and weight change of the carbon as Eq.(3).

$$\Delta w_O = \Delta w - \Delta w_C \quad (3)$$

Reduction degree f_O is defined by the ratio of weight decrease of oxygen and oxygen content in the initial briquette ($f_O = \Delta w_O / w_{Oi}$). Because the samples B1, B2 and B3 have different carbon content, the gasification degree of coke is defined as follows.

If the carbon content is less than theoretically required value for the reduction of iron oxide (for example, sample B1 and B2), the reaction degree is defined by the ratio of weight decrease of carbon and initial carbon content ($f_C = \Delta w_C / w_{Ci}$). In the case of higher carbon content than theoretically required value (for example, sample B3), the reaction degree is defined as the ratio of weight decrease of carbon and the carbon weight required for the complete reduction of iron oxide ($f_C = \Delta w_C / w_C^*$).

3. PRELIMINARY TEST

3.1 Weight change in heating-up condition

A preliminary experiment was conducted to measure the weight change of a single briquette in nitrogen atmosphere in heating-up conditions. Results obtained for the three briquettes were shown in **Fig.2**. The three sample briquettes B1, B2 and B3 had 19, 25 and 28 % respectively in final

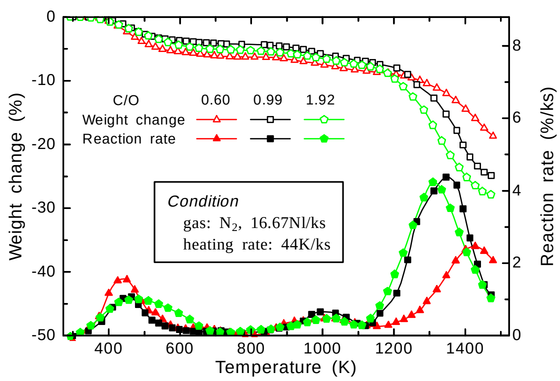


Fig. 2 Weight change and reaction rate in heating-up condition.

weight decrease showing three characteristic reactions proceeded at temperature of around 450, 1000 and 1300 K (100 K higher for B1). These reactions corresponded to the evaporation of water and the thermal decomposition of binder, the reduction of Fe_2O_3, and the reduction of FeO at respective temperatures. From these results, it was found that the reaction rate of thermal decomposition of the binder was measured from weight decrease independently by selecting the temperature region. Rates of reduction and gasification of a single briquette were obtained by simultaneous measurements of weight change and gas flow rate change.

3.2 Selections of preheating temperature and time

Reduction experiment is conducted at the fixed temperature. In the experiments, it is desired to shorten the time required for heating-up to experimental temperature as quickly as possible. Because no weight change was observed at around 823 K in **Fig.2**, this temperature was selected as a preheating temperature.

For determination of preheating time, the temperature at the center of briquette was measured by the thermocouple at 823 K in nitrogen atmosphere, and then, weight change of the briquette after thermal decomposition was also measured. As the result, the time of 1.8 ks required until the briquette temperature arrived at the furnace temperature. Weight change of the briquette was not observed during preheating time mentioned above.

On the other hand, 3.6 ks was required to preheat a sample briquette to the temperature of 373 K before thermal decomposition of binder.

3.3 Experimental method at fixed temperature

In the experiment at a fixed temperature, the position of a briquette sample for preheating was determined according to the measured longitudinal temperature distribution in the reaction tube. An experiment measuring rate of reduction reaction of briquette or rate of thermal decomposition started after the sample has been moving down to the level of reaction temperature in the reaction tube.

Experimental conditions for the decomposition and for the reduction of briquettes at the fixed temperature are shown in Table 2. Flow rate of N_2 gas was 9.5 l/ks.

Table 2 Experimental conditions in decomposition of binder and reduction of oxidized-iron briquette.

Conditions		Decomposition	Reduction
Preheating	Temp. (K)	373	823
	Time (ks)	4.2	2.4
Reaction	Temp. (K)	443－675	1272－1495
	Time (ks)	3.6－3.3	5.4－3.6

3.4 Temperature change of briquette sample during reductions

In the reaction of briquette sample, the reduction reaction proceeds with gasification of coke included in the briquette. As the gasification of coke is a significant endothermic reaction, the effect of the heat of reaction on the briquette temperature has to be investigated during reaction. Briquette temperature during reactions was measured by the thermocouple inserted into the center of the briquette in the temperature range of 950 K to 1350 K. No temperature decrease was observed in the experiments. It was estimated that enough preheating and higher thermal conductivity of the briquette sample led to temperature change.

3.5 Residual carbon and oxygen in the briquette after reduction

The contents of residual carbon and oxygen were chemically analyzed for the briquette after reduction. **Fig.3** shows comparison between the values analyzed and obtained from the measurement of weight and gas volume changes. The agreement proved that the measurement of the changes of weight and gas volume were reasonable experimental method.

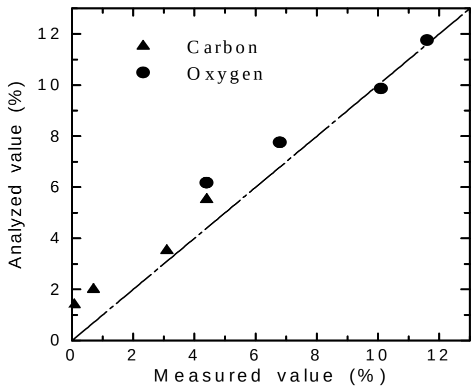


Fig. 3 Comparison between chemically analyzed values of residual carbon and oxygen in the briquette and the values obtained by the measurement of weight and gas volume changes.

4. EXPERIMENTAL RESULTS

4.1 Effect of the carbon content on the reaction rates

Fig.4 shows the effect of carbon content on reaction rates of oxidized iron and coke in the briquette. Both reaction rates increased with increase of carbon content (C/O) in the briquette.

4.2 Weight change by thermal decomposition of binder

The weight decrease observed by the thermal decomposition of the briquette B1 was shown in **Fig.5**. This figure showed the thermal decomposition proceeded smoothly and finished around 2.5 ks. The reaction rate was expressed by the first order reaction given as Eq.(4).

$$\ln(1 - f_b) = -k_b t \qquad (4)$$

On the basis of experimental data in Fig.3, the rate constant k_b was determined as Eq.(5).

$$k_b = 159.2 \exp\left(\frac{-37.2 \times 10^3}{RT}\right) \tag{5}$$

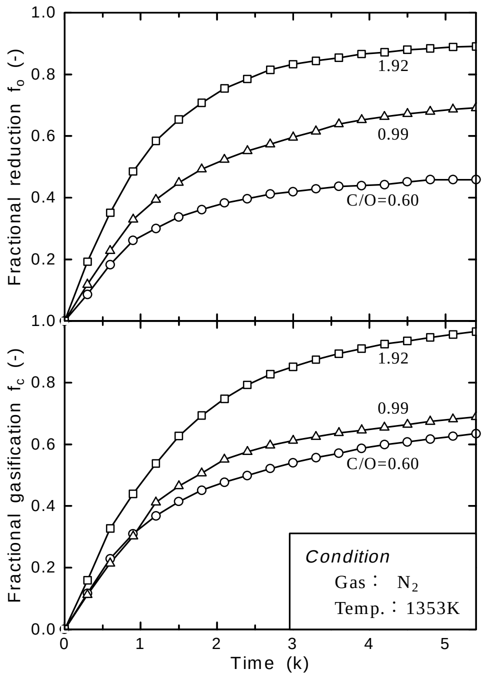


Fig. 4 Effect of C/O ratio on reduction rate and coke gasification in the briquette.

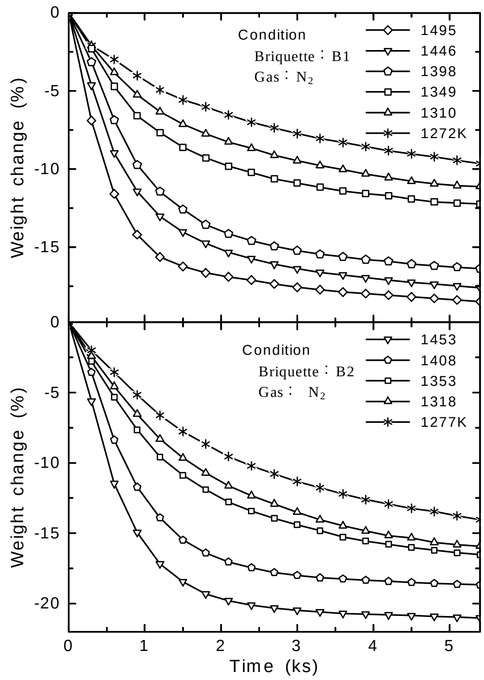


Fig. 6 Weight change of briquette during reduction.

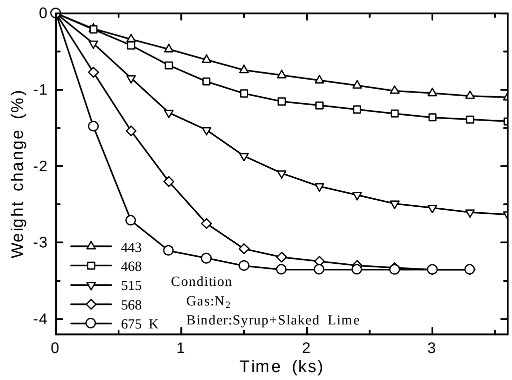


Fig. 5 Weight change of briquette during thermal decomposition.

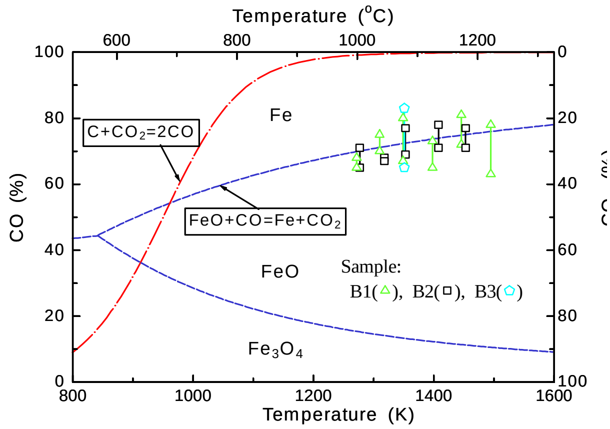


Fig. 7 Relation between temperature and partial pressure of CO in the gas produced by reduction.

4.3 Weight change during reduction

The experiments were conducted in high temperature region for the simultaneous reduction and gasification reactions. The weight decrease observed for the reduction reaction of the briquettes B1 and B2 in the temperature range of 1270 to 1500 K was shown in **Fig.6.** This figure showed high reaction rate at higher temperature and the retardation of reaction rate at later stage of reaction.

Relation between weight change (Δw_O , Δw_C) and gas compositions for CO and CO_2 is expressed by Eq.(6) from the mass balance. Gas composition (y_{CO} , y_{CO_2}) generated by the reductions was calculated by using Eq.(6).

$$\frac{y_{CO_2}}{y_{CO_2} + y_{CO}} = \frac{\Delta w_O}{\Delta w_C} \frac{12}{16} \qquad (6)$$

In order to investigate the reaction mechanism of the briquettes in high temperature region, outlet gas compositions were plotted in the reduction equilibrium diagram of Fe-C-O system as shown in **Fig.7**. This figure showed outlet gas has almost equilibrium gas. This means the over all reaction rate of briquettes were governed by the gasification reaction of coke in conditions.

Figure 8 illustrates the gasification curves obtained from the results shown in Fig.6. Measured data were analyzed by applying first order reaction kinetics. The gasification was separated into two stages giving different rate constants as shown in **Fig.9**.

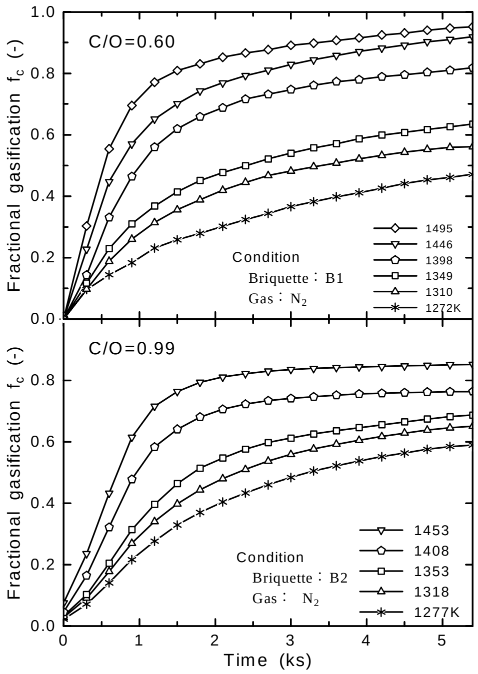


Fig. 8 Effect of temperature on the gasification rate of coke in the briquette.

Figure 10 shows the temperature dependencies of reaction rate constants for the former (k_{c1}) and the later period (k_{c2}) in the briquette reduction. On applying two equations, relation between the temperature and the gasification degree (f_C^*) at the function of two straight lines (mark ●) at the initial and the later stages are shown by the straight relation as shown in **Fig.11**. The upper and lower regions of the line mean the areas for the initial and the later periods of the briquette reduction respectively. Similar result was obtained from briquette sample B2. These results

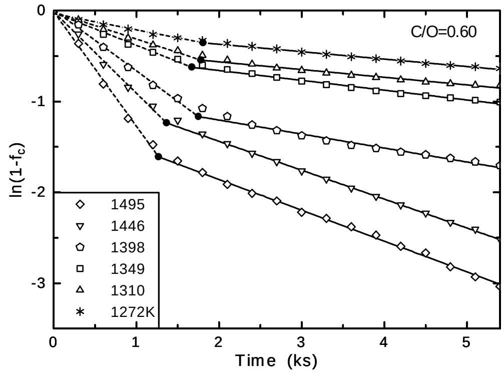


Fig. 9 Relation between ln(1-f_c) and time.

are summarized as follows.

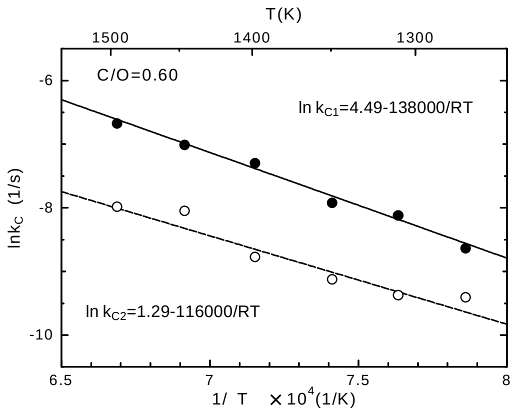


Fig.10 Temperature dependence of reaction rate constants for gasification of coke.

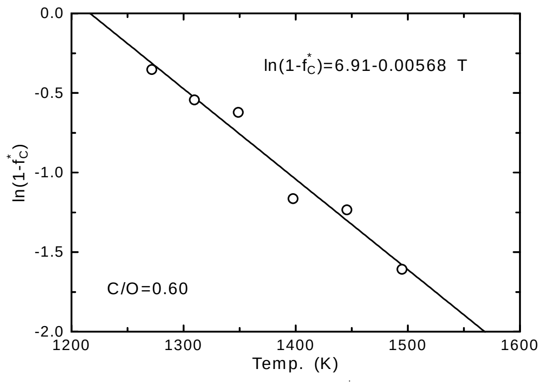


Fig. 11 Relation between ln(1-f_c^*) and temperature.

$$\left.\begin{aligned} &\ln(1-f_C) = -k_{C1}t \qquad (f_C \le f_C^*) \\ &\ln(1-f_C) = -k_{C2}t + \left(1+\frac{k_{C2}}{k_{C1}}\right)\ln(1-f_C^*) \\ &\qquad\qquad (f_C > f_C^*) \end{aligned}\right\} \tag{7}$$

The reaction rate constants for the two stages and characteristic degree of gasification (f_c^*) which separates the gasification stages, are expressed by the following equations for the two kinds of briquettes.

On the briquette sample B1,

$$\left.\begin{aligned} &k_{C1} = 89.12\exp(-138\times10^3/\mathrm{R}T) \\ &k_{C2} = 3.633\exp(-116\times10^3/\mathrm{R}T) \\ &\ln(1-f_C^*) = 6.91-0.00568T \end{aligned}\right\} \tag{8}$$

On the briquette sample B2,

$$\left.\begin{aligned} &k_{C1} = 27.94\exp(-123\times10^3/\mathrm{R}T) \\ &k_{C2} = 0.2114\exp(6.8\times10^3/\mathrm{R}T) \\ &\ln(1-f_C^*) = 8.18-0.00675T \end{aligned}\right\} \tag{9}$$

The reduction of iron oxide is thought to proceed in equilibrium state as explained previously, therefore the reduction degree of iron oxide is obtained from the gasification degree as described below.

$$f_O = \frac{16w_C^*}{12w_{Oi}}(1-\eta_{CO})f_C \tag{10}$$

4.4 Comparison between measured and calculated weight changes

Applying Eqs. (4), (5) and Eqs. (7) to (10), simulation computation was conducted for the weight decrease of the briquette in isothermal reaction processes. **Figure 12** showed a comparison between observed and calculated weight decreases under the conditions of different kinds of briquettes and different temperatures. Good agreement proved the mechanisms and rate constants obtained were reasonable and can be applied to the process analysis of the smelting reduction of the briquette for oxidized iron-scrap in a moving bed reactor.

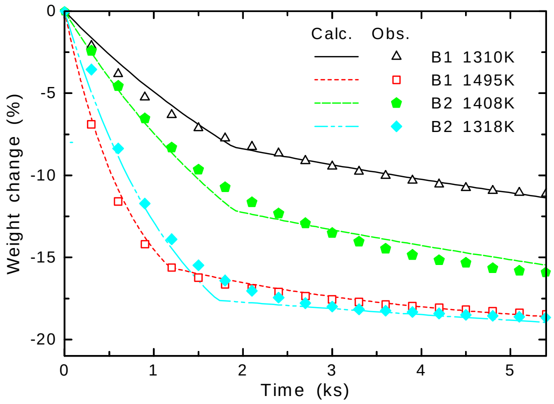


Fig.12 Comparison between measured data and calculated one with weight change of briquettes.

5. CONCLUSION

The carbon-contained briquette of oxidized iron-scrap like mill scale was investigated for the use as new raw materials for hot metal production.

Three kinds of briquette having different amount of coke breeze were prepared. Reaction rates for the reduction of iron oxide, the gasification of coke and the thermal decomposition of binder of the briquette were measured by the measurements of both changes of weight and gas volume under the conditions of elevating and fixed temperatures in the nitrogen atmosphere.

The rate equations and reaction rate constants obtained were reasonable and expected to be applied to the process analysis for the smelting reduction of the oxidized iron-scrap briquette.

NOMENCLATURE

f_b Thermal decomposition degree of binder [-]
f_C Gasification degree of carbon [-]
f_C^* Critical gasification degree of carbon [-]
f_O Reduction degree [-]
k Reaction rate constant [s^{-1}]
R Gas constant [$J \cdot mol^{-1} \cdot K^{-1}$]
t Reaction time [s]
T Temperature [K]
v_r Volume of generated gas [Nl]
w Weight [g]
w_C^* Carbon weight required for reduction [g]
Δw Weight decrease [g]
y Gas concentration [%]
η_{CO} Gas utilization [-]
Subscription
C Carbon
O Oxygen
b Binder
i initial

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