

# Kinetics of reduction of titano-magnetite powder by H<sub>2</sub>

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**Abstract:** The reduction of titano-magnetite powder containing 56.9 mass% of iron and 9.01 mass% of TiO<sub>2</sub> with H<sub>2</sub>-Ar gas mixtures was investigated in isothermal experiments by using thermo-gravimetric analyzer (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM). TGA measurements were carried out from 967 to 1173K under the hydrogen partial pressure ( $P_{H_2}$ ) range from 50.5 to 101kPa. The results showed that under the conditions of lower temperatures and lower hydrogen partial pressures, the reductive reaction was very slow. Nevertheless, the reaction rate increased with the increasing temperature and  $P_{H_2}$ . It was found that the double reactions, reduction of titano-magnetite to produce wüstite and ilmenite and reduction of wüstite and ilmenite to generate iron and titanium-containing phase, occurred simultaneously during the reduction of titano-magnetite with hydrogen. The experimental results indicated that the hydrogen diffusion in wüstite and ilmenite layer was the rate controlling step for the first reaction (reduction of titano-magnetite to produce wüstite and ilmenite), the reduction rate of the second reaction (reduction of wüstite and ilmenite to generate iron and titanium-containing phase) was controlled by interfacial chemical reaction. The apparent activation energies were as high as 98kJ/mol and 115kJ/mol for the first and second reaction respectively.

**Keywords:** Titano-magnetite, thermo-gravimetric analysis, hydrogen reduction, kinetics

## 1. Introduction

Due to the shortage of resources and the enhancement of environmental protection consciousness, the gas-based reduction of iron ores became a important subject of study and an interest in recent years,<sup>[1-5]</sup> especially the hydrogen reduction of iron oxides,<sup>[6-9]</sup> which can contribute to energy saving and low CO<sub>2</sub> emission.

Titanium-containing iron ores from New Zealand, which were found throughout the world in large deposits, with a lower price than the conventional hematite iron ores, have been becoming alternative sources of iron.<sup>[10-12]</sup> The iron ores are mainly composed of titano-magnetite (TTM). Previous investigations showed that the gaseous reduction of titano-magnetite was slower than that of hematite or magnetite iron ores due to the existence of titanium.<sup>[10, 11, 13]</sup> McAdam<sup>[13]</sup> studied the reduction kinetics of titano-magnetite by CO-CO<sub>2</sub>. From this study the author proposed that the rate of wüstite growth from the reduction of Fe<sub>3-x</sub>Ti<sub>x</sub>O<sub>4</sub> solid solutions obeyed a parabolic law. However, in the subsequent reduction step from wüstite to iron, the interface between wüstite of iron moved almost with linear rate. Park et al.<sup>[10]</sup> also investigated the reduction of titania-ferrous ore and found that the reduction path at temperatures above 1173K as follows: Fe<sub>3-x</sub>Ti<sub>x</sub>O<sub>4</sub> → FeO + Fe<sub>3-x-δ</sub>Ti<sub>x+δ</sub>O<sub>4</sub> → Fe + Fe<sub>3-x-δ</sub>Ti<sub>x+δ</sub>O<sub>4</sub> → Fe + xTiO<sub>2</sub>.

However, the information on the reduction of titano-magnetite by hydrogen is still not sufficient, especially in the kinetics and understanding of the rate-controlling processes. It is necessary to carry out a study on the kinetics of reduction of titano-magnetite by hydrogen for the future applications.

In the present paper, the reduction kinetics and mechanism of titano-magnetite powder using hydrogen was investigated and a new model, easier to use and to perform theoretical analysis, was developed.

## 2. Material and experimental procedure

### 2.1 Material

The chemical compositions of titano-magnetite examined in this paper are presented in Table 1. The size of ore particle was in a range of 150-160  $\mu\text{m}$ . The specific surface area was  $0.8\text{m}^2/\text{g}$  for the titano-magnetite. The XRD pattern of raw material is shown in Fig.1. XRD analysis indicated the titano-magnetite used was a solid solution of magnetite ( $\text{Fe}_3\text{O}_4$ ) and  $\text{Fe}_2\text{TiO}_4$  with a chemical formula of  $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$  ( $x \approx 0.27$ ). This result was close to the one given by the references [10].

**Table 1** Chemical composition of titano-magnetite powder (wt%)

Element	TFe	CaO	MgO	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{TiO}_2$
Titano-magnetite	56.9	0.17	3.23	2.99	3.78	9.01

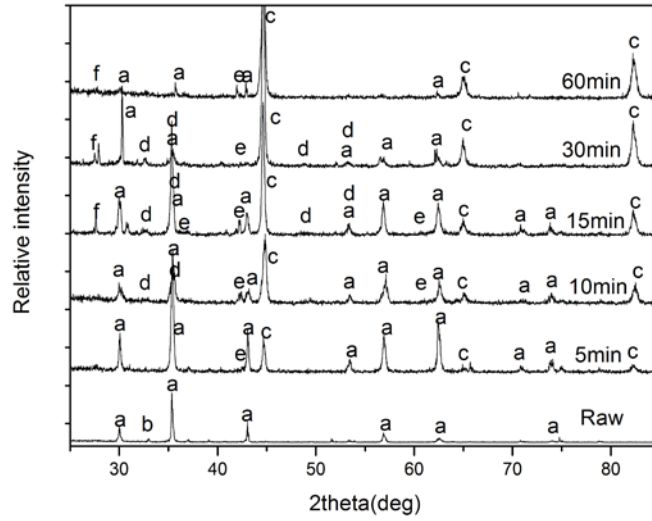
### 2.2 Experimental procedure

The weight change of titano-magnetite powders during reduction was monitored using a HCT-2 thermal analysis system, which includes a TG microbalance with a precision of  $\pm 0.1\mu\text{g}$ . In each experimental run the ore powders of 100mg in weight was used and filled into an alumina crucible. When crucible with the sample was placed in the heating furnace, argon was introduced in the system. Then, the furnace was heated up from room temperature to a required reduction temperature with a heating rate of 20K/min in argon atmosphere. When the thermal balance was established, the argon gas was stopped and the reducing gas mixture was introduced. The weight decrease of due to the reduction was then monitored continuously with a certain time interval of 1 point/second to enable a quantitative-kinetic analysis of the results. When certain period of time, the introduced reducing gas was changed to argon again, and the sample was cooled to the room temperature.

The hydrogen and the argon used in the experiments were in high purity ( $< 5\text{ ppmO}_2$ ). The composition of reducing gas was achieved using mass and volumetric precision gas flow controllers (Alicant Scitific, Model MC-500SCCM-D). In all the experimental runs, a constant flow rate of 50ml/min remained during the reduction. This level was found sufficient for diminishing the resistance of the gas-boundary layer around the sample being negligible.

XRD (Model, TTRIII, Japan) measurement were carried out for samples. The morphologies of these samples were

observed using SEM (Model S250MK3, CAMBRIDGE) technique.



a:TTM, b:Fe<sub>2</sub>O<sub>3</sub>, c:Fe, d:FeTiO<sub>3</sub>, e:FeO, f:TiO<sub>2</sub>.

**Fig. 1** XRD patterns of samples reduced by H<sub>2</sub> at 1123K, in the progress of reduction.

### 3. Results and Discussion

At temperatures above 843K, the existence of wüstite phase as an intermediate product in the course of magnetite reduction has been proved by Jozwiak.et.al.<sup>[14]</sup> Reaction of TTM started with the reduction of magnetite in the magnetite- ulvospinel solid solution to wüstite<sup>[11]</sup>. Therefore, the main reduction path can be expressed as:



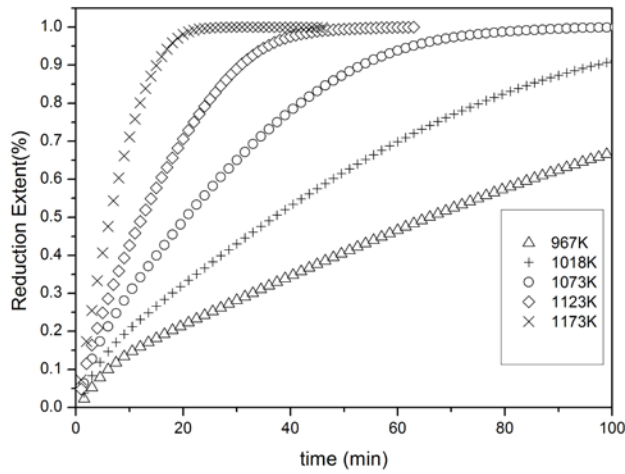
The extent of reduction was calculated using Eq. (2),

$$R = \frac{w_t}{w} \quad (2)$$

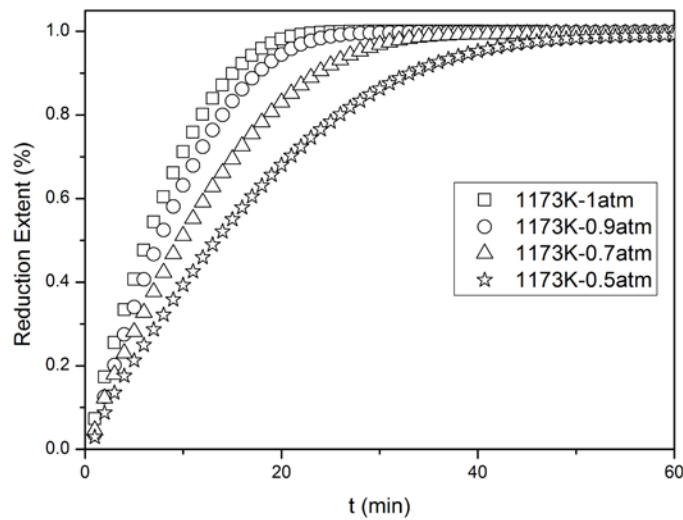
where  $w_t$  is the lost weight of sample after time  $t$ ,  $w$  is the theoretical total lost weight of the sample. If titano-magnetite were reduced completely,  $w$  is calculated to be  $0.2053w_0$ , where  $w_0$  is initial weight of titano-magnetite sample.

#### 3.1 Effect of temperature

The isothermal reduction of titano-magnetite by hydrogen was studied using pure H<sub>2</sub> in the temperature range of 967 to 1173K. The curves of reduction extent against time are presented in Fig. 2, which showed that after 100 minutes, iron oxides were reduced to metallic iron completely at temperatures above 1073K. However, the reactions were very slow at low temperature, especially at 967K. Even the reactions proceeded at 967K over a period of 100 minutes, the reduction extent was only 67%. Also, in the temperature range of 967 to 1123K, the reduction rate slowly decreased with increasing extent of reduction.



**Fig. 2** Reduction curves of titano-magnetite powder reduced by pure H<sub>2</sub> at different temperatures



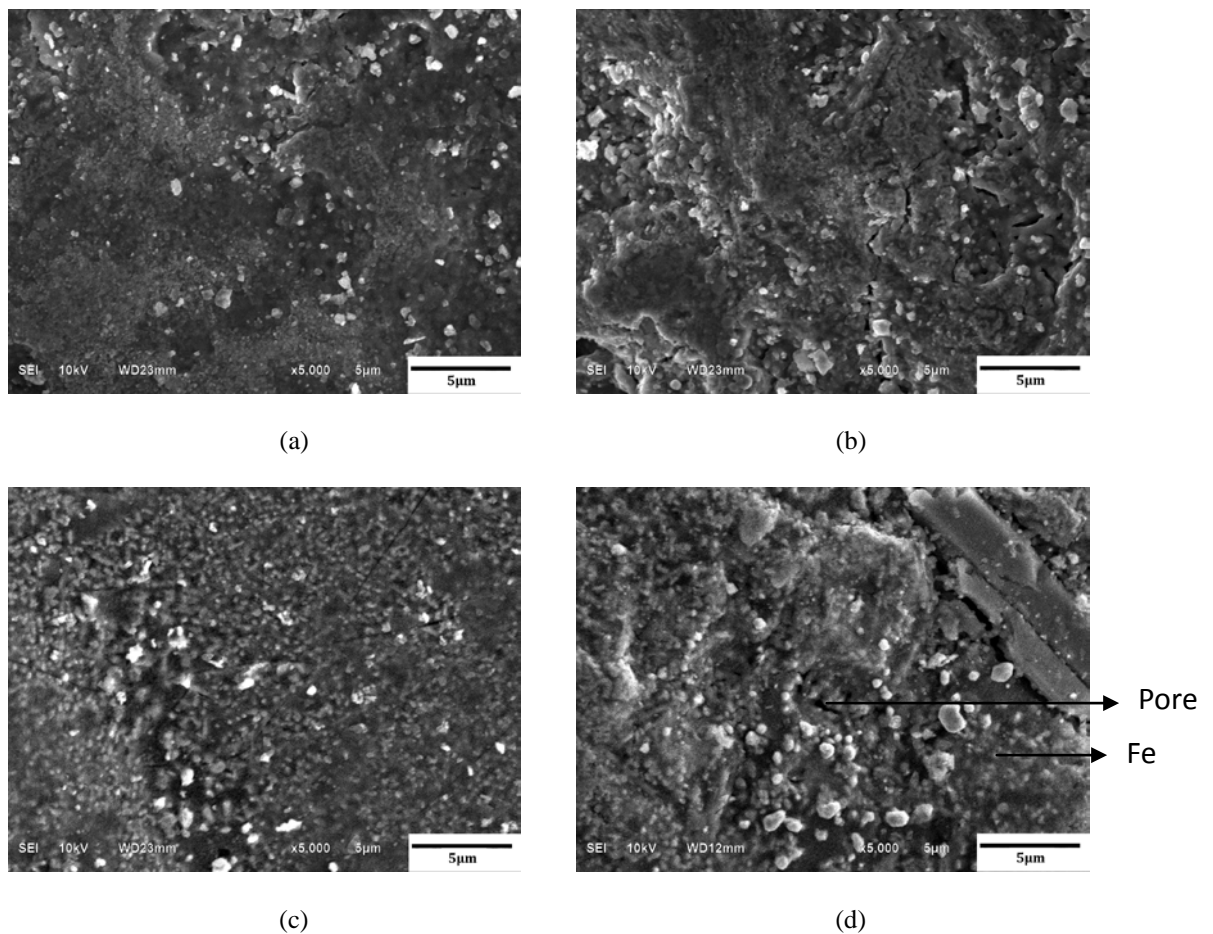
**Fig.3** Reduction curves of titano-magnetite powder reduced at 1173K with different hydrogen partial pressure.

### 3.2 Effect of partial pressure of hydrogen

The effect of partial pressure of hydrogen on the reduction of titano-magnetite was studied by the reaction of titano-magnetite with H<sub>2</sub>-Ar gas mixture at 1173K. The ratio of partial pressure of hydrogen to the sum of pressures of H<sub>2</sub> and Ar,  $P_{H_2}/P_{H_2}+P_{Ar}$ , was changed in the range of 0.5 to 1.0. The reduction curves are presented in Fig. 3, from which it can be obtained that at low hydrogen partial pressures, the reduction was slow and the increase in partial pressure of hydrogen caused a visible increase in reduction degree and rate.

### 3.3 Phases of reduced products during the reduction of titano-magnetite

Samples in the progress of reduction at 1123K with pure H<sub>2</sub> were analysed by XRD, as shown in Fig. 1. Metallic iron was observed after 5min of reduction indicating that the final product iron generated from the start. After 60min, the peaks for metallic iron became dominant in the XRD pattern. The intermediate phases (wüstite and ilmenite) and the final products (iron and titanium-containing phase) were detected in the course of reduction. It was suggested that magnetite in the titano-magnetite was firstly reduced to wüstite, thereafter to iron, and ilvospinel was reduced to ilmenite first, then to TiO<sub>2</sub>. It can be concluded that the two reactions, the reduction of titano-magnetite to produce wüstite and ilmenite, as well as the reduction of wüstite to generate iron and titanium-containing phase, simultaneously proceeded from the beginning of the reactions to the end.



**Fig. 4** Morphologies of samples reduced by pure hydrogen at 1123K. (a) after 3min reduction (b) after 15min reduction (c) after 30min reduction (d) after 60min reduction

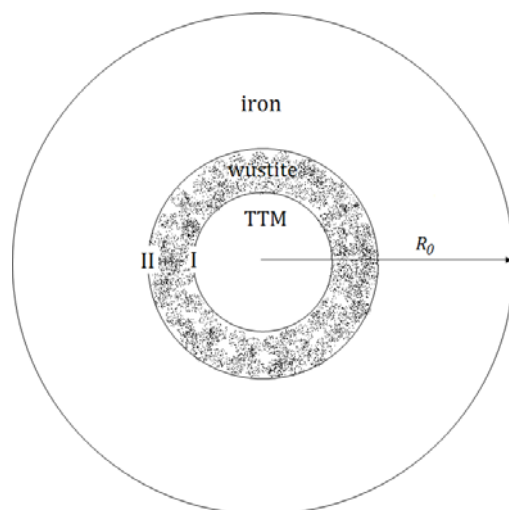
### 3.4 SEM analysis

Figures 4(a) to (d) present SEM images of samples reduced at 1123K for different time. It can be learned that with the reaction progressing, there are small metallic iron grains formation, and thereafter, the small metallic iron grains grow and conglomerate with the generation of pores, finally to form the fine structure. The results of Fig.4(c) and (d) indicated that the product layer is porous and is beneficial to H<sub>2</sub> diffusion.

### 3.5 Reaction kinetics

#### 3.5.1 Model

As mentioned earlier, the results of XRD suggested that the double reactions, namely the reduction of titano-magnetite to produce wüstite and ilmenite, and the reduction of wüstite and ilmenite to generate iron and titanium-containing phase, occurred simultaneously. So, the reduction of titano-magnetite can be described as the one that the reduction proceeds first with chemical reaction between titano-magnetite and  $H_2$  at the outer surface of particles with the forming wüstite and ilmenite. Once wüstite and ilmenite forms, the second reaction will proceed immediately. From the above viewpoint, it could be estimated that the reduction of titano-magnetite proceeded topochemically and it was assumed that there were two reaction fronts each linked to one of the single reactions in the course of reduction as shown in Fig. 5.



**Fig. 5** Interface progressions for titano-magnetite reduced by hydrogen

As clearly showed in Figure.4 many pores formed in outer product layer (iron layer), which would be beneficial to hydrogen  $H_2$ , as known that has smallest molecule favorable to diffuse. It could be reasonable to assume that the reduction rate of wüstite to iron was not controlled by the diffusion of  $H_2$  in the iron layer, and was most likely being controlled by the chemical reaction at the II interface (Fig.5). However, in the process of reduction of titano-magnetite to wüstite, due to the growth of the iron layer, and wüstite layer, the diffusion of hydrogen through the wüstite layer was slow. Moreover, there was a large part of hydrogen would be consumed during the reaction at the I interface (Fig.5). Hence, the diffusion of hydrogen in the product layer might become the rate-controlling step in the reduction of titano-magnetite to wüstite and ilmenite.

Chou et al.<sup>[15, 16]</sup> have proposed a new model to describe the gas-solid reaction, in which the formulae are in the analytic form expressing the reacted fraction as an explicit function and the parameters have specific physical meaning. However, it cannot be used to describe the kinetics of double reactions. To solve this problem and on this basis, the authors<sup>[17]</sup> developed a new model that can describe the kinetics of double reductive reactions by considering the diffusion or chemical reaction controlling mechanism.

In order to provide a deeper understanding of experimental results, this model will be applied to this reduction process. The formula for the reduction of titano-magnetite with hydrogen under isothermal condition is proposed as follow<sup>[17]</sup>:

$$\xi = 1 - \alpha_1 \left( 1 - \sqrt{\frac{2K_H^{0\beta} D_H^0 (\sqrt{P_{H_2}} - \sqrt{P_{H_2}^{eq1}})}{R_0^2 V_{m1}} \exp\left(-\frac{\Delta E_{app1}}{RT}\right) t} \right)^3 - \alpha_2 \left( 1 - \frac{K_0 P_{H_2} \exp\left(-\frac{\Delta E_{app2}}{RT}\right) t}{R_0 V_{m2}} \right)^3 \quad (3)$$

where '1' represents the first reaction, '2' represents the second reaction;  $\alpha_1$  and  $\alpha_2$  are coefficients depending on the oxygen loss of each single reaction,  $K_H^{0\beta}$ ,  $K_0$  are constants independent of temperature;  $D_H^0$  is diffusion coefficient of hydrogen in product layer;  $P_{H_2}^{eq}$  is hydrogen partial pressure in equilibrium with hydrogen at the reaction interface and should be related to temperature T;  $V_{m1}$  and  $V_{m2}$  are coefficients that depend on substance and reaction,  $R_0$  is the radius of the particle,  $\Delta E_{app}$  is the apparent activation energy. If the value of  $P_{H_2}^{eq}$  is very small or the temperature

coefficient of  $P_{H_2}^{eq}$  can be neglected, then  $\frac{2K_H^{0\beta} D_H^0 (\sqrt{P_{H_2}} - \sqrt{P_{H_2}^{eq1}})}{R_0^2 V_{m1}}$  will be constant as the hydrogen partial pressure and the particle radius are fixed.

#### A. The effect of temperature on the reduction extent

Define

$$B_{T1} = \frac{1}{(2K_H^{0\beta} D_H^0 / V_{m1}) (\sqrt{P_{H_2}} - \sqrt{P_{H_2}^{eq1}}) R_0^2} \quad (4)$$

$$B_{T2} = \frac{1}{(K_0 / V_{m2}) P_{H_2} / R_0} \quad (5)$$

where  $B_T$  is a function of  $P_{H_2}$  and  $R_0$ .  $B_T$  will be constant when the hydrogen partial pressure and the particle size are fixed. Combining (3), (4) and (5), we have

$$\xi = 1 - \alpha_1 \left( 1 - \sqrt{\frac{\exp\left(-\frac{\Delta E_{app1}}{RT}\right)}{B_{T1}} t} \right)^3 - \alpha_2 \left( 1 - \frac{\exp\left(-\frac{\Delta E_{app2}}{RT}\right)}{B_{T2}} t \right)^3 \quad (6)$$

This is the formula representing the effect of temperature on the reduction extent. It may be seen from Eq.(6) that the higher the temperature, the larger the reduction extent  $\xi$ . It is in accordance with our commonsense, as the higher the temperature the faster the reaction. Nevertheless, the increasing rate in different temperature ranges will be different. The increasing rate will decrease as temperature increases.

#### B. The effect of hydrogen partial pressure on the reduction extent

Here, we define

$$B_{P1} = \frac{1}{(2K_H^0 \beta D_H^0 / V_{m1}) \exp(-\frac{\Delta E_{app1}}{RT}) / R_0^2} \quad (7)$$

$$B_{P2} = \frac{1}{(K_0 / V_{m2}) (\exp(-\frac{\Delta E_{app2}}{RT}) / R_0)} \quad (8)$$

where  $B_p$  is a function of  $T$  and  $R_0$ .  $B_p$  will be constant as the temperature and the particle size are fixed. Combining (3), (7) and (8), one obtains

$$\xi = 1 - \alpha_1 \left( 1 - \sqrt{\frac{\sqrt{P_{H_2}} - \sqrt{P_{H_2}^{eq1}}}{B_{P1}} t} \right)^3 - \alpha_2 \left( 1 - \frac{P_{H_2} t}{B_{P2}} \right)^3 \quad (9)$$

This is the formula representing the effect of hydrogen partial pressure on the reduction extent. It may be seen from Eq. (9) that the higher the hydrogen partial pressure, the larger the reduction extent.

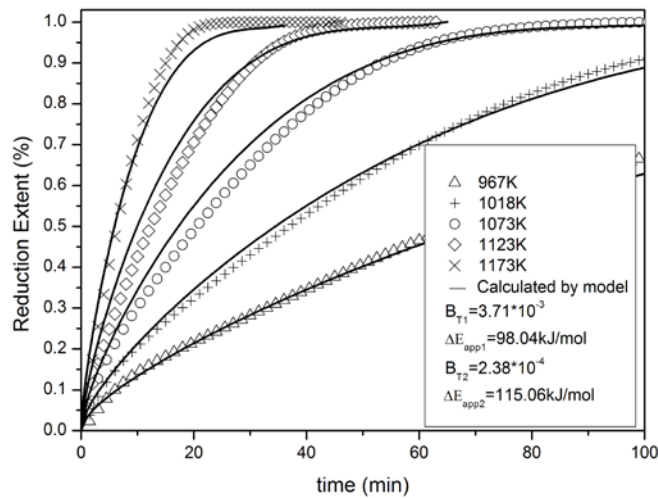
### 3.5.2 Application of the new model

Duo to  $x$  is very small, and for simplicity, it would be reasonable to only consider the main reactions, titano-magnetite  $\rightarrow$  wüstite and wüstite  $\rightarrow$  iron. Based on this consideration,  $\alpha_1$ ,  $\alpha_2$  could be calculated approximately equal to 0.25 and 0.75, respectively. Normally, the value of  $P_{H_2}$  is high and the value of  $P_{H_2}^{eq}$  is very small and can be neglected. So, in this study,  $P_{H_2}^{eq}$  was set down as 0.

#### A. Effect of temperature

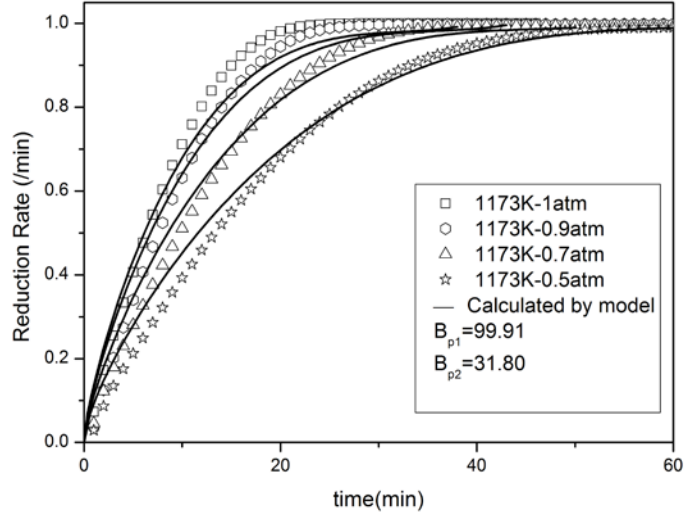
Eq. (6) can be used to describe the reduction kinetics of titano-magnetite with hydrogen at a certain temperature. The fitting results are shown in Fig. 6. The model describing the effect of temperature on the reduction extent of titano-magnetite is as follows:

$$\xi = 1 - 0.25 \left( 1 - \sqrt{\frac{\exp(-\frac{98042.5}{RT})}{0.003712} t} \right)^3 - 0.75 \left( 1 - \frac{\exp(-\frac{115058.1}{RT})}{0.000238} t \right)^3 \quad (10)$$



**Fig. 6** A comparison of experimental data with model estimated reaction extents for reduction of titano-magnetite powder by pure  $H_2$  at different temperatures





**Fig. 7** A comparison of experimental data with model for reduction of titano-magnetite powder at 1173K with different hydrogen partial pressure

#### B. Effect of partial pressure of hydrogen

Eq. (9) can be used to describe the reduction kinetics of titano-magnetite with hydrogen at different partial pressure of hydrogen. Fig. 7 shows the fitted results and experimental data of reduction titano-magnetite at 1173K with different hydrogen partial pressure. The equation describing the effect of hydrogen partial pressure on the reduction extent of titano-magnetite is as follows:

$$\xi = 1 - 0.25 \left( 1 - \sqrt{\frac{P_{H_2}}{99.91} t} \right)^3 - 0.75 \left( 1 - \frac{P_{H_2} t}{31.80} \right)^3 \quad (11)$$

At the same time, the models for other rate controlling mechanism in reference [17] were used to fit the experimental results and found that those models could not describe the reduction well. It indicates that the foregoing essential model hypothesis is reasonable.

#### 4. Conclusions

The kinetics of reduction of titano-magnetite powder by  $H_2$ -Ar gas mixture was investigated using thermo-gravimetric analyzer from 967 to 1173K. The following results can be summarized.

1) At lower temperatures, the reduction of titano-magnetite was much slower. Increasing the temperature and  $H_2$  partial pressure was found beneficial to facilitate the reduction of titano-magnetite. From the results of SEM, it can be concluded that the porous iron layers formed in the reduction was facilitating the hydrogen diffusion.

2) The double reactions, reduction of titano-magnetite to produce wüstite and ilmenite and reduction of wüstite and ilmenite to generate iron and titanium-containing phase, were found to occur simultaneously in the course of reduction of titano-magnetite with hydrogen. The hydrogen diffusion in wüstite and ilmenite layer was the rate controlling step for the first reaction (reduction of titano-magnetite to produce wüstite and ilmenite). However, the reduction rate

controlling step for the second reaction (reduction of wüstite and ilmenite to generate iron and titanium-containing phase) was interfacial chemical reaction.

3) The present model can be applied to describe the reduction kinetics of titano-magnetite using hydrogen, the model predicted curves agree well with the experimental results.

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