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 H3PO4 dosage, roasting temperature, and roasting time on TiO2 grade were investigated. A Ti-rich material containing 88.54% TiO2, 0.42% (CaO+MgO) was obtained when finely ground titanium slag was roasted with 7.5% H3PO4 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 TiO2 (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, TiO2 has become the predominant white pigment for paints, paper, plastics, etc [1,2]. TiO2 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 environ-mental problems [4,5]. In the chloride process, titanium dioxide pigment is produced from rutile, titanium slag and some TiO2-rich sand ilmenite, via a TiCl4 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 TiO2 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>
<thead>
<tr>
<th>Chemical compositions of titanium slag (mass fraction, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
</tr>
<tr>
<td>72.42</td>
</tr>
<tr>
<td>Al₂O₃</td>
</tr>
<tr>
<td>2.65</td>
</tr>
</tbody>
</table>

Table 1

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 (d60 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% H₂SO₄ for the first stage leaching, 2 h with 40% H₂SO₄ 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 Kα 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 TiO₂ 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 TiO₂ grade, which is increased rapidly as the phosphoric acid dosage increases from 0 to 10%. As the phosphoric acid content increases to 10%, the TiO₂ 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.

3.2 Effects of roasting temperature

The effects of roasting temperature on the TiO₂ grade were studied in the temperature range of 900−1200 °C. Parameters were kept constant during the tests as 7.5% H₃PO₄ and 2 h roasting. Figure 2 shows that the TiO₂ grade is improved with the roasting temperature increasing from 900 °C to 1000 °C; beyond 1000 °C, TiO₂ grade starts to decrease. Therefore, the roasting temperature of 1000 °C is recommended, at which the TiO₂ grade of 88.54% could be achieved.

3.3 Effect of roasting time

To study the effect of roasting time on the TiO₂ 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% H₃PO₄ added. Figure 3 shows that as the roasting time increases from 1 h to 2.5 h, TiO₂ 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](image-url) Effect of roasting time on TiO$_2$ grade (7.5% H$_3$PO$_4$)

### 3.4 Final product

The main chemical compositions of the product prepared under the conditions of 7.5% H$_3$PO$_4$ added, roasting at 1000 °C for 2 h are shown in Table 2. As shown in Table 2, the product contains 88.54% TiO$_2$, and 0.42% (CaO+MgO). The XRD pattern in Fig. 4 shows that it is TiO$_2$ (rutile) and meets the requirements of the chloride process.

![Fig. 4](image-url) XRD pattern of product

<table>
<thead>
<tr>
<th>TiO$_2$</th>
<th>MgO</th>
<th>SiO$_2$</th>
<th>TiFe</th>
<th>MnO</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>88.54</td>
<td>0.31</td>
<td>7.73</td>
<td>2.15</td>
<td>0.13</td>
<td>0.64</td>
<td>0.11</td>
<td>0.02</td>
</tr>
</tbody>
</table>

### 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$_2$O$_5$, MgTi$_2$O$_5$ and MnTi$_2$O$_5$ [18]. Its stoichiometric composition is M$_3$O$_5$, which is consistent with the compositional invariance [19]. The so-called M$_3$O$_5$ is insoluble in HCl, NaOH, H$_3$PO$_4$ and cold H$_2$SO$_4$ solution. Therefore, it is difficult to upgrade titanium slag by direct acid leaching.

TiO$_2$ is a weak acidic oxide, and occurs as a complex anion Ti$_n$O$_{2n+1}^{(n+1)-}$ in titanium slag. P$_2$O$_5$ is a strong acidic oxide. Due to the bonding force between PO$_4^{3-}$ and Mg$^{2+}$, Mn$^{2+}$, Fe$^{2+}$, Al$^{3+}$ in M$_3$O$_5$ is greater than that of Ti$_n$O$_{2n+1}^{(n+1)-}$, 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$_3$PO$_4$, 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$_3$PO$_4$ dosages at different temperatures were studied. The results are shown in Figs. 5 and 6.

![Fig. 5](image-url) XRD patterns of titanium slag roasting with different dosages of H$_3$PO$_4$ (Roasting temperature 1000 °C, roasting time 2 h)

As shown in Fig. 5, the diffraction peak of the M$_3$O$_5$ is weakened, the diffraction peak of TiO$_2$ (rutile) strengthens and silicate mineral disappears with the H$_3$PO$_4$ increasing. TiO$_2$ (rutile), M$_3$O$_5$ and silicate
mineral are the major phases recorded in the sample roasted without H₂PO₄. For the sample roasted with 7.5 % H₂PO₄, the major phases are TiO₂ (rutile), M₆O₇, SiO₂ and Mg₅(PO₄)₂. The results indicate that titanium slag roasted with H₂PO₄ promotes titanium phases changing to TiO₂ (rutile), silicate mineral changing to SiO₂, and the solid solution structure of anovositive and silicate mineral is destroyed. Therefore, impurities in titanium slag could be removed by acid leaching. However, because of the gallertartig generated during SiO₂ and leaching in the acid, SiO₂ cannot be removed effectively [20]. The results well explain the high content of SiO₂ in the final product.

The results in Fig. 6 show that the major phase of the sample changes little when it was roasted at 600 °C, TiO₂ (rutile) appears and the diffraction peak of the M₆O₇ weakens at 800 °C. As the temperature is raised to 1000 °C, two diffraction peaks of Mg₅(PO₄)₂ and a diffraction peak of SiO₂ appear at diffraction angles between 20° and 25°. The results indicate that upon heat treatment, the slag sample displays changes in phase structure, namely M₆O₇ changes to TiO₂ (rutile) and silicate mineral changes to SiO₂.

4 Conclusions

1) Ti-rich material containing 88.54% TiO₂ and 0.42% (CaO+MgO) was obtained under the conditions of roasting at 1000 °C for 2 h with 7.5% H₂PO₄, 2 h with 25% H₂SO₄ for the first stage leaching, 2 h with 40% H₂SO₄ for the second stage leaching. Ca and Mg in titanium slag are effectively removed by activation roasting followed by acid leaching.

2) Structures of anovositive solid solution and silicate minerals are destroyed in the roasting. As a result, titanium components in titanium slag are transformed into TiO₂ (rutile) while impurities are transformed into acid-soluble phosphate and quartz.

References


钛渣活化焙烧酸浸制备富钛料

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摘 要：提出了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 TiO₂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 TiO₂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 TiO₂。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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