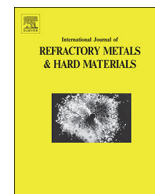




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A new kinetic model for hydrogen reduction of metal oxides under external gas diffusion controlling condition

Jie Dang*, Yijie Wu, Zepeng Lv, Zhixiong You, Shengfu Zhang, Xuwei Lv

College of Materials Science and Engineering, Chongqing University, Chongqing 400044, PR China



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ABSTRACT

The reduction of metal oxides by hydrogen is a very significant reaction in metallurgical industries. Particularly, hydrogen reduction is one of the effective methods to reduce CO₂ emission in iron and steel industry. The mathematical modeling of H₂ reduction process would help to define the operating parameters and to get a better control of the reduction process. In this study, a new kinetic model regarding hydrogen reduction of metal oxides controlled by external gas diffusion has been proposed. The model has incorporated numbers of parameters such as temperature, size of the metal oxides, diffusion coefficient constant, hydrogen partial pressure, density of metal oxides and time. Furthermore, the shape of metal oxides (spherical, cylindrical, lamellar particles) was considered as well, and the models for the reduction of metal oxides with different shapes were combined to a formula. Also, the developed model can be applied to describe the reduction kinetics under both isothermal and non-isothermal conditions. Because the model is in the analytic function, therefore, it is convenient for usage and theoretical analysis. Application of the developed model to practical systems validated that its predicted values agreed very well with the experimental data.

1. Introduction

Arising from the public concern on global warming issue, clean energies are recommended to replace carbon-based fossil energies and thus to reduce CO₂ emission from the heavy industries [1], for instance the iron and steel industry. Hydrogen, as an energy vector and clean energy, could be used as a reducing agent in the reduction of iron oxides [2] and other metal oxides, such as the nickel oxide [3], molybdenum oxides [4, 5], and is one of the most potential and promising reductant candidates to decrease CO₂ emission.

The mathematical modeling of H₂ reduction process is important in order to interpret laboratory data and in design and scale-up, and it will help to define the operating parameters and to get a better control of the reduction process. A number of valuable kinetic models which can be used to describe reduction kinetics of metal oxides by hydrogen have been published. In these models, several controlling steps have been considered and discussed. Avrami [6–8] has developed the nucleation and growth model, which can be used to describe the reduction kinetics of metal oxides at low temperature. The volume reaction model [9–11], Jander's model [12], Cater's model [13] and Ginstling-Brounshtein's model [14] were also proposed to describe both the chemical reaction controlled reduction and diffusion in the product layers controlled reduction. In general, the controlling steps for the reduction can be

nucleation, chemical reaction, diffusion in the product layers or external gas diffusion controlling. Our previous model [15] regarding hydrogen reduction of metal oxides considered both the chemical reaction and diffusion in the product layer as well. As reviewed, the models for nucleation, chemical reaction and diffusion in the product layers controlling mechanisms were all developed. However, to our knowledge, there has been very little research on the kinetic model for the reduction of metal oxides with hydrogen (being the single reduction agent) under external gas diffusion controlling condition, although it is very important in the industry.

Therefore, the work on which this paper reports was undertaken to develop a model to describe the reduction of metal oxides with hydrogen under external gas diffusion controlling condition. The model allows the incorporation of numbers of parameters into the overall scheme but does not involve any complex numerical calculation. Comparing with the empirical formulae (Jander's model [12], Cater's model [13]), another major progress is that our formulae has revealed the physical meaning of parameter “*k*” that appears in the empirical formulae. Furthermore, these formulae proposed in this study are analytic with a form of explicit function and enable the easy performance of a theoretical analysis.

* Corresponding author.

E-mail address: jiedang@cqu.edu.cn (J. Dang).<https://doi.org/10.1016/j.ijrmhm.2018.07.011>

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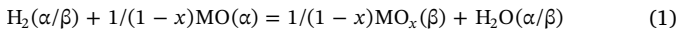
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2. Reduction mechanism of metal oxides by hydrogen

First, it is assumed that the metal oxides particles have a uniform size (uniform diameter for spherical and cylindrical particles, uniform thickness for lamellar ones), and the size remains constant during the reduction. The reductive process is assumed to be composed of eleven steps.

- (i) Hydrogen in the bulk gas phase diffuses into the gas boundary layer.
- (ii) Hydrogen in the boundary gas layer diffuses to the surface of metal oxides particles.
- (iii) Diffusion of hydrogen through the porous product layer to the reaction interface.
- (iv) Physisorption of hydrogen molecules.
- (v) Chemisorption of hydrogen molecules at the interface.
- (vi) Chemical reaction on the metal oxides/product layer interface.



where M represents metals, α represents metal oxides, β represents the product phase.

- (vii) Chemical desorption of H₂O molecules.
- (viii) Physical desorption of H₂O molecules.
- (ix) H₂O diffuses through the porous product layer to the surface of the particle.
- (x) H₂O diffuses into the gas/particle boundary layer.
- (xi) H₂O diffuses to the bulk gas phase.

Generally, the chemical reaction at the reacted interface or gas diffusion in the product layer is the controlling step [16], and this mainly depends on the substance, reaction, reaction temperature, particle size and even gas concentration. However, if the flow velocity of gas is not sufficient for diminishing the diffusion resistance of gas in the gas boundary layer, the gas diffusion in the boundary layer would become the controlling step during the reaction.

3. The theoretical model

Three types of particle with different shapes are taken into consideration: spherical, cylindrical and lamellar particles.

3.1. Spherical particles

Fig. 1 shows the spherical particle of metal oxides, where x is the

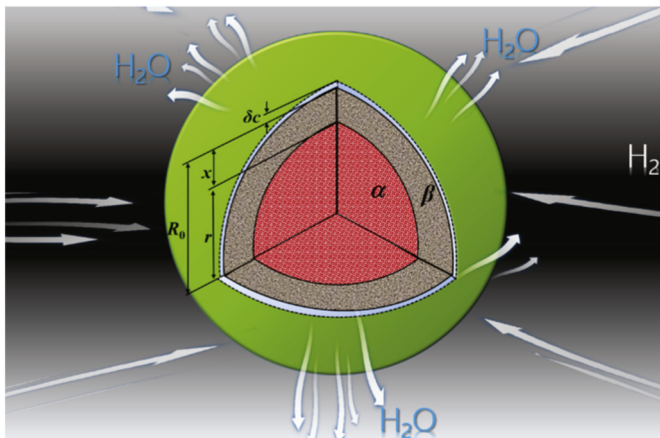


Fig. 1. Schematic diagram of reduction of spherical metal oxides by H₂: α -Metal oxides; β -Reduction product; R_0 -Radius of the particle; r -Radius of α -phase at time t ; x -Thickness of β -phase; δ_c -the thickness of boundary layer.

thickness of the product layer, R_0 is the radius of the particle, r represents the unreduced metal oxides and δ_c is the thickness of gas boundary layer. Because the raw material is assumed to be nonporous, the H₂ reduction obeys the core-shrinking mechanism and a porous product layer will be formed in the outside of the unreduced metal oxides. The reduction extent ξ at radius r can be determined in terms of the following equation:

$$\xi = 1 - \left(\frac{r}{R_0}\right)^3 \quad (2)$$

Differentiating Eq. (2) with respect to time t , it can be obtained that

$$\frac{d\xi}{dt} = -\frac{3r^2}{R_0^3} \frac{dr}{dt} \quad (3)$$

In the case of diffusion in the gas boundary layer controlling, the radial decrease rate of α should be proportional to the flux of H₂, $J_{H_2}^\beta$, namely

$$\frac{dr}{dt} = -\frac{M}{\rho} \frac{R_0^2}{r^2} J_{H_2}^\beta \quad (4)$$

where M is molecule weight of metal oxides, and ρ is the density of metal oxides.

Based on the Fick's first law, the flux of H₂ can be written as

$$J_{H_2} = -D_{H_2} \left(\frac{C_\delta - C_b}{\delta_c}\right) \quad (5)$$

in which D_{H_2} is the diffusion coefficient of H₂ in the gas boundary layer; C_b is the H₂ concentration in the bulk phase and C_δ is H₂ concentration at the interface of metal oxides and gas boundary layer; δ_c is the thickness of gas boundary layer.

If the gas can be considered as ideal gas, then

$$C = \frac{P}{RT} \quad (6)$$

Combining Eqs. (3)–(6), one can obtain,

$$\frac{d\xi}{dt} = \frac{3MD_{H_2}}{RT\rho R_0\delta_c} (P_{H_2}(b) - P_{H_2}(\delta)) \quad (7)$$

where $P_{H_2}(b)$ is the H₂ partial pressure in the bulk phase, and $P_{H_2}(\delta)$ is the H₂ partial pressure at the interface of metal oxides and gas boundary layer.

If the diffusion coefficient of H₂ is written as

$$D_{H_2} = D_0 \exp\left(-\frac{\Delta E_{app}}{RT}\right) \quad (8)$$

Eq. (9) can then be obtained,

$$\frac{d\xi}{dt} = \frac{3MD_0}{RT\rho R_0\delta_c} (P_{H_2}(b) - P_{H_2}(\delta)) \exp\left(-\frac{\Delta E_{app}}{RT}\right) \quad (9)$$

where D_0 is a constant independent of temperature, ΔE_{app} is the apparent activation energy.

Integrating and rearranging Eq. (9) yields

$$\xi = \frac{3MD_0}{RT\rho R_0\delta_c} (P_{H_2}(b) - P_{H_2}(\delta)) \exp\left(-\frac{\Delta E_{app}}{RT}\right) t \quad (10)$$

In the practical production, most metals oxides are reduced under the non-isothermal condition, for example, the iron reduction in a shaft furnace (the temperature increases during the reduction with descending of the burden). Hence, it is significant and necessary to establish the non-isothermal reduction model.

The simple case of increasing temperature with a constant rate η is considered in the present study. The relation of temperature T with time t is given as Eq. (15)

$$T = T_0 + \eta t \quad (11)$$

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