Oxidation kinetics of a low-grade vanadiferous titanomagnetite concentrate with high titanium

Jinsheng Liu¹², Gongjin Cheng¹², Jianxing Liu¹², Hongrui Yue¹², Xueyong Ding¹, Xiangxin Xue¹²,*

¹ School of Metallurgy, Northeastern University, Shenyang 110819, China
² Liaoning Key Laboratory of Recycling Science for Metallurgical Resources, Shenyang 110819, China
* Corresponding author’s e-mail: xuexx@mail.neu.edu.cn

Abstract: In order to better develop and utilize the low-grade vanadiferous titanomagnetite concentrate with high titanium (LVCHT) and provide reference for the treatment of similar minerals. Oxidation process and kinetics of the LVCHT were investigated in this study. The results show that LVCHT presents weight loss at temperatures less than 600 °C, which is attributed to the removal of moisture and volatile components. Above 600 °C, the weight gain of LVCHT is due to the persistence of oxidative behavior, and the oxidation process is most likely controlled by external diffusion, and the associated activation energies (Ea) and the value of k₀ are 29.89 kJ/mol and 0.64, respectively.

1. Introduction
Vanadiferous titanomagnetite is a polynmetallic symbiotic ore with mainly iron, titanium and vanadium, accompanied by a variety of valuable elements (chromium, cobalt, nickel, copper, scandium, gallium and platinum, etc.), rich reserves and wide distribution [1-4]. Recently, a large amount of low-grade vanadiferous titanomagnetite has been discovered in northwest Liaoning, China [5]. However, its special ore phase composition and physical and chemical properties prevent it from being effectively utilized. The technologies used to process vanadiferous titanomagnetite are blast furnace - converter steelmaking, direct reduction - electric furnace melting and direct reduction - magnetic separation [6-9]. Moreover, several researches have shown that pre-oxidation can significantly improve the utilization efficiency of low-grade vanadiferous titanomagnetite ore when processing it [10-12]. Therefore, in order to improve the utilization efficiency of low-grade vanadiferous titanomagnetite concentrate with high titanium (LVCHT) as much as possible, this paper investigates its oxidation process and oxidation kinetics to provide reference for the treatment of similar minerals.

2. Experimental
2.1. Raw Material
The LVCHT samples used in this research were obtained from a mineral processing enterprise in Northwest area of Liaoning Province, China. The LVCHT is black and the main chemical composition of LVCHT is presented in Table 1, which shows that the LVCHT sample has a total iron (TFe) mass fraction of 43.34 %, TiO₂ of 17.60 %, and a small amount of CaO, SiO₂, MgO and Al₂O₃. Compared with the vanadiferous titanomagnetite concentrate produced in other regions in China, the content of...
TiO₂ in the LVCHT is higher, but the grade of TFe is obviously lower [13]. The XRD patterns of LVCHT are shown in Figure 1. It can be seen that the LVCHT is mainly composed of titanomagnetite, ilmenite, titanite etc. The content of titanium magnetite is close to 64 %, but it contains a large amount of Ti elements, which is the main reason for the low TFe and low recovery efficiency.

| TFe  | TiO₂ | SiO₂ | Al₂O₃ | CaO | MnO | MgO | K₂O | Na₂O |
|------|------|------|-------|-----|-----|-----|-----|-----|
| 43.34 | 17.60 | 10.98 | 2.61  | 5.06 | 0.66 | 0.87 | 0.05 | 0.04 |

Figure 1. XRD patterns of the LVCHT

2.2. Procedure and Methods
In this study, oxidation process and kinetics of the LVCHT were studied using a thermogravimetric analyzer (HCT-4, Henven Experimental Equipment Co., Beijing, China). Every time, about 50 mg LVCHT sample was picked and oxidized at a predetermined temperature for a certain time, both the heating and holding temperature roasting process were carried out under pure air flow (200 ml/min). During the whole process, the temperature and weight data of the LVCHT samples were monitored by a high-precision electronic balance and thermocouple, and received and stored by the computer finally.

3. Results and Discussion
3.1. Thermal analysis of oxidation program
Figure 2 shows the TG-DTA plots of oxidation process of LVCHT at different temperatures. It can be seen that the LVCHT presents weight loss at temperatures less than 600 °C, with specific weight loss points of 105.78 °C, 228.35 °C, 353.69 °C and 543.56 °C, respectively. Which is mainly attributed to the removal of moisture and volatile components. Combined with the DTA curve, a peak of heat absorption occurs at 108.53 °C, also indicating the beginning of moisture loss. 355.73 °C and 551.87 °C present exothermic peak, which indicates that the oxidation reaction has occurred, but the removal of moisture still dominates, thus exhibiting the weight loss phenomenon. Above 600 °C, the weight gain is due to the persistence of oxidative behavior, main chemical reactions that occur are following Eqs. (1) – (3). Finally, after raising the temperature to 1000 °C, LVCHT increased its mass by a total of 5.6 %.

\[
4Fe_{2.75}Ti_{0.25}O_4(s) + O_2(g) = FeTiO_3(s) + 5Fe_2O_3(s) \tag{1}
\]
\[
4FeTiO_3(s) + 3O_2(g) = 2Fe_2O_3(s) + 4TiO_2(s) \tag{2}
\]
\[
4FeTiO_3(s) + 2Fe_2O_3(s) + O_2(g) = 4Fe_5TiO_4(s) \tag{3}
\]
3.2. Oxidation degree
The oxidation degree ($\alpha$) was calculated using the following formula:

$$\alpha = \frac{m_t - m_i}{m_0} \times 100\% \quad (4)$$

where $m_t$ denotes the mass of LVCHT after an oxidation time, mg; $m_i$ denotes the initial mass of the LVCHT, mg; and $m_0$ denotes the total mass of the gained oxygen after complete oxidation, mg.

The effect of temperature on the oxidation degree was investigated, and the results are shown in Figure 3. It can be seen that increasing the temperature can significantly improve the oxidation degree of LVCHT, and after 120 min roasting, the oxidation degree at 1000 °C is 16.92 % higher than that at 700 °C, which is almost completely oxidized. In addition, higher temperature also enables LVCHT to reach a high plateau of oxidation degree earlier.

3.3. Oxidation kinetics
The gas-solid reaction such as oxidation and reduction can be treated with an unreacted shrink nucleus model. The main control steps of the reaction are external diffusion, internal diffusion and chemical reaction. The reaction kinetics equations of different control steps are given in Table 2. According to the kinetic equation of $F_1(\alpha)$, $F_2(\alpha)$ and $F_3(\alpha)$, the relationship between kinetic equations and oxidation time was fitted in Figure 4, and model fitting parameters has been shown in Table 3.

For kinetic equation of LVCHT oxidation, the better the linear relationship between calculated $-\ln(1 - \alpha)$ and $t$, the closer the kinetic model is to the actual situation. Which indicates that the oxidation process of LVCHT is most likely controlled by external diffusion.
Table 2. Kinetic equations of oxidation program

| Name | Control step       | Kinetic equation | NO. |
|------|--------------------|------------------|-----|
| $F_1(\alpha)$ | External diffusion | $-\ln(1 - \alpha) = kt$ | (5) |
| $F_2(\alpha)$ | Internal diffusion | $[1 - (1 - \alpha)^{1/3}]^2 = kt$ | (6) |
| $F_3(\alpha)$ | Chemical reaction  | $1 - (1 - \alpha)^{1/3} = kt$ | (7) |

Figure 4. Relationship between kinetic equations and oxidation time

Table 3. Oxidation process dynamics model fitting parameters

| Model | Temperature/℃ | $k$    | $R^2$ |
|-------|----------------|--------|-------|
| $F_1(\alpha)$ | 700             | 0.01714 | 0.9821 |
|        | 800             | 0.02119 | 0.9832 |
|        | 900             | 0.02663 | 0.9875 |
|        | 1000            | 0.04262 | 0.9892 |
| $F_2(\alpha)$ | 700             | 0.00180 | 0.9797 |
|        | 800             | 0.00244 | 0.9849 |
|        | 900             | 0.00334 | 0.9924 |
|        | 1000            | 0.00569 | 0.9862 |
| $F_3(\alpha)$ | 700             | 0.00445 | 0.9761 |
|        | 800             | 0.00519 | 0.9733 |
|        | 900             | 0.00609 | 0.9714 |
|        | 1000            | 0.00798 | 0.9594 |

3.4. Activation energy calculation

After obtaining the rate constant $k$ at each temperature, the activation energy $E_a$ of the oxidation process of LVCHT can be easily estimated according to the following Arrhenius equation:

$$\ln k = \ln k_0 - \frac{E_a}{RT}$$  \hspace{1cm} (8)

where $E_a$ represents the activation energy (kJ/mol), $k_0$ represents the prefactor, $R$ represents the molar constant of gas (8.314 J·mol$^{-1}$·K$^{-1}$), $T$ represents the oxidation temperature (K).

The results of the fitting calculations for relationship between function $\ln k$ and $T^{-1}$ are shown in Figure 5 and Table 4. Therefore, when external diffusion, internal diffusion and chemical reaction are the controlling steps of the LVCHT oxidation process, the associated activation energies ($E_a$) are 29.89 kJ/mol, 38.20 kJ/mol and 19.39 kJ/mol, and the values of $k_0$ are 0.64, 0.19 and 0.05, respectively.
Figure 5. Relationship between function $\ln k$ and $T^{-1}$

Table 4. Activation energy result calculated by Arrhenius equation

| Parameters | $F_1(\alpha)$ | $F_2(\alpha)$ | $F_3(\alpha)$ |
|------------|----------------|----------------|----------------|
| $Ea/(kJ/mol)$ | 29.89 | 38.20 | 19.39 |
| $k_0$ | 0.64 | 0.19 | 0.05 |

4. Conclusion

Oxidation process and kinetics of the LVCHT were investigated in this study. The results show that LVCHT presents weight loss at temperatures less than 600 °C, which is attributed to the removal of moisture and volatile components. Above 600 °C, the weight gain of LVCHT is due to the persistence of oxidative behavior, and the oxidation process is most likely controlled by external diffusion. When external diffusion, internal diffusion and chemical reaction are the controlling steps of the LVCHT oxidation process, the associated activation energies ($Ea$) are 29.89 kJ/mol, 38.20 kJ/mol and 19.39 kJ/mol, respectively.

Acknowledgments

This project is supported by the National Natural Science Foundation of China (grant nos.51674084, 21908020 and U1908226) and the National Key R&D Program of China (No. 2017YFB0603801).

References

[1] W. Li, G.Q. Fu, M. Chu, M.Y. Zhu, Influence of V$_2$O$_5$ Content on the Gas-Based Direct Reduction of Hongge Vanadium Titanomagnetite Pellets with Simulated Shaft Furnace Gases, Jom, 70 (2018): 76-80.
[2] S.W. Prabowo, R.J. Longbottom, B.J. Monaghan, D. Del Puerto, M.J. Ryan, C.W. Bumby, Sticking-Free Reduction of Titanomagnetite Ironsand in a Fluidized Bed Reactor, Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science, 50 (2019): 1729-1744.
[3] W. Li, N. Wang, G.Q. Fu, M.S. Chu, M.Y. Zhu, Influence of TiO$_2$ addition on the oxidation induration and reduction behavior of Hongge vanadium titanomagnetite pellets with simulated shaft furnace gases, Powder Technology, 326 (2018): 1729-1744.
[4] M. Gan, Y.F. Sun, X.H. Fan, Z.Y. Ji, W. Lv, X.L. Chen, T. Jiang, Preparing high-quality vanadium titanomagnetite pellets for large-scale blast furnaces as ironmaking burden, Ironmaking & Steelmaking, 47 (2020): 130-137.
[5] C.B. Xu, Y.M. Zhang, T. Liu, J. Huang, Characterization and Pre-Concentration of Low-Grade Vanadium-Titanium Magnetite Ore, Minerals, 7 (2017):137-147.
[6] Y.L. Sui, Y.F. Guo, T. Jiang, G.Z. Qiu, Reduction kinetics of oxidized vanadium titanomagnetite
pellets using carbon monoxide and hydrogen, Journal of Alloys and Compounds, 706 (2017): 546-553.

[7] H.L. Song, J.P. Zhang, X.X. Xue, Kinetics on Chromium-Bearing Vanadia-Titania Magnetite Smelting with High-Basicity Pellet, Processes, 9 (2021):811-824.

[8] G.J. Cheng, X.X. Xue, T. Jiang, P.N. Duan, Effect of TiO₂ on the Crushing Strength and Smelting Mechanism of High-Chromium Vanadium-Titanium Magnetite Pellets, Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science, 47 (2016): 1713-1726.

[9] W. Li, G.Q. Fu, M.S. Chu, M.Y. Zhu, An effective and cleaner process to recovery iron, titanium, vanadium, and chromium from Hongge vanadium titanomagnetite with hydrogen-rich gases, Ironmaking & Steelmaking, 48 (2021): 33-39.

[10] X.B. Li, T. Wu, Q.S. Zhou, T.G. Qi, Z.H. Peng, G.H. Liu, Kinetics of oxidation roasting of molybdenite with different particle sizes, Transactions of Nonferrous Metals Society of China, 31 (2021): 842-852.

[11] F. Pan, Q.S. Zhu, Z. Du, H.Y. Sun, Oxidation Kinetics, Structural Changes and Element Migration during Oxidation Process of Vanadium-titanium Magnetite Ore, Journal of Iron and Steel Research International, 23 (2016): 1160-1167.

[12] W. Li, G.Q. Fu, M.S. Chu, M.Y. Zhu, Investigation of the oxidation induration mechanism of Hongge vanadium titanomagnetite pellets with different Al₂O₃ additions, Powder Technology, 360 (2020): 555-561.

[13] W. Lv, X.W. Lv, Y.Y. Zhang, S.P Li, K. Tang, B. Song, Isothermal oxidation kinetics of ilmenite concentrate powder from Panzhihua in air, Powder Technology, 320 (2017): 239-248.