Oxidation Kinetics of Cement-bonded Natural Ilmenite Pellets

Kang SUN, Masao ISHII, Reijiro TAKAHASHI and Jun-ichiro YAGI

Research Institute of Mineral Dressing and Metallurgy, Tohoku University, Katahira, Aoba-ku, Sendai, Miyagi-ken, 980 Japan.

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The oxidation kinetics was studied thermogravimetrically with three kinds of cement-bonded natural ilmenite pellets. Appreciable temperature rise was found inside the pellets during their oxidation with pure oxygen. In order to suppress the temperature rise, a series of oxidation experiments was carried out with diluted oxygen (9.8mol%O₂-N₂) in the temperature range from 1073 to 1273 K. The experimental data were analyzed in the light of the unreacted core shrinking model resulting in that the oxidation rate was mainly controlled by the intrapellet diffusion of oxygen and the intrinsic chemical reaction. The temperature dependence of the kinetic parameters was also determined.

KEY WORDS: oxidation; kinetics; ilmenite; cement-bonded pellet; thermogravimetry; unreacted core shrinking model; mixed control; intrapellet diffusivity; reaction rate constant.

1. Introduction

As titanium industry progresses, the available resources of high grade natural rutile are becoming less and less. This enforces us to make use of the abundant ilmenite deposits. As a result, a number of processes has been proposed for upgrading ilmenite.¹⁾ No matter which process we choose, the reduction of ilmenite is an important step. Furthermore, both experimental results and industrial experience have proved that preoxidation is beneficial for the reduction, especially, for the reduction of the poorly weathered ores. Therefore, it is very important to study the oxidation kinetics of ilmenite.

In spite that the oxidation kinetics of ilmenite has been studied by several researchers,²⁻⁴⁾ the effect of reaction heat on the oxidation rate has been ignored. According to our experiments, the temperature rise inside the pellet was too great to be negligible during the oxidation with pure oxygen. In order to clarify the kinetics of the oxidation of ilmenite without the influence of such a nonisothermal effect, the oxidation kinetics was studied with oxygen diluted with nitrogen. The relationship between the temperature rise inside the pellet and the oxygen concentration of the gaseous mixture was measured experimentally and based on which the acceptable value of the bulk concentration of oxygen was selected.

From the viewpoint of commercial production, pelletization is beneficial for the gas solid contact and easy for operation, especially, the technique of cement-bonded pellet can also reduce energy consumption and environmental pollution. In order to clarify the fundamental phenomena and eventually control the industrial process, it is essential to study the kinetic behavior of a single cement-bonded pellet.

The purpose of this paper is to study the kinetic

behavior of the oxidation of natural ilmenite with cement-bonded pellets under approximately isothermal condition and to measure the kinetic parameters according to heterogeneous kinetic theory.

2. Experimental

2.1. Apparatus and Procedure

The oxidation kinetics was studied thermogravimetrically with cement-bonded ilmenite pellets from 1073 to 1273 K by applying 9.8mol%O₂-N₂ which will be termed as "diluted oxygen" in the following discussion. The

Fig. 1. Schematic diagram of the experimental apparatus.
1: Load transducer, 2: Platinum wire, 3: Alumina tube, 4: Pellet, 5: Electric furnace, 6: Alumina balls, 7: Bridge box, 8: Dynamic strain meter, 9: Recorder, 10: Temperature controller.

Table 1. Chemical composition of the three kinds of natural ilmenite. (mass%)

	TiO ₂	TFe	FeO	Fe ₂ O ₃	MnO	SiO ₂	Al ₂ O ₃	P ₂ O ₅	Cr ₂ O ₃	V ₂ O ₅	MgO	CaO
AOO*	52.21	26.40	26.14	16.71	1.73	1.52	1.00	0.005	0.02	0.12	0.40	0.14
COO*	51.13	29.94	34.69	7.91	2.11	2.51	0.98	0.052	0.04	0.12	0.31	0.15
MOO*	55.05	25.97	30.63	7.93	2.90	1.73	1.16	0.075	0.01	0.06	0.31	0.15

* AOO, COO and MOO stand for the three kinds of original ore from Australia, China and Malaysia, respectively.

Fig. 2. X-ray diffraction patterns of the three kinds of ilmenite samples.
(a) AOO, (b) COO, (c) MOO.

experimental apparatus used is shown schematically in **Fig. 1**. The inner diameter of the alumina tube was 50 mm ϕ . The lower part of the alumina tube was filled with alumina balls for preheating the gaseous reactant. The uniform temperature zone within ± 2 K was about 20 cm in height above the alumina ball bed. The gas flow rate was controlled at 1.67×10^{-4} m³/sec (NTP).

After the output of the measuring system attained to a steady state, a pellet was suspended in the uniform temperature zone with a piece of platinum wire connected to a load transducer during nitrogen flowing. Then, an experiment was started by shifting the inert gas nitrogen with gaseous reactant, diluted oxygen. The weight change of the pellet, from which the fractional conversion of the oxidation was calculated, was detected with the load transducer and the signal was recorded automatically.

Fig. 3. Particle size distribution of the three kinds of samples after being crushed.

Bulk temperature was measured with a Pt/Pt-Rh (13 mass%) thermocouple before and after each run of experiment.

2.2. Samples

Three kinds of natural ilmenite ores from Australia, China and Malaysia were used. Their chemical composition is listed in **Table 1**. The mineral composition of the samples was analyzed by means of X-ray diffraction (XRD). The structure of the partially oxidized ilmenite pellets was examined by the aids of an optical microscope. According to the XRD patterns shown in **Fig. 2**, these natural ilmenite ores consisted principally of ferrous titanate (FeTiO₃). However, Australia ore (AOO) and Malaysia ore (MOO) contained a little pseudobrookite (Fe₂TiO₅). Small amount of TiCaO₃ formed after dehydration at 1173 K from the main constituent of the cement, CaO, and the TiO₂ in the original ilmenite. After the samples were crushed individually, almost same size distribution of the particles was arranged as shown in **Fig. 3**.

2.3. Pelletization

Pellets containing 8.0 mass% Portland cement were prepared from the ilmenite ores with a disk pelletizer which was 30 cm in diameter. The chemical composition of the Portland cement was listed in **Table 2**. Green pellets were cured under saturated water vapor atmosphere at 323 K for one week and then dried at 373 K in air for two days and finally dehydrated at 1173 K under oxygen-free nitrogen atmosphere for one hour. According to the results of preliminary experiments, both free water and combined water contained originally in the

Table 2. Chemical composition of the Portland cement.
(mass%)

CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO
65.6	20.9	4.7	2.7	1.75

Table 3. Density and porosity of the dehydrated pellets.

Pellets	ACP	CCP	MCP
Apparent density $\rho_a \times 10^{-3}$ (kg·m ⁻³)	3.12	3.17	3.02
True density $\rho_s \times 10^{-3}$ (kg·m ⁻³)	4.26	4.32	4.35
Porosity ε (—)	0.268	0.266	0.306

pellets were sufficiently removed after the above-mentioned treatments. For simplicity, hereafter, the three kinds of cement-bonded pellets made of ilmenite ores from Australia, China and Malaysia will be abbreviated as ACP, CCP and MCP, respectively. After dehydration, the strength of the pellets which were 12.5 to 13.0 mm in diameter was greater than 100 kg per pellet and their density and porosity measured according to JIS M 8716-1971 and JIS M 8717-1971 were given in **Table 3**.

Because the kinetic behavior of the oxidation of the three kinds of pellets was very similar, only the results measured with ACP will be mainly described in the following sections.

3. Experimental Results

3.1. Reaction of the Oxidation

The XRD results of the three kinds of cement-bonded ilmenite pellets oxidized at the bulk temperature of 973, 1073 and 1273 K with pure oxygen for two hours showed that they consisted of different products. The pellets oxidized at 973 K mainly consisted of hematite (Fe₂O₃) and rutile (TiO₂); those oxidized at 1073 K were almost composed of pseudorutile (Fe₂Ti₃O₉) and hematite, and those oxidized at 1273 K were principally converted into ferric pseudobrookite (Fe₂TiO₅) and rutile. This phenomenon indicates that the oxidation mechanism changes with temperature.²⁾

As a representative within the temperature range from 1073 to 1273 K, **Figure 4** illustrates the XRD patterns of ACP oxidized with pure oxygen at the bulk temperature of 1073 K (as will be explained later, the real maximum temperature inside the pellet was higher than 1223 K) for 2 h showing that the completely oxidized ACP consisted principally of pseudorutile and hematite. Therefore, the oxidation can be expressed stoichiometrically as Eq. (1) within this temperature range.

This result agreed with that reported by Rao and Rigaud²⁾ who derived their conclusion by means of differential thermal analysis (DTA) and XRD, and also was confirmed by the results of characteristic X-ray analyses of the oxidized layer as will be explained in detail in Sec. 3.4.

3.2. Measurement of Temperature Rise inside Pellet

It was observed that the oxidation rate of the ilmenite

Fig. 4. XRD patterns of the two-hour oxidized ACP at 1073 K.

Fig. 5. Temperature rise inside pellet during the oxidation of ACP with pure oxygen and bulk temperature being 1073 K.

pellet with pure oxygen was considerably fast in the bulk temperature range from 1023 to 1273 K, and thermodynamic estimation suggested that the oxidation generate great amount of reaction heat. As a result, marked temperature rise inside the pellet was brought about. Consequently, the oxidation of the ilmenite pellets with pure oxygen can not be analyzed as an isothermal reaction.

The temperature rise inside a pellet during oxidation was measured directly by inserting a sheathed CA thermocouple, which was 1.0 mm in outer diameter, into the pellet center. A typical experimental result measured with ACP under the condition of bulk temperature being 1073 K is shown in **Fig. 5**. The maximum temperature rise was about 150 K. In other words, the real maximum temperature at the reaction front would be higher than 1223 K when the bulk temperature was maintained at 1073 K.

3.3. Oxidation Experiment with Diluted Oxygen

In order to accurately measure the kinetic parameters appearing in the rate equation derived on the basis of isothermal assumption, it is necessary to avoid the influence of the temperature rise experimentally. An effective way is to slow down the reaction rate so as to make the temperature rise as small as possible. This was realized in our experiment by using oxygen diluted with nitrogen as the inert component.

The observed relationship between the maximum

temperature rise and the bulk concentration of oxygen used is shown in Fig. 6. This diagram shows that the maximum temperature rise was only about 20 K when the bulk concentration of oxygen was 10 mol%. Therefore, it is reasonable to analyze the oxidation of the cement-bonded ilmenite pellets as an isothermal reaction as long as the bulk concentration of oxygen being lower than 10 mol%. A 9.8 mol% O_2-N_2 mixture was used throughout our experiment.

As observed experimentally, during the oxidation of the ilmenite pellets with pure oxygen, the reaction rate was obviously slow in the lower temperature range than 1023 K, and when bulk temperature was higher than 1473 K, sintering impaired significantly the oxidation rate. In addition, reaction mechanism changed unless the bulk temperature was higher than 1023 K and lower than 1173 K (real maximum temperature at reaction front was over 1320 K). In order to avoid these problems, a series of experiments was conducted with the diluted oxygen within the temperature range from 1073 to 1273 K. Observed oxidation curves at different temperature levels

were illustrated in Fig. 7.

3.4. Morphology of the Oxidized Pellets

The cross-section of the partially oxidized ilmenite pellets showed that the oxidation macroscopically proceeded topochemically, but it was very difficult to take clear photographs because of their similar reflectivity of the unreacted core and the product layer. However, the microstructure of the reacted layer was very complicated as shown in Fig. 8. Fine stripes with different colors, which represented different phases, segregated during oxidation. The results of characteristic X-ray analysis showed that the dark phase was rich in titanium, however, the bright phase was rich in iron. This segregation was understood as the results of the reaction expressed by Eq. (1).

4. Theoretical Analysis

4.1. Rate Equations

According to the unreacted core shrinking model, the following rate equation can be derived for the isothermal

Fig. 6. Relationship between the maximum temperature rise inside pellet and the bulk concentration of oxygen during the oxidation of ACP when bulk temperature was 1073 K.

Fig. 7. Oxidation curves of ACP measured with diluted oxygen at different temperatures.

Fig. 8. Photomicrographs of Australian ilmenite particles before and after oxidation.

(a) original ilmenite particles

(b) line analysis of titanium in the original ilmenite particle

(c) ilmenite particle after oxidation at 1073 K.

The bright parts are rich in iron and the dark parts are rich in titanium.

mixed control reaction system.⁵⁾

$$\frac{t-t_f}{F} = \frac{\rho_s(1-\varepsilon)x_s r_o}{bMc_o} \left[\frac{r_o}{6D_e} (3F-2F^2) + \frac{K}{k(1+K)} \right] \quad (2)$$

where,

$$t_f = \frac{\rho_s(1-\varepsilon)x_s r_o}{bMc_o} \frac{3-3F+F^2}{3k_f} \quad (3)$$

$$F = 1 - (1-x)^{1/3} \quad (4)$$

In the course of a heterogeneous reaction, the formation and growth of the newly formed nuclei usually proceed so slowly that they will probably predominate the overall reaction rate. Under such a condition, the so-called Prout-Tompkins' equation is applicable.⁶⁾

Fig. 9. Mixed control plots of the oxidation of ACP with 9.8mol% O₂-N₂, the solid lines are the regression results.

Fig. 10. Oxidation results of ACP with diluted oxygen plotted according to the nucleation and growth model, the solid lines are the regression results.

$$N(x) \equiv \ln[x/(1-x)] = k_n t + C \quad (5)$$

where C is a constant.

Reaction rate data measured with the cement-bonded ilmenite pellets using diluted oxygen were analyzed on the basis of the rate equations mentioned above. As a representative, results measured with ACP are given in Figs. 9 and 10 which show that only the unreacted core shrinking model agrees satisfactorily with the experimental results because the experimental data analyzed according to Eq. (5) do not fall into straight lines as illustrated in Fig. 10.

4.2. Kinetic Parameters

As shown in Fig. 9, the relationship of $(t-t_f)/F$ vs. $3F-2F^2$ calculated according to Eq. (2) resulted in straight lines. The effective diffusivity of oxygen through the product layer and the rate constant of the intrinsic chemical reaction were calculated from the slope and intercept of the lines, respectively.

With the values of the rate constants and the effective diffusivity of the gaseous species obtained above, their temperature dependence was determined in terms of Arrhenius equation and the results were given in Fig. 11.

According to Evans *et al.*,⁷⁾ the effective diffusivity of gaseous species through a solid medium can be expressed as follows.

$$D_e = (\varepsilon/\tau) D_{1,2} \quad (6)$$

In order to understand the dependence of the structure of the product layer on reaction temperature, it is more reasonable to consider the relationship between the structural parameter defined in Eq. (6), ε/τ , and temperature. The results are also given in Fig. 11 showing that ε/τ is almost independent of temperature within this temperature range. The molecular diffusivity of the O₂-N₂ system, $D_{1,2}$, was estimated according to

Fig. 11. Arrhenius plot of the kinetic parameters measured with ACP.

Table 4. Temperature dependence of the kinetic parameters measured with three kinds of cement-bonded natural ilmenite pellets.

Pellets	Rate constant	Effective diffusivity	Structural parameter
ACP	$k = 1.01 \times 10^4 \exp(-123 \times 10^3/RT)$	$D_e = 1.87 \times 10^{-3} \exp(-8.35 \times 10^3/RT)$	$(\varepsilon/\tau) = 0.018 \exp(7.40 \times 10^3/RT)$
CCP	$k = 4.89 \exp(-46.4 \times 10^3/RT)$	$D_e = 8.14 \times 10^{-4} \exp(-41.5 \times 10^3/RT)$	$(\varepsilon/\tau) = 0.773 \exp(-25.8 \times 10^3/RT)$
MCP	$k = 1.75 \exp(-103.8 \times 10^3/RT)$	$D_e = 8.15 \times 10^{-3} \exp(-20.2 \times 10^3/RT)$	$(\varepsilon/\tau) = 0.077 \exp(-4.45 \times 10^3/RT)$

Chapman-Enskog's equation⁸⁾ for determining ε/τ .

$$D_{1,2} = 5.9958 \times 10^{-24} [T^3 (M_1^{-1} + M_2^{-1})]^{1/2} / (p \sigma_{12}^2 \Omega_{D,12}) \quad (7)$$

The expressions of the temperature dependence of the aforementioned kinetic parameters measured with the three kinds of pellets were summarized in **Table 4**. The difference in the effective diffusivity of oxygen through the product shell measured with different kinds of pellets was mainly contributed to the difference in their original chemical composition. During the oxidation, only the ferrous material was oxidized to ferric material, and it was this reaction that resulted in the change in the structure of the product layer. As shown in Table 1, because the content of FeO in COO was more than that in AOO, it is easy to understand that the effective diffusivity of oxygen measured with CCP was greater than that measured with ACP even though their original porosity was almost the same.

5. Discussion

5.1. Rate Controlling Step

The relative importance of each step during oxidation was described numerically in terms of their resistance fraction. The resistance fraction of each step, namely, mass transfer through the stagnant gaseous film, the intrapellet diffusion of gaseous species and the intrinsic chemical reaction was evaluated according to the method described in Ref. 9). Their expressions are given below:

Resistance fraction of the mass transfer of gaseous species through the stagnant gaseous film around the pellet:

$$R_f = 1/k_f/A \quad (8)$$

Resistance fraction of the intrapellet diffusion of oxygen:

$$R_d = r_o F / [D_e (1 - F)] / A \quad (9)$$

Resistance fraction of the intrinsic chemical reaction:

$$R_c = 1/[k(1 - F)^2] / A \quad (10)$$

where A is the total resistance:

$$A = 1/k_f + r_o F / [D_e (1 - F)] + 1/[k(1 - F)^2] \quad (11)$$

The mass transfer coefficient k_f was estimated according to Ranz-Marshall's equation.¹⁰⁾

$$N_{Sh} = 2.0 + 0.6 N_{Rep}^{1/2} N_{Sc}^{1/3} \quad (12)$$

The value of the viscosity contained in the expression of N_{Sc} and N_{Rep} was estimated according to Bird *et al.*'s equation.⁸⁾

The results are illustrated in **Fig. 12** showing that both the intrapellet diffusion and the intrinsic chemical reaction played a predominant role during the oxidation of natural ilmenite pellets and the resistance of mass transfer of the gaseous species through the stagnant gaseous film was very small except in the initial stage of the reaction.

5.2. Validity

In order to examine the validity of the kinetic

Fig. 12. Resistance fraction of the mass transfer of gaseous species through the stagnant gaseous film around pellet, intrapellet diffusion and the intrinsic chemical reaction, during the oxidation of ACP with diluted oxygen.

Fig. 13. Comparison of the calculated fractional conversion with the measured data, ACP, diluted oxygen. Lines are calculated results and points are measured data.

parameters of the oxidation of natural ilmenite pellets, **Fig. 13** compares the measured fractional conversion with those of calculation which was conducted with the parameters obtained in Sec. 4.2., showing that their agreement was satisfactory. Similar results were also obtained for CCP and MCP.

6. Conclusions

(1) The oxidation of the cement-bonded natural ilmenite pellets proceeded topochemically from the macroscopic point of view. In the temperature range from 1073 to 1273 K, the main reaction was stoichiometrically expressed as follows:

(2) When ilmenite pellets were oxidized with pure oxygen, the temperature rise inside the pellet was about 150 K when bulk temperature was 1073 K, which was too great to be negligible. However, the oxidation results measured with 9.8mol% O₂-N₂ were reasonably interpreted according to the isothermal unreacted core shrinking model.

(3) Within the temperature range from 1073 to 1273 K, the intrapellet diffusivity of oxygen and the

intrinsic chemical reaction rate constant were obtained for the three kinds of cement-bonded natural ilmenite pellets as shown in Table 4.

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Nomenclature

- b : stoichiometric coefficient of solid reactant in Eq. (1) (—)
 c_o : concentration of O_2 in the bulk gaseous phase ($\text{mol} \cdot \text{m}^{-3}$)
 D_e : effective diffusivity of O_2 ($\text{m}^2 \cdot \text{s}^{-1}$)
 k : reaction rate constant ($\text{m} \cdot \text{s}^{-1}$)
 k_f : gaseous mass transfer coefficient ($\text{m} \cdot \text{s}^{-1}$)
 k_n : constant in Eq. (5) (s^{-1})
 M : molar weight of FeTiO_3 ($\text{kg} \cdot \text{mol}^{-1}$)
 M_1 : molar weight of oxygen ($\text{kg} \cdot \text{mol}^{-1}$)
 M_2 : molar weight of nitrogen ($\text{kg} \cdot \text{mol}^{-1}$)
 p : pressure (Pa)
 r_o : radius of the pellet (m)
 R : gas constant ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)
 T : absolute temperature (K)
 t : reaction time (s)

- x : fractional conversion (—)
 x_s : mass fraction of the solid reactant in the pellet (—)
 ε : porosity of the pellet (—)
 ρ_s : true density of the pellet ($\text{kg} \cdot \text{m}^{-3}$)
 σ_{12} : collision diameter (m)
 τ : tortuosity factor of the reacted layer (—)
 $\Omega_{D,12}$: collision integral (—)

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