

PROCESSING OF TiO₂ FROM TITANIUM-BEARING BLAST FURNACE SLAG AS TITANIUM SOURCE

Received – Priljeno: 2015-10-14

Accepted – Prihvaćeno: 2016-02-18

Preliminary Note – Prethodno priopćenje

The titanium dioxide (TiO₂) was prepared by efficient decomposition of titanium-bearing blast furnace slag (TBBFS) in molten salt system. The as-prepared TiO₂ were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Almost complete leaching of Ti was achieved when TBBFS was carried out at 500 °C for about 3 h with NaOH/TBBFS mass ratio of 3:1 and NaOH to NaF molar ratio of 3:1. The XRD pattern showed that the containing titanium product obtained under optimal conditions was Na₂TiO₃. The average size of the rutile TiO₂ obtained was about 1.0 μm and the content was up to 99,23 %.

Key words: metallurgy, blast furnace, slag, TiO₂, leaching

INTRODUCTION

TiO₂ has attracted much attention because of its superior chemical and physical properties, and potential applications in gas sensing, photo-catalysis, and lithium-ion batteries [1-4]. There are one of the largest vanadium-titanium magnetite ore deposited in the Panzhihua region of China [5]. At present, approximately 53 % of the Ti is concentrated into the titanium-bearing blast furnace slag (TBBFS) by iron blast furnaces process, in which the concentration of TiO₂ is 19 % – 22 %.

Because of the dispersed distributions of Ti in various mineral phases, such as titanite, perovskite and Ti-rich diopside, TBBFS is one of the most difficult slags to be treated. For example, Sui et al [6] enriched the Ti components in the perovskite phase and TiO₂ content in the slag can be enhanced to 35 wt. % – 45 wt. %. Zhang et al [7] obtained rutile crystal TiO₂ by high-temperature modification and the mass fraction of Ti in rutile phase was about 64 wt. %. Xiong et al [8] leached Ti from TBBFS by sulfuric acid method and the leaching efficiency was about 74 %.

In this paper, the purpose of the present investigation is to prepare TiO₂ by efficient decomposition of TBBFS in molten salt system. Moreover, the phase identification and transformation in the molten salt process are investigated.

EXPERIMENTAL

TBBFS from Panzhihua Iron and Steel Corporation was used in this study. The composition of TBBFS was

listed in Table 1. The reagents used in the experiments were all of analytical grade, and de-ionized water was used in all the experiments.

Table 1 **The Composition of TBBFS / wt. %**

CaO	SiO ₂	TiO ₂	Al ₂ O ₃
24,92	27,74	19,23	13,64
MgO	ΣFe	Others	
8,04	4,78	1,65	

In all the roasting experiments, the TBBFS of 10, 0 g was thoroughly mixed with different amounts of NaOH and NaF in the crucible. Each crucible was roasted at a specified temperature for specified time in a muffle furnace. To determine TiO₂ leaching efficiency, the roasted sample was dissolved by 5 wt. % HCl (the release of Ti from TBBFS was negligible in HCl) [9]. After the complete dissolution of the sample, unreacted residues were separated from the solution by filtration because it could not be dissolved in the diluted HCl solution. The concentration of titanium in the filtrate can be analyzed by ICP-OES for the measurement of Ti leaching efficiency.

In all the experiments, except otherwise stated, element analysis was performed by ICP-OES (Optimal 5300DV, Perkin-Elmer, USA). X-ray diffraction (XRD) patterns were carried out with Cu Kα radiation (λ = 0,15406 μm) (X'Pert PRO MPD, PANalytical, Netherland) at 40 kV and 30 mA. The particle morphologies were observed by a scanning electron microscope (SEM) using JEOL JSM 6300 microscope, at an acceleration voltage of 25 kV.

RESULTS AND DISCUSSION

The effect of temperature on the Ti leaching efficiency was carried out in the temperature range of 400

X. Li, H.H. Yu, Z. H. Fang, Z. G. Yuan, School of Material Science and Engineering, Shenyang Ligong University, Shenyang, China;
X. X. Xue, School of Material and Metallurgy, Northeastern University, Shenyang, China

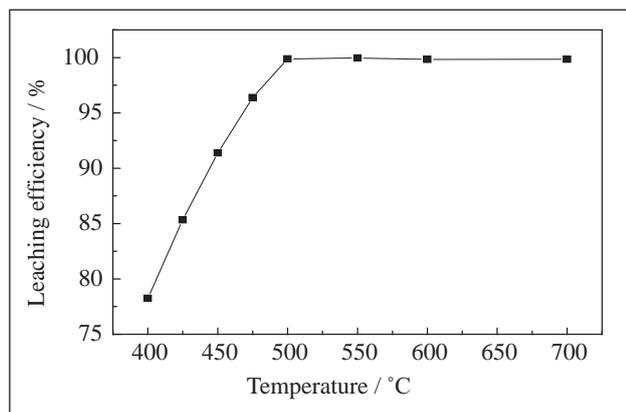


Figure 1 Effect of temperature on titanium leaching efficiency

– 700 °C. The results in Figure 1 indicate that the temperature has significant influence on the Ti leaching efficiency. The Ti leaching efficiency increases with the increase of reaction temperature, especially in the initial stage of reaction, showing clear temperature dependence. Almost complete extraction of Ti was achieved when the roasted temperature was more than 500 °C.

In addition, Figure 2 shows that Ca(OH)₂ is formed during 400 – 450 °C, CaO is identified and CaTiO₃ is disappeared during 500 – 600 °C. Meanwhile, only Na₂TiO₃ phase is identified. However, according to the phase diagram in the Na₂O – TiO₂ system [10], both Na₂TiO₃ and Na₄TiO₄ should be formed in the temperature range of 400 – 600 °C. A hypothesis for this discrepancy might be that the Ti-O bonds in CaTiO₃ are so strong that they could not be disrupted under the roasting conditions. Hence, only ion-exchange process takes place between Ca²⁺ and Na⁺, while the structure of TiO₃²⁻ remains stable.

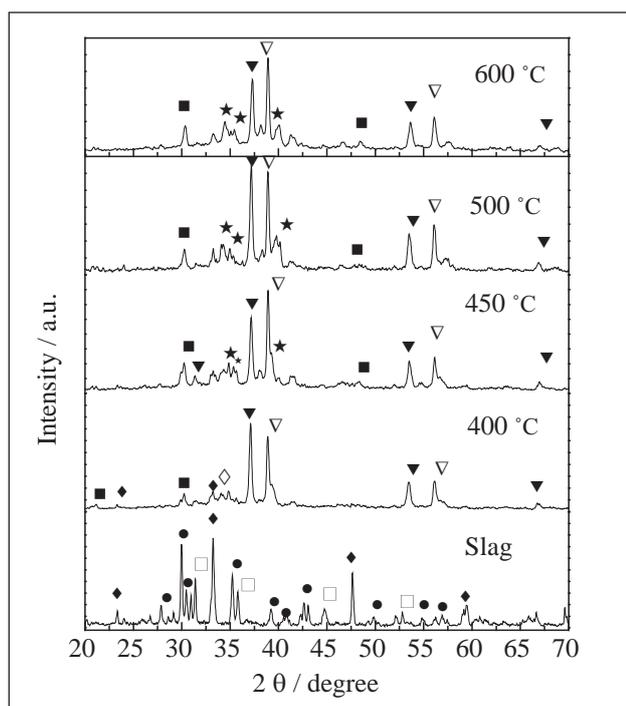


Figure 2 XRD patterns of roasted samples at various temperature (♦: CaTiO₃, ●: diopside, □: spinel, ▽: NaF, ★: Na₂TiO₃, ▼: CaO, ■: Na₂SiO₃, ◇: Ca(OH)₂)

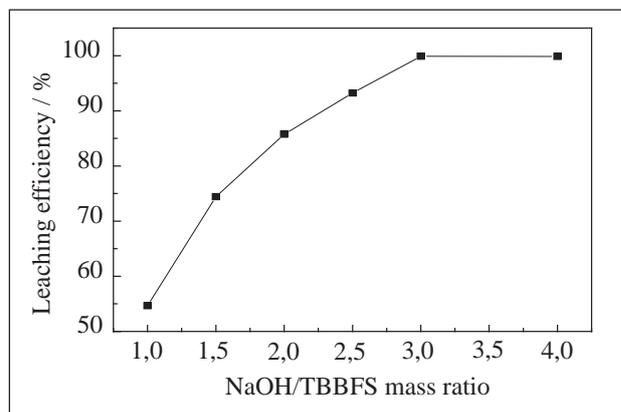
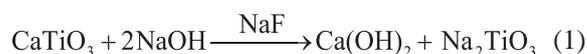
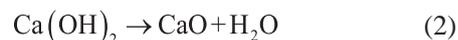


Figure 3 Effect of NaOH/TBBFS mass ratio on titanium leaching efficiency

Thus, it is believed that the decomposition of CaTiO₃ under the roasting conditions can be represented by the following equations:



The product Ca(OH)₂ is further decomposed:



In Figure 3, NaOH/TBBFS mass ratios ranging from 1:1 to 4:1 were adopted to investigate titanium leaching efficiency at 500 °C. The results show that the titanium leaching efficiency is improved with the increase of NaOH/TBBFS mass ratio until reaching a plateau of 99,8 % at 3:1. NaOH is the main reactants and the increase of its quantity favors the TBBFS reaction thermodynamically and accelerates the slag decomposition process. NaOH also acts as a fluidizing and fluxing agent in the reaction mixtures. The increase of NaOH decreases the solution viscosity and facilitates the diffusion of reactants during the reaction. Excess of NaOH is necessary to maintain the liquidity of the reactants and ensure sufficient reactions while the extra NaOH could not significantly affect the economy of the whole process because of the recycling procedure in the overall process.

To study the effect of NaF addition, the sample was roasting at 500 °C with and without NaF. XRD patterns

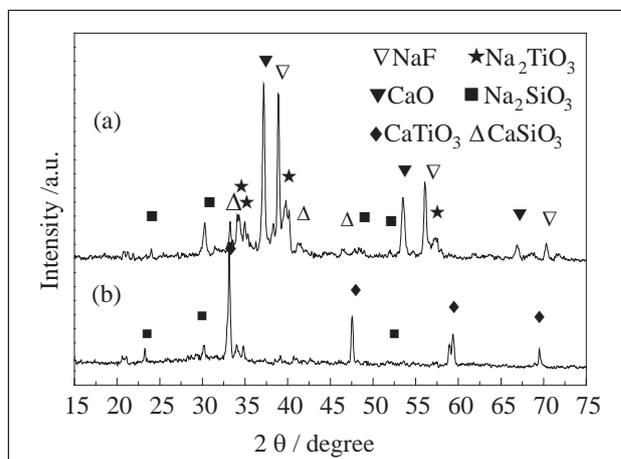


Figure 4 XRD patterns of samples with various addition conditions a: with NaF, b: Without NaF

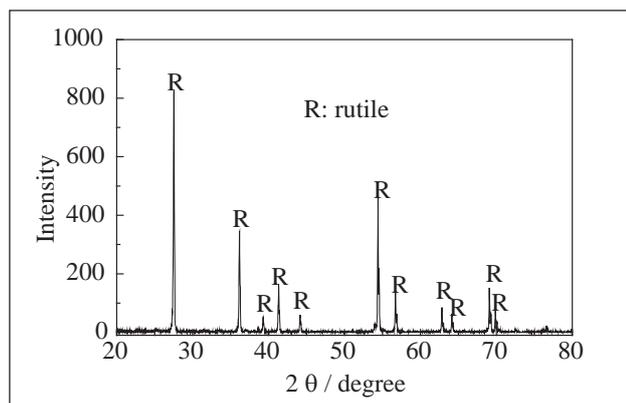


Figure 5 XRD pattern of TiO₂

show that CaTiO₃ are not be disrupted under the roasting conditions (Figure 4(b)) and the Ti leaching efficiency in the condition is only 72,4 %. A hypothesis for this discrepancy may be that the Ti - O bonds in CaTiO₃ are so strong that they could not be disrupted under the roasting conditions. However, in the Figure 4(a), Na₂TiO₃, CaO and NaF are identified and the Ti leaching efficiency in the condition is 99,8 %. It is interesting to note that no fluorine- containing salt is identified. Thus, it is inferred that NaF do not involve in reaction with TBBFS, and it acts as a fluidizing and fluxing agent in the reaction mixtures.

The phase transformation was carried out by refluxing the sodium titanate in H₂SO₄ solutions (pH = 0,3) at 105 °C for 5 h. The hydrous titanium dioxide obtained was calcined at 450 °C and the corresponding XRD pattern and SEM image were shown in Figure 5 and 6, respectively. The XRD pattern in Figure 5 indicates the well crystallized rutile phase is obtained. The SEM image in Figure 6 shows that the average size of powder is about 1,0 μm. The chemical composition of product is TiO₂ 99,23 %, ΣFe 0,068 %, MnO 0,032 %, Al₂O₃ 0,059 % and SiO₂ 0,064 %. It could be used as pigment after further treatment.

CONCLUSIONS

The experimental results on the decomposition of TBBFS in NaOH-NaF system indicate that the temperature and NaOH/TBBFS mass ratio have significant influence on the titanium leaching efficiency. Almost complete extraction of titanium is achieved in the optimal conditions of temperature 500 °C, NaOH/TBBFS mass ratio 3:1, NaOH/NaF molar ratio 3:1. At these optimal conditions, the containing titanium product is Na₂TiO₃ which could be dissolved in dilute HCl solution. The average size of TiO₂ obtained is about 1,0 μm, the phase is rutile, and the content is up to 99,23 %.

Acknowledgements

Financial support for this work by the National Natural Science Foundation of China (No.U1360204 and

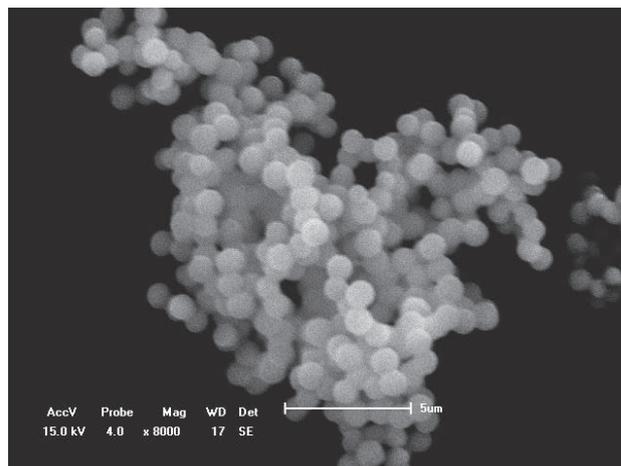


Figure 6 SEM image of TiO₂

No.50234040), Liaoning Province Education Administration Foundation (L2013089) and Open Foundation of Shenyang Ligong University Key Laboratory .

REFERENCES

- [1] B. Wang, H. Xin, X. D. Li, J. Cheng, G. Yang, F. Nie, Mesoporous CNT@TiO₂-C nanocable with extremely durable high rate capability for Lithium-ion battery anodes, *Scientific Reports* 4 (2014), 1-6.
- [2] C. Y. Cho, J. H. Moon, Hierarchically porous TiO₂ electrodes fabricated by dual templating methods for dye-sensitized solar cells, *Advanced Materials* 23 (2011), 2971 - 2975.
- [3] Z. Chen, I. Belharouak, Y. K. Sun, K. Amine, Titanium-based anode materials for safe lithium-ion batteries, *Advanced Functional Materials* 23 (2013), 959 - 969.
- [4] C. Jiang, J. Zhang, Nanoengineering titania for high rate lithium storage: a review, *Journal of Materials Science and Technology* 29 (2013), 97-122.
- [5] X. Lei, X. X. Xue, H. Yang, Preparation of UV-visible light responsive photocatalyst from titania-bearing blast furnace slag modified with (NH₄)₂SO₄, *Transactions of Nonferrous Metals Society of China* 22 (2012), 1771- 1777.
- [6] M. Wang, L. Li, L. Zhang , L. N. Zhang, G. Tu, Z. Sui, Effect of oxidation on enrichment behavior of TiO₂ in titanium-bearing slag, *Rare Metals* 2 (2006), 106- 110.
- [7] W. Zhang, L. Zhang, J. Zhang, N. Feng, Crystallization and coarsening kinetics of rutile phase in modified Ti-bearing blast furnace slag, *Industrial and Engineering Chemistry Research* 51 (2012), 12294- 12298.
- [8] Y. Xiong, C. Li, B. Liang, J. Xie, Leaching behavior of air cooled Ti-bearing blast- furnace slag in hydrochloric acid, *the Chinese Journal of Nonferrous Metals* 18 (2008)3, 557-563.
- [9] C. Sasikumar, D. S. Rao, S. Srikanth. Dissolution studies of mechanically activated Manavalakurichi ilmenite with HCl and H₂SO₄, *Hydrometallurgy* 8(2007), 154-169.
- [10] R. S. Roth, T. Negas, L. P. Cook, *Phase Diagrams for Ceramists*, The American Ceramic Society, Ohio, 1981, pp. 88.

Note: The responsible translator for English language is K. Bei, Hangzhou Qihang translation Co.LTD, China