

## Preparation of Ti-rich material from titanium slag by activation roasting followed by acid leaching

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**Abstract:** A method of activation roasting followed by acid leaching using titanium slag was introduced to prepare Ti-rich material. The effects of  $H_3PO_4$  dosage, roasting temperature, and roasting time on  $TiO_2$  grade were investigated. A Ti-rich material containing 88.54%  $TiO_2$ , 0.42% (CaO+MgO) was obtained when finely ground titanium slag was roasted with 7.5%  $H_3PO_4$  at 1000 °C for 2 h, followed by a two-stage leaching in boiling dilute sulfuric acid for 2 h. The XRD patterns show that the product is titanium dioxide with a rutile structure. Mechanism studies show that structures of anosovite solid solution and silicate minerals are destroyed in the roasting process. As a result, titanium components in titanium slag are transformed into  $TiO_2$  (rutile) while impurities are transformed into acid-soluble phosphate and quartz.

**Key words:** titanium slag; activation roasting; acid leaching; Ti-rich material; rutile

### 1 Introduction

Titanium dioxide is the best quality inorganic pigment. Because of its whiteness, high refractive index and light-scattering ability,  $TiO_2$  has become the predominant white pigment for paints, paper, plastics, etc [1,2].  $TiO_2$  pigment can be manufactured by either the older sulfate or the newer chloride processes [2,3]. The sulfate process is the first commercial technology used to convert ilmenite or titanium slag to titanium dioxide. In this process, ilmenite and titanium slag are leached with sulfuric acid, and large quantities of waste and toxic by-products are produced, resulting in serious environmental problems [4,5]. In the chloride process, titanium dioxide pigment is produced from rutile, titanium slag and some  $TiO_2$ -rich sand ilmenite, via a  $TiCl_4$  stage at high temperatures [6]. Due to the advantages of the chloride process such as the yield of high-quality product, environmentally friendly and the smaller amount of waste product, the chloride process is more favorable for the  $TiO_2$  pigment production. However, the chloride process has higher requirement for the qualification of the feedstock, in which the contents of Ca and Mg have to be low [7,8].

Ilmenite resources are rich in Panzhihua, accounting

for 90.54% of total ilmenite reserves in China [9]. The titanium slag produced by electric smelting of Panzhihua ilmenite concentrate has high contents of Ca and Mg; thus, it is unsuitable for chloride. For upgrading titanium slag, several methods have been studied, which are primarily focused on the destruction of its refractory nature [10–12]. The treatments of titanium slag mainly included oxidation roasting, oxidation-reduction roasting, sulphidization, chlorination and salt roasting, in which impurities were subsequently removed by water or diluted hydrochloric acid leaching [13–15]. Canada QIT Company has successfully produced high-quality titanium-rich material from titanium slag, and achieved commercial production, but the kernel technology is unknown to the outside. Many other processes, however, demand oxidation and reduction at a high-temperature pretreatment. Furthermore, in the acid leaching, they require high temperature and high pressure. High-energy consumption, environmental pollution and high requirements for equipment limit the industrial application of those processes.

In the present work, a titanium slag manufactured by smelting ilmenite in electric arc furnace was provided by Panzhihua Iron & Steel Company, China. A process was proposed to upgrade titanium slag. Impurities in titanium slag such as Ca and Mg are effectively removed.

The product obtained is suitable as a raw material for chloride.

## 2 Experimental

### 2.1 Material

The main chemical compositions of the titanium slag are shown in Table 1. All chemicals and reagents used in this study are of analytical grade.

**Table 1** Chemical compositions of titanium slag (mass fraction, %)

TiO <sub>2</sub>	TFe	SiO <sub>2</sub>	MgO	CaO
72.42	7.02	5.37	8.21	1.36
Al <sub>2</sub> O <sub>3</sub>	MnO	P	S	Ig
2.65	0.74	0.0035	0.045	0.10

### 2.2 Method

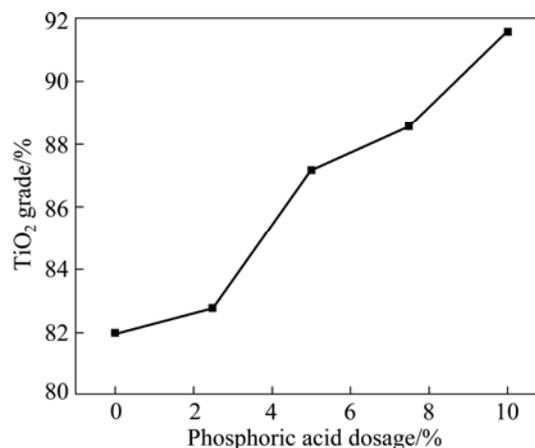
The slag samples were finely ground to size less than 74 μm, and mixed with phosphoric acid to pelletize. The pellets were then dried in an oven at 110 °C for 24 h and roasted at various temperatures in a tube furnace (*d*60 mm) with free-access air. After a period of time, the roasted samples were drawn out of the reactor and allowed to cool down to the room temperature. The roasted samples were then ground to size less than 74 μm. Specified amount of preheated sulfuric acid of known concentration, as well as the roasted samples, was loaded into the glass reactor for a two-stage leaching, 2 h with 25% H<sub>2</sub>SO<sub>4</sub> for the first stage leaching, 2 h with 40% H<sub>2</sub>SO<sub>4</sub> for the second leaching. The stirring speed was maintained at 500 r/min by a digital controlled stirrer. At the end of the runs, the slurry was filtered under vacuum. The leached residues were washed with water and then calcined at 900 °C for 30 min. The final product was analyzed chemically; the crystal structures of the titanium slag and the treated samples were characterized by X-ray diffraction (Cu K<sub>α</sub> radiation, λ=1.54056 Å, D/Max2200, Rigaku, Japan).

## 3 Results and discussion

### 3.1 Effects of phosphoric acid dosage

To study the effects of phosphoric acid dosage on TiO<sub>2</sub> grade, several experiments were conducted. Parameters were kept constant during tests, as 1000 °C and 2 h roasting. Figure 1 indicates that the phosphoric acid dosage has a significant influence on the TiO<sub>2</sub> grade, which is increased rapidly as the phosphoric acid dosage increases from 0 to 10%. As the phosphoric acid content increases to 10%, the TiO<sub>2</sub> grade reaches 91.57%. It can be explained that roasting with phosphoric acid damages the stable structure of anosovite in titanium slag.

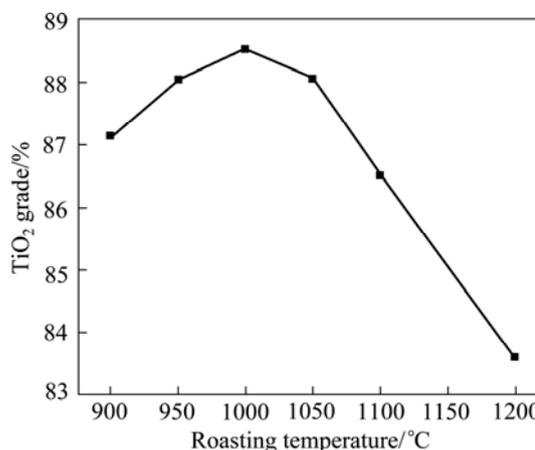
Impurities, which are dissolved in anosovite, are more likely to be leached with acid.



**Fig. 1** Effect of phosphoric acid dosage on TiO<sub>2</sub> grade

### 3.2 Effects of roasting temperature

The effects of roasting temperature on the TiO<sub>2</sub> grade were studied in the temperature range of 900–1200 °C. Parameters were kept constant during the tests as 7.5% H<sub>3</sub>PO<sub>4</sub> and 2 h roasting. Figure 2 shows that the TiO<sub>2</sub> grade is improved with the roasting temperature increasing from 900 °C to 1000 °C; beyond 1000 °C, TiO<sub>2</sub> grade starts to decrease. Therefore, the roasting temperature of 1000 °C is recommended, at which the TiO<sub>2</sub> grade of 88.54% could be achieved.



**Fig. 2** Effect of roasting temperature on TiO<sub>2</sub> grade (7.5% H<sub>3</sub>PO<sub>4</sub>)

### 3.3 Effect of roasting time

To study the effect of roasting time on the TiO<sub>2</sub> grade, experiments were conducted with different roasting duration periods (1–2.5 h) whilst keeping the roasting temperature fixed at 1000 °C and 7.5% H<sub>3</sub>PO<sub>4</sub> added. Figure 3 shows that as the roasting time increases from 1 h to 2.5 h, TiO<sub>2</sub> grade increases inconspicuously and always stays at about 88%. The results indicate that roasting time has little effect on the experiment. In this

work, in order to make the titanium slag and phosphoric acid react completely, the roasting time is selected to be 2 h.

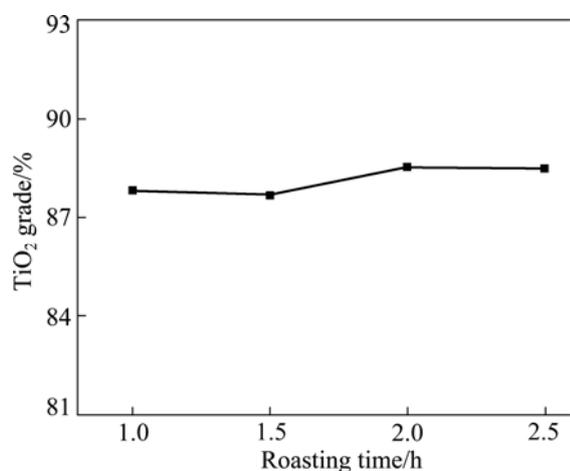


Fig. 3 Effect of roasting time on TiO<sub>2</sub> grade (7.5% H<sub>3</sub>PO<sub>4</sub>)

### 3.4 Final product

The main chemical compositions of the product prepared under the conditions of 7.5% H<sub>3</sub>PO<sub>4</sub> added, roasting at 1000 °C for 2 h are shown in Table 2. As shown in Table 2, the product contains 88.54% TiO<sub>2</sub>, and 0.42% (CaO+MgO). The XRD pattern in Fig. 4 shows that it is TiO<sub>2</sub> (rutile) and meets the requirements of the chloride process.

Table 2 Main chemical compositions of product (mass fraction, %)

TiO <sub>2</sub>	MgO	SiO <sub>2</sub>	TFe	MnO	Al <sub>2</sub> O <sub>3</sub>	CaO	S
88.54	0.31	7.73	2.15	0.13	0.64	0.11	0.02

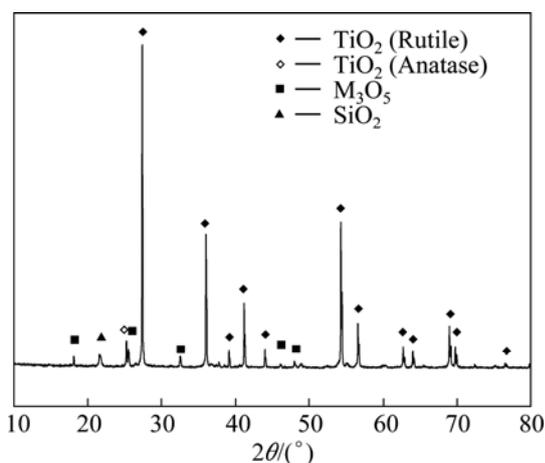


Fig. 4 XRD pattern of product

### 3.5 Mechanism analysis

For conversion to titanium slag, ilmenite was mixed with coal and subjected to a reduction smelting at 1500–1700 °C [16,17]. The main crystalline phase in

titanium slag is typically pseudobrookite. Pseudobrookite is a solid solution of FeTi<sub>2</sub>O<sub>5</sub>, MgTi<sub>2</sub>O<sub>5</sub> and MnTi<sub>2</sub>O<sub>5</sub> [18]. Its stoichiometric composition is M<sub>3</sub>O<sub>5</sub>, which is consistent with the compositional invariance [19]. The so-called M<sub>3</sub>O<sub>5</sub> is insoluble in HCl, NaOH, H<sub>3</sub>PO<sub>4</sub> and cold H<sub>2</sub>SO<sub>4</sub> solution. Therefore, it is difficult to upgrade titanium slag by direct acid leaching.

TiO<sub>2</sub> is a weak acidic oxide, and occurs as a complex anion  $Ti_nO_{3n+1}^{2(n+1)-}$  in titanium slag. P<sub>2</sub>O<sub>5</sub> is a strong acidic oxide. Due to the bonding force between PO<sub>4</sub><sup>3-</sup> and Mg<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Al<sup>3+</sup> in M<sub>3</sub>O<sub>5</sub> is greater than that of  $Ti_nO_{3n+1}^{2(n+1)-}$ , impurities are then released from anosovite in form of a phosphate glass phase [11]. In the present study, with the phosphoric acid added, under the conditions of high temperature and oxygen, the slag phase was changed as follows: 1) The Ti(III)-oxide in the slag was converted to Ti(IV)-oxide (rutile); 2) The Fe(II) oxide was converted to Fe(III) oxide; 3) Impurities reacted with phosphoric acid to generate phosphate; 4) Silicate minerals reacted with phosphoric acid to generate a new silicon material phase.

According to the analysis, after roasting with H<sub>3</sub>PO<sub>4</sub>, the stable structure of the anosovite was destroyed; resulting in the fact that impurities were released, while the new titanium phase (rutile) was insoluble in dilute sulfuric acid. Therefore, the impurities in titanium slag can be removed by acid leaching to obtain a Ti-rich material. To identify the mechanism of activation roasting, XRD analyses of titanium slag samples roasted with different H<sub>3</sub>PO<sub>4</sub> dosages at different temperatures were studied. The results are shown in Figs. 5 and 6.

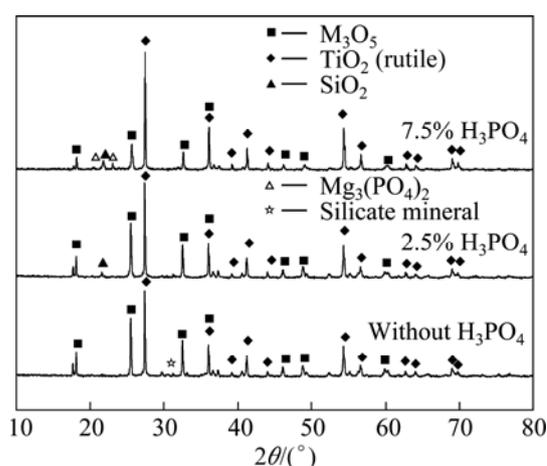
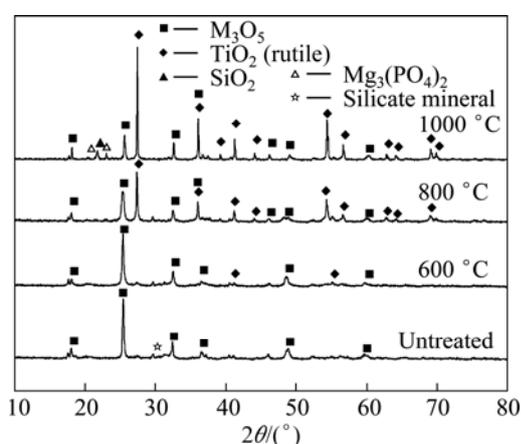


Fig. 5 XRD patterns of titanium slag roasting with different dosages of H<sub>3</sub>PO<sub>4</sub> (Roasting temperature 1000 °C, roasting time 2 h)

As shown in Fig. 5, the diffraction peak of the M<sub>3</sub>O<sub>5</sub> is weakened, the diffraction peak of TiO<sub>2</sub> (rutile) strengthens and silicate mineral disappears with the H<sub>3</sub>PO<sub>4</sub> increasing. TiO<sub>2</sub> (rutile), M<sub>3</sub>O<sub>5</sub> and silicate

mineral are the major phases recorded in the sample roasted without  $\text{H}_3\text{PO}_4$ . For the sample roasted with 7.5 %  $\text{H}_3\text{PO}_4$ , the major phases are  $\text{TiO}_2$  (rutile),  $\text{M}_3\text{O}_5$ ,  $\text{SiO}_2$  and  $\text{Mg}_3(\text{PO}_4)_2$ . The results indicate that titanium slag roasted with  $\text{H}_3\text{PO}_4$  promotes titanium phases changing to  $\text{TiO}_2$  (rutile), silicate mineral changing to  $\text{SiO}_2$ , and the solid solution structure of anosovite and silicate mineral is destroyed. Therefore, impurities in titanium slag could be removed by acid leaching. However, because of the gallertartig generated during  $\text{SiO}_2$  and leaching in the acid,  $\text{SiO}_2$  cannot be removed effectively [20]. The results well explain the high content of  $\text{SiO}_2$  in the final product.



**Fig. 6** XRD patterns of titanium slag roasted at different temperatures ( $\text{H}_3\text{PO}_4$  content 7.5%, roasting time 2 h)

The results in Fig. 6 show that the major phase of the sample changes little when it was roasted at 600 °C,  $\text{TiO}_2$  (rutile) appears and the diffraction peak of the  $\text{M}_3\text{O}_5$  weakens at 800 °C. As the temperature is raised to 1000 °C, two diffraction peaks of  $\text{Mg}_3(\text{PO}_4)_2$  and a diffraction peak of  $\text{SiO}_2$  appear at diffraction angles between 20° and 25°. The results indicate that upon heat treatment, the slag sample displays changes in phase structure, namely  $\text{M}_3\text{O}_5$  changes to  $\text{TiO}_2$  (rutile) and silicate mineral changes to  $\text{SiO}_2$ .

## 4 Conclusions

1) Ti-rich material containing 88.54%  $\text{TiO}_2$  and 0.42% ( $\text{CaO}+\text{MgO}$ ) was obtained under the conditions of roasting at 1000 °C for 2 h with 7.5%  $\text{H}_3\text{PO}_4$ , 2 h with 25%  $\text{H}_2\text{SO}_4$  for the first stage leaching, 2 h with 40%  $\text{H}_2\text{SO}_4$  for the second stage leaching. Ca and Mg in titanium slag are effectively removed by activation roasting followed by acid leaching.

2) Structures of anosovite solid solution and silicate minerals are destroyed in the roasting. As a result, titanium components in titanium slag are transformed into  $\text{TiO}_2$  (rutile) while impurities are transformed into

acid-soluble phosphate and quartz.

## References

- [1] CHEN Guo, XIONG Kun, PENG Jin-hui, CHEN Jin. Optimization of combined mechanical activation-roasting parameters of titania slag using response surface methodology [J]. *Advanced Powder Technology*, 2010, 21(3): 331–335.
- [2] LASHEEN T A. Sulfate digestion process for high purity  $\text{TiO}_2$  from titania slag [J]. *Frontiers of Chemical Engineering in China*, 2009, 3(2): 155–160.
- [3] ZHANG Yong-jie, QI Tao, ZHANG Yi. A novel preparation of titanium dioxide from titanium slag [J]. *Hydrometallurgy*, 2009, 96(1–2): 52–56.
- [4] XUE Tian-yan, WANG Li-na, QI Tao, CHU Jing-long, QU Jing-kui, LIU Chang-hou. Decomposition of acid dissolved titanium slag from Australia by sodium hydroxide [J]. *Rare Metals*, 2009, 28(6): 564–569.
- [5] LU Hui, XIE Gang, YU Xiao-hua, XIE Hong-yan. Removal of silicon and aluminum from EAF titanium-containing slag and pre-oxidation roasting kinetics of the leached slag [J]. *The Chinese Journal of Process Engineering*, 2010, 10(3): 513–521. (in Chinese)
- [6] GUEGUIN M. Process of producing synthetic rutile from titaniferous product having a high reduced titanium oxide content: USA, 4629607[P]. 1986-12-16.
- [7] SAHU K K. An overview on the production of pigment grade titania from titania-rich slag [J]. *Waste Management & Research*, 2006, 24(1): 74–79.
- [8] YANG Xiao-qin, SUN Zhao-hui. Study on preparation the high quality titanium material for titanium white by chloride process [J]. *Conservation and Utilization of Mineral Resources*, 2007(5): 38–42. (in Chinese)
- [9] GUO Yu-feng, XIAO Chun-mei, JIANG Tao, QIU Guan-zhou, HUANG Zhu-cheng, DONG Hai-gang. Enrichment of moderate and low grade titania feedstock by activated roasting-acidic leaching [J]. *The Chinese Journal of Nonferrous Metals*, 2005, 15(9): 1446–1451. (in Chinese)
- [10] FILIPPOU D, HUDON G. Iron removal and recovery in the titanium dioxide feedstock and pigment industries [J]. *JOM Journal of the Minerals, Metals and Materials Society*, 2009, 61(10): 36–42.
- [11] Van DYK J P, PISTORIUS P C. Evaluation of a process that uses phosphate additions to upgrade titania slag [J]. *Metallurgical and Materials Transactions B*, 1999, 30(4): 823–829.
- [12] ZHANG Li, LI Guang-qiang, SUI Zhi-tong. Oxidation kinetics of titaniferous slag [J]. *The Chinese Journal of Nonferrous Metals*, 2002, 12(5): 1069–1073. (in Chinese)
- [13] GUÉGUIN M, CARDARELLI F. Chemistry and mineralogy of titania-rich slags. Part 1: Hemo-ilmenite, sulphate, and upgraded titania slags [J]. *Mineral Processing and Extractive Metallurgy Review*, 2007, 28(1): 1–58.
- [14] PISTORIUS P, MOTLHAMME T. Oxidation of high-titanium slags in the presence of water vapour [J]. *Minerals Engineering*, 2006, 19(3): 232–236.
- [15] WANG Ming-yu, LI Liao-sha, ZHANG Li, ZHANG Lin-nan, TU Gan-feng, SUI Zhi-tong. Effect of oxidation on enrichment behavior of  $\text{TiO}_2$  in titanium-bearing slag [J]. *Rare Metals*, 2006, 25(2): 106–110.
- [16] CHEN G, CHEN J, PENG J, SRINIVASAKANNAN C. Dissociation of  $\text{Ti}_2\text{O}_3$  from titania slag under mechanical activation [J]. *Journal of Alloys and Compounds*, 2011, 509(24): L244–L247.
- [17] LI Yu, LEI Ying, ZHANG Li-bo, PENG Jin-hui, LI Chang-long. Microwave drying characteristics and kinetics of ilmenite [J]. *Transactions of Nonferrous Metals Society of China*, 2011, 21(1):

- 202–207.
- [18] DONDI M, CRUCIANI G, BALBONI E, GUARINI G, ZANELLI C. Titania slag as a ceramic pigment [J]. *Dyes and Pigments*, 2008, 77(3): 608–613.
- [19] VILLIERS J P R, GÖSKE J, TULING A. Disintegration in high grade titania slags: Low temperature oxidation reactions and associated fracture mechanics of pseudobrookite [J]. *Mineral Processing and Extractive Metallurgy*, 2005, 114(2): 73–79.
- [20] LI Jing, ZHANG Zuo-tai, ZHANG Mei, GUO Min, WANG Xi-dong. The influence of SiO<sub>2</sub> on the extraction of Ti element from Ti-bearing blast furnace slag [J]. *Steel Research International*, 2011, 82(6): 607–614.

## 钛渣活化焙烧酸浸制备富钛料

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**摘要:** 提出了一种钛渣活化焙烧酸浸制备富钛料的方法, 对磷酸用量、焙烧温度和焙烧时间对富钛料 TiO<sub>2</sub> 品位的影响进行研究。将细磨钛渣与 7.5%磷酸在 1000 °C 下焙烧 2 h, 再将焙烧产物经过两段硫酸沸腾浸出, 可获得 TiO<sub>2</sub> 品位为 88.54%, CaO 与 MgO 总量为 0.42%的富钛料。经 XRD 鉴定, 该富钛料主要物相为金红石结构的 TiO<sub>2</sub>。机理研究表明, 钛渣添加磷酸后焙烧, 黑钛石固溶体结构和硅酸盐矿物结构遭到破坏, 从而使钛渣中的钛组分转变为金红石物相, 杂质组分转变为可酸溶的磷酸盐和石英。

**关键词:** 钛渣; 活化焙烧; 酸浸; 富钛料; 金红石

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