

Gas-Solid Reaction Kinetics for Upgrading Ilmenite(イメルナイトの高品位化に関する気固反 応の速度論的研究)

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号	1320
発行年	1992
URL	http://hdl.handle.net/10097/10127

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授 与 各 位	博 士 (工 学)
学位授与年月日	平成 4 年 11 月 11 日
学位授与の根拠法規	学位規則第 5 条第 2 項
最 終 学 歴	昭 和 60 年 9 月 中国長沙鋳冶研究院冶金系修士課程修了
学 位 論 文 題 目	Gas-Solid Reaction Kinetics for Upgrading Ilmenite (イルメナイトの高品位化に関する気固反応の速度論的研究)
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論 文 内 容 要 旨

1. Outline of the Research Field.

The tendency that the resources of high grade natural rutile are becoming less and less as titanium industry progresses enforces us to make use of the abundant ilmenite deposits. Both preoxidation and reduction of ilmenite play important roles in upgrading this material, therefore it is very important to study the kinetics of these two processes.

The present research work includes the following three main parts :

- (a) the kinetics of the oxidation and reduction of a single pellet made of natural ilmenite ;
- (b) the kinetics of the oxidation and reduction of synthetic ilmenite ;
- (c) the reduction kinetics of natural ilmenite in a fluidized bed.

2. Oxidation Kinetics of a Single Natural Ilmenite Pellet

The oxidation kinetics of natural ilmenite was studied thermogravimetrically with cement-bonded pellets made of three kinds of ilmenite ores which were from Australia, China and Malaysia, respectively. The experimental apparatus is schematically shown in Fig. 1.

The results of X-ray diffraction (XRD) analysis with samples before and after oxidation showed that the reaction mechanism changed with temperature. Furthermore, appreciable

temperature rise was found inside the pellet during the oxidation with pure oxygen by inserting a fine sheathed thermocouple into the pellet. In order to circumvent the change in reaction mechanism and to suppress the temperature rise, a series of experiments was carried out with diluted oxygen (9.8 mol% O₂-N₂) from 1073 to 1273 (bulk temperature).

The experimental data measured with the diluted oxygen were analyzed according to the unrected core shrinking model. It was found that the oxidation rate was mainly limited by the intrapellet diffusion of oxygen through the product layer and the intrinsic chemical reaction.

3. Nonisothermal Behavior of the Oxidation of Natural Ilmenite Pellet

The oxidation kinetics of an ilmenite pellet with pure oxygen can not be interpreted with isothermal kinetic models because of the remarkable temperature rise inside the pellet. Instead, this subject was analyzed with an unsteady nonisothermal kinetic model developed by treating the mass transfer as a pseudo-steady state process and the heat transfer within the pellet as an unsteady state process, respectively. Fairly good agreement between the model prediction and experimental data was obtained by solving the governing differential equations numerically with the kinetic parameters determined experimentally.

The effect of heat accumulation inside the pellet was evaluated and it was found that the pseudo-steady state assumption for heat transfer within the pellet was invalid especially in the initial stage. According to the resistance fraction of each step and the value of Biot number, the total oxidation rate was mainly controlled by the intrapellet diffusion of oxygen and the overall heat transfer rate was mainly limited by the poor heat conduction through the product layer.

4. Reduction Kinetics of a Single Natural Ilmenite Pellet

The hydrogen reduction kinetics of natural ilmenite was studied thermogravimetrically with the apparatus and the three kinds of cement-bonded pellets used in previous sections. Special attention was focused on the kinetic behavior of the reduction of the complex intermediate compounds, such as pseudorutile (Fe₂Ti₃O₉) and pseudobrookite (Fe₂TiO₅) as well as the stepwise reaction kinetics of the reduction of the preoxidized ilmenite pellet.

Preoxidation of the ilmenite pellets accelerated the subsequent reduction and the reduction rate increased with preoxidation temperature.

The reduction of the preoxidized pellets proceeded in stepwise manner. The first step was the conversion of the ferric material to ferrous one (Reaction I) and followed by the second step, the further reduction of the ferrous material to metallic iron and rutile (Reaction II).

The kinetics of the direct reduction of the ilmenite pellets was analyzed with a one-interface kinetic model and that of the reduction of preoxidized ilmenite pellets was interpreted with a

two-interface kinetic model as shown in Fig. 2.

Reaction I finished within several minutes and the overall reduction was mainly consisted of Reaction II. The rate-controlling step was evaluated in terms of resistance fraction of each step concerned, according to which the intrapellet diffusion of the gaseous species played an important role in the reduction of the ilmenite pellets.

5. Kinetics of the Oxidation and Reduction of Synthetic Ilmenite

In order to remove the influence of impurities, the kinetics of oxidation and reduction was studied with synthetic ilmenite. According to the XRD results, the synthetic ilmenite consisted of pure FeTiO_3 .

The kinetics of the oxidation and reduction of the synthetic ilmenite was studied thermogravimetrically with slabs (15mm ϕ x 1mm) using the same apparatus as that mentioned above, and the experimental results were analyzed with similar kinetic models as that stated previously.

There are two phases in the oxidized ilmenite, one of which is dark in color and rich in titanium and the other is bright in color and rich in iron. As shown in Fig. 3, microscopically, the distribution of titanium and iron in the oxidized layer is not uniform and the mineral composition of the titanium-rich phase changes between ferric pseudobrookite ($\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$) and pseudorutile ($\text{Fe}_2\text{O}_3 \cdot 3\text{TiO}_2$) but the iron-rich phase almost consists of pure hematite (Fe_2O_3).

6. Kinetics of the Reduction of Natural Ilmenite in a Fluidized Bed

As proved by the cold experiments, the fluidization was smooth and uniform when the gas superficial velocity was (5~6) u_m , and the amount of solid sample was about 50g, and no slugging phenomenon was observed.

The hydrogen reduction kinetics of Australian ilmenite in a bubbling fluidized bed was studied with the apparatus shown schematically in Fig. 4. The reaction rate was measured by the following two methods: (a) analyzing the chemical composition of the exit gas with a mass spectrometer; (b) determining the reduction degree by oxidizing the solid samples taken at different reaction time intervals.

The reduction kinetics was interpreted in the light of a kinetic model developed on the basic concept of the "two-phase theory" and the governing differential equations were solved numerically by means of finite difference approximation.

Fairly good agreement between the kinetic model predictions and that of measurement obtained. It was further found that the concentration distribution of hydrogen in emulsion phase and bubble phase was different, whereas, the distribution of the local reduction degree of

powders in the two phases was almost uniform, moreover, both the mass transfer and the intrinsic chemical reaction played an important role during the reduction.

7. Conclusions

The main results and conclusions of the present research work were summarized.

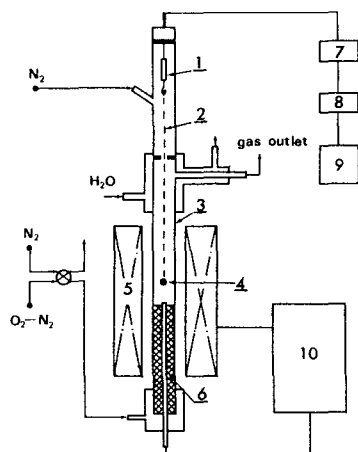


Fig. 1
Schematic diagram of the experimental apparatus for studying the kinetics of a single pellet

- | | |
|----------------------|----------------------------|
| 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 |

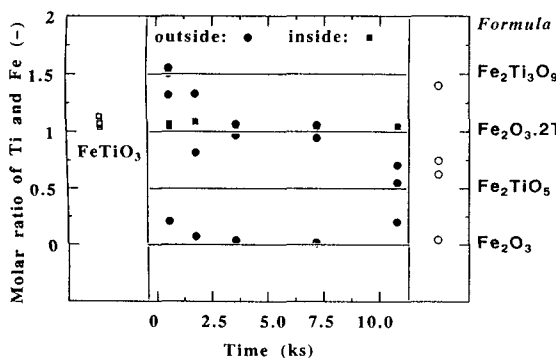


Fig. 3
Results of point analyses of the original synthetic ilmenite, partially reacted (1173K) and completely oxidized (1073K, 12h) samples

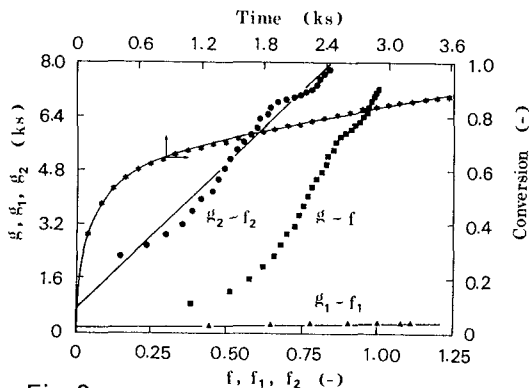


Fig. 2
Comparison of the two-interface kinetic model with that of the one-interface kinetic model

$$\begin{aligned}
 g &= t/F & f &= 3F - 2F^2 \\
 g_1 &= t/(1 - \xi) & f_1 &= 1 + \xi - 2\xi^2 \\
 g_2 &= (t - t_c)/(\zeta_c - \zeta) & f_2 &= 3(\zeta + \zeta_c) - 2(\zeta^2 + \zeta\zeta_c + \zeta_c^2)
 \end{aligned}$$

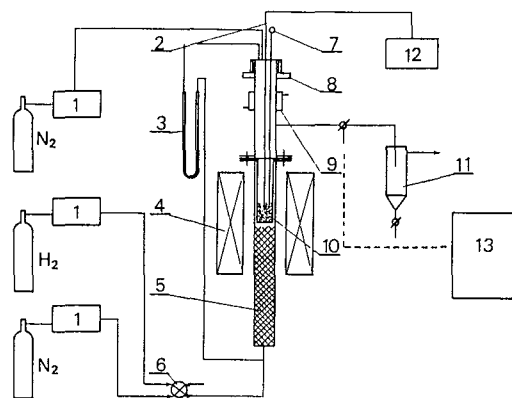


Fig. 4
Schematic diagram of the experimental apparatus for studying the reduction kinetics of ilmenite in a fluidized bed

- | | |
|-------------------------|----------------------|
| 1. Mass flow meter, | 2. Thermocouple, |
| 3. Manometer, | 4. Electric furnace, |
| 5. Alumina ball bed, | 6. 4-way cock, |
| 7. Solid sampler, | 8. O-ring, |
| 9. Water cooling parts, | 10. Fluidized bed, |
| 11. Dust catcher, | 12. Recorder |

審査結果の要旨

イルメナイトから金属チタン、あるいは、 TiO_2 を製造する場合、第一のプロセスとしてイルメナイトの高品位化が重要である。本研究においては、天然イルメナイトから作成した非焼成ペレットならびに試薬から作成した合成イルメナイトの酸化還元反応の速度論的研究を行い、反応メカニズムの解明ならびに速度パラメータの測定を行うとともに、流動層による天然イルメナイト粉末の還元挙動を検討した結果をまとめたものであり、全編7章からなっている。

第1章は緒論であり、従来の研究を概括し、本研究の目的を述べている。

第2章では、天然イルメナイトから作成した非焼成ペレットの9.8mol% O_2 - N_2 系ガスによる酸化反応を未反応核モデルにより解析し、粒子内拡散と化学反応の混合律速になることを示すとともに、速度パラメータの値を求めている。

第3章では、天然イルメナイトから作成した非焼成ペレットの純酸素による酸化反応の速度および粒子内部の温度変化を測定し、熱移動と物質移動を考慮した非等温未反応核モデルで解析した。その結果、この酸化反応は主として酸素の粒子内拡散により支配されており、また、温度分布が生じる原因は反応完結層の低有効熱伝導率によることを示した。

第4章では、予備酸化した天然イルメナイトの水素による還元反応速度の測定ならびに2段反応モデルによる解析を行い、この反応が主として粒子内拡散と化学反応の混合律速であることを示し、その速度パラメータの値を求めている。また、イルメナイトペレットの予備酸化は還元反応速度を増大させるのに有効であることを示しているが、これは工業的な利用のため重要である。

第5章においては、純粋なイルメナイトの反応特性を検討するため、試薬からイルメナイトを合成し、その酸化還元実験を行った。測定結果を未反応核モデルで解析し、速度パラメータの値を求めているが、天然イルメナイトの場合と近い値を示した。鉍物組織を顕微鏡で観察すると酸化後はTi濃度の高い相とFe濃度の高い相が存在し、均一相にならないことを示している。

第6章では、イルメナイトの高品位化の工業的プロセスを検討するため、粉末イルメナイトの流動層による還元実験を行っている。この場合、還元反応は均一反応となり、均一反応モデルを組み入れた二相モデルにより還元挙動を解析している。

第7章は結論である。

以上要するに本論文は、イルメナイトの酸化還元反応のメカニズムと速度を天然および合成イルメナイトについて求めるとともに、工業的応用を考慮したイルメナイト粉末の流動還元プロセスを反応工学的に解析したもので、イルメナイトの高品位化のために有益な知見を得ており、金属工学の発展に寄与することが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。