The titanium dioxide ($\text{TiO}_2$) was prepared by efficient decomposition of titanium-bearing blast furnace slag (TBBFS) in molten salt system. The as-prepared $\text{TiO}_2$ 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 $\text{Na}_2\text{TiO}_3$. The average size of the rutile $\text{TiO}_2$ obtained was about 1.0μm and the content was up to 99.23%.

Key words: metallurgy, blast furnace, slag, $\text{TiO}_2$, leaching

INTRODUCTION

$\text{TiO}_2$ 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 $\text{TiO}_2$ is 19 % – 22 %. Because of the dispersed distributions of Ti in various mineral phases, such as titanaugite, 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 $\text{TiO}_2$ content in the slag can be enhanced to 35 wt. % – 45 wt. %. Zhang et al [7] obtained rutile crystal $\text{TiO}_2$ 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 $\text{TiO}_2$ 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>
<thead>
<tr>
<th>CaO</th>
<th>$\text{SiO}_2$</th>
<th>$\text{TiO}_2$</th>
<th>$\text{Al}_2\text{O}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.92</td>
<td>27.74</td>
<td>19.23</td>
<td>13.64</td>
</tr>
<tr>
<td>MgO</td>
<td>Fe</td>
<td>Others</td>
<td></td>
</tr>
<tr>
<td>8.04</td>
<td>4.78</td>
<td>1.65</td>
<td></td>
</tr>
</tbody>
</table>

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 TiO$_2$ 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 ($\lambda = 0.15406 \mu$m) (X’Pert PRO MPD, PANalytical, Netherlands) 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
– 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 CaTiO\(_3\) is disappeared during 500 – 600 °C. Meanwhile, only Na\(_2\)TiO\(_3\) phase is identified. However, according to the phase diagram in the Na\(_2\)O – TiO\(_2\) system [10], both Na\(_2\)TiO\(_3\) and Na\(_4\)TiO\(_4\) should be formed in the temperature range of 400 – 600 °C. A hypothesis for this discrepancy might be that the Ti-O bonds in CaTiO\(_3\) are so strong that they could not be disrupted under the roasting conditions. Hence, only ion-exchange process takes place between Ca\(^{2+}\) and Na\(^{+}\), while the structure of TiO\(_3^{2-}\) remains stable.

Thus, it is believed that the decomposition of CaTiO\(_3\) under the roasting conditions can be represented by the following equations:

\[
\text{CaTiO}_3 + 2\text{NaOH} \xrightarrow{\text{NaF}} \text{Ca(OH)}_2 + \text{Na}_2\text{TiO}_3
\]  

(1)

The product Ca(OH)\(_2\) is further decomposed:

\[
\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O}
\]  

(2)

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
show that CaTiO_3 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 CaTiO_3 are so strong that they could not be disrupted under the roasting conditions. However, in the Figure 4(a), Na_2TiO_3, 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 TiO_2 99.23 %, ΣFe 0.068 %, MnO 0.032 %, Al_2O_3 0.059 % and SiO_2 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 Na_2TiO_3 which could be dissolved in dilute HCl solution. The average size of TiO_2 obtained is about 1,0 μm, the phase is rutile, and the content is up to 99.23 %.

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REFERENCES


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