Decomposition kinetics of titanium slag in sodium hydroxide system

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A B S T R A C T

A novel process was proposed for preparing titanium dioxide by the decomposition of titanium slag in sodium hydroxide system under atmospheric pressure. The kinetics on the decomposition of titanium slag was mainly investigated. The results on effect of reaction temperature, particle size and NaOH-to-slag mass ratio on titanium extraction show that the temperature and particle size have significant influence on the titanium extraction. The experimental data of titanium extraction indicate that the shrinking core model with chemical reaction controlled process is most applicable for the decomposition of titanium slag, with the apparent activation energy of 40.8 kJ mol−1. Approximately 95–98% of titanium in the titanium slag could be extracted under the optimal reaction conditions. In addition, the content of TiO2 obtained in the product is up to 99.3%.

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1. Introduction

White pigment (titanium dioxide, TiO2) is used in various fields such as coatings, fillers for plastic and paper, adsorbents, cosmetics, catalysts and gas sensors due to its high chemical stability, heat stability, and exceptional optical, mechanical and electronic properties (Chen and Liu, 2006; Fujishima et al., 2000; Grätzel, 2003). Industrial production methods of TiO2 pigment include sulphate process and (Chen and Liu, 2006; Fujishima et al., 2000; Grätzel, 2003). Industrial production methods of TiO2 pigment include sulphate process and chloride process. The sulphate process is based on the digestion of the ilmenite with sulfuric acid, followed by thermal hydrolysis of the titanium (IV) ions in highly acidic solutions, and then by the calcination of the obtained titanium(IV) hydrous oxides. Titanium slag used in the chloride process is first chloridized, forming TiCl4 vapor, which is subsequently oxidized at very high temperature, yielding solid rutile powder. In the case of the sulphate process, about 8 ton of ~20 wt.% spent sulphuric acid and 4 ton of copperas are brought with for each ton of TiO2 production, resulting in serious environmental problems (Liang et al., 2005). Therefore, about 60% of the TiO2 pigments in the world are manufactured by the chloride process at the present time. Furthermore, the increasing output of titanium slag could enhance the growing potential of chloride process (Dai, 2007). However, the chlorination and oxidation in chloride process involve high reaction temperature of over 1000 °C, which is a high energy consuming process.

Recently, a novel metallurgical process for ilmenite and titanium slag has been developed by Institute of Process Engineering, Chinese Academy of Sciences (Qi et al., 2005; Liu et al., 2006; Tong et al., 2007). In this process, ilmenite or titanium slag was first decomposed by concentrated KOH solution under atmospheric pressure, forming the intermediate product with high titanium content and low iron content, which can be converted into pigment grade titanium dioxide after further treatment. However, the recycling of large amount of KOH solution occupies the most process energy consumption. In order to optimize the process and to reduce energy consumption, a new method to reduce the amount of alkali greatly, was proposed in this paper.

In the present study, the titanium slag, used as the raw material to prepare titanium dioxide, is manufactured by smelting ilmenite in an electric arc furnace, with anthracite as reductants (Pistorius, 2002). In this process, the titanium slag was first decomposed in NaOH system at lower temperature. Then the intermediate product was treated by water, providing what might be described as slurry containing solid titanium oxide and by-products in solution. Titanium oxide can be separated from the mixture by filtration and purified by the following refluxing in diluted acid solution. The general flow sheet of this process was shown in Fig. 1. In comparison with the chlorination and oxidation in chloride process, the reaction temperature in this process is dropped by 500 °C.

The purpose of the present investigation is to obtain essential information on the kinetics of decomposition of titanium slag in sodium hydroxide system with respect to the reaction mechanism.
Moreover, the phase identification and transformation of the products were also investigated.

2. Experimental

2.1. Materials

The solid NaOH was reagent grade (Beijing Chemical Plant). Deionized water was used through the experiments whenever needed. Water for analysis was super purified by a water super-purification machine (Milli-Q, Millipore). The titanium slag used in the present work was bought from Guoai Ferroalloy Company (He Bei province, China). The detailed chemical composition of the slag was examined by ICP-OES (Optima 5300DV, PerkinElmer, USA) and the analytic results are listed in Table 1.

2.2. Experimental apparatus and procedure

The titanium slag was dried, ground and dry-sieved to different narrow size fractions. The mineralogical analysis of the sample was investigated by XRD (Philips 1140, Cu Kα, 40 mA current, 30 kV voltage). The result in Fig. 2 indicates that the main crystalline phase of titanium slag is Ti$_3$O$_5$ (TiO$_2$·Ti$_2$O$_3$) with minor Ti$_2$O$_3$.

Experiments were performed in a muffle furnace using nickel crucibles. The NaOH was first dissolved with water to make a 60 wt.% solution, and the titanium slag was prepared as already described. The concentrated NaOH solution and titanium slag were then homogeneously mixed in the nickel crucibles and put into the muffle furnace when the temperature reached the preset value, with free access of air. The water added in the former procedure would evaporate away because of the atmospheric pressure condition. The temperature of the muffle furnace was controlled by a programmable temperature controller, with a precision of ±1 °C. All experimental data were the average of two or three parallel experiments.

The reaction of titanium slag with NaOH system yields sodium titanate (Na$_2$TiO$_3$) and could be described as follows:

$$2\text{Ti}_3\text{O}_5 + 12\text{NaOH} + \text{O}_2 = 6\text{Na}_2\text{TiO}_3 + 6\text{H}_2\text{O} \quad (1)$$

To calculate the titanium extraction, approximately 1.0 g product was taken out at appropriate time intervals during a run. The sample was dissolved in diluted HCl solution, and the dissolution reaction took place as follows:

$$\text{Na}_2\text{TiO}_3 + 4\text{HCl} = \text{TiO}_{2^{+}} + 2\text{Na}^{+} + 4\text{Cl}^{-} + 2\text{H}_2\text{O} \quad (2)$$

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, and the titanium extraction was calculated by the following formula:

$$X_{\%} = \left( \frac{V \times M_{\text{Ti}}}{m_p} \times \frac{G_{\text{Ti}}}{G_{\text{Ti}}} \times C_{\text{Ti}} \right) \times 100 \quad (3)$$

Where $X_{\%}$ is the titanium fractional conversion, $M_{\text{Ti}}$ is the titanium concentration in HCl solution measured by ICP-OES after the

Table 1

<table>
<thead>
<tr>
<th>Ti</th>
<th>ΣFe</th>
<th>MnO</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>55.1</td>
<td>0.90</td>
<td>2.82</td>
<td>2.17</td>
<td>0.84</td>
<td>0.64</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Fig. 1. Brief flow sheet of the new process for titanium dioxide production.

Fig. 2. XRD pattern of the titanium slag.

Fig. 3. Effect of particle size on titanium extraction.
dissolution of the product (g L\(^{-1}\)), \(G_t\) and \(G_i\) are the total mass of the reaction product and titanium slag respectively (g), \(m_p\) is the mass of the product sample dissolved in HCl solution (g), \(C_{Ti}\%\) is the titanium mass fraction in the slag, \(V\) is the volume of HCl solution used to dissolve the product sample (L).

### 3. Results and discussion

#### 3.1. Decomposition of titanium slag

##### 3.1.1. Effect of particle size

The dependence of particle size on titanium extraction was carried out in NaOH system at 450 °C with NaOH-to-slag mass ratio of 1.5:1 by using the three particle size fractions of titanium slag: 75–125, 58–75 and 48–58 µm. The results presented in Fig. 3 show that titanium extraction increases with the decrease of the particle size, which is attributed to the fact that the decrease of particle size increases specific surface of the slag, as well as its reactivity. Thus, subsequent experiments were performed by using 48–58 µm size fraction of titanium slag.

##### 3.1.2. Effect of NaOH-to-slag mass ratio

According to reaction (1) and the chemical analysis results of titanium slag, 5 g of titanium slag needs about 5 g of sodium hydroxide (the mass ratio is 1:1) for complete reaction. Sodium hydroxide acts as a fluidizing and fluxing agent in the reaction mixture. Excess of sodium hydroxide was necessary to maintain the liquidity of the reactants and ensure sufficient reactions while the extra sodium hydroxide could not significantly affect the economy of the whole process because of the recycling procedure in the overall process (Chandra et al., 1996).

NaOH-to-titanium slag mass ratios of 1.2:1, 1.5:1, 1.8:1 were adopted to investigate the influence of NaOH-to-slag mass ratio on titanium extraction at 450 °C by using 48–58 µm size fraction of titanium slags. The results in Fig. 4 show that the titanium extraction is improved with the increase of NaOH-to-slag mass ratio, while little increase is appeared between the ratio of 1.8:1 and 1.5:1. The ratio of 1.5:1 is therefore recommended, at which the titanium extraction of 94% could be achieved.

##### 3.1.3. Effect of temperature

Temperature dependence of the alkali decomposition process can be used to estimate the apparent free energy and elucidate the macro-kinetics of the process. The effect of temperature on the titanium extraction was carried out in the temperature range of 400–475 °C by using 48–58 µm size fraction of titanium slag with NaOH-to-slag mass ratio of 1.5:1. The results in Fig. 5 indicate that the temperature has significant influence on the titanium extraction. The titanium extraction increases with the increase of reaction temperature, especially in the initial stage of reaction. For example, the titanium...
extraction reached 90% within 45 min at 475 °C. The reason is that the viscosity of molten NaOH system decreases with the increasing temperature, which in turn enhances the mass transfer in the liquid-solid interface.

3.2. Kinetics study

Decomposition of titanium slag in NaOH system in the temperature range of 400–475 °C is a typical liquid–solid reaction, which could be analyzed with the shrinking core model (Levenspiel, 1972). According to the assumption, the particle of titanium slags is spherical and the reaction between sodium hydroxide and titanium slag is first-order for NaOH, the following two kinetic equations apply for different rate-controlling step:

**Chemical reaction controlled process**

\[ 1 - (1 - X)^{1/3} = MKC_A t / \rho r = k_1 t \]  \hspace{1cm} (4)

**Diffusion through ash layer controlled process**

\[ 1 + 2(1 - X) - 3(1 - X)^{2/3} = 6bMC_A t / \rho r^2 = k_2 t \]  \hspace{1cm} (5)

where \( X \) is the titanium fraction reacted at time \( t \) (min), \( M \) is the molecular weight of the titanium slag (kg mol\(^{-1}\)), \( K_c \) is the first-order rate constant (m min\(^{-1}\)), \( C_A \) is the NaOH concentration (mol m\(^{-3}\)), \( \rho \) is the density of the particle (kg m\(^{-3}\)), \( r \) is the initial radius of the particle (m), \( D \) is the diffusion coefficient (m\(^2\) min\(^{-1}\)), \( b \) is the stoichiometric coefficient, and \( k_1 \) (m min\(^{-1}\)), \( k_2 \) (m min\(^{-1}\)) are the apparent rate constants.

Based on the titanium fractional conversion \( X \) at time \( t \) given in Fig. 5, \( 1 - (1 - X)^{1/3} \) and \( 1 + 2(1 - X) - 3(1 - X)^{2/3} \) were calculated, respectively, which were subsequently plotted with reaction time \( t \) according to Eqs. (4) and (5). The results show that Eq. (4) gives better linear tendency (from 0 to 80 min) at each reaction temperature, taking the temperature of 400 °C for example as shown in Fig. 6. Plots of \( 1 - (1 - X)^{1/3} \) vs. time shown in Fig. 7 indicate the extraction of titanium at 450–475 °C gives a good correlation with the chemical reaction controlled kinetic Eq. (4). Therefore, decomposition of titanium slag in the NaOH system is a chemical reaction controlled process in the temperature range of 450–475 °C by using 48–58 μm size fraction of titanium slag with NaOH-to-slag mass ratio of 1.5:1.

![Fig. 8. Activation energy plot of decomposition process of titanium slag.](image)

![Fig. 9. SEM images of titanium slag and products at 450 °C for different reaction time, a: 0 min; b: 10 min; c: 45 min; d: 80 min.](images)
The apparent rate constant was determined from the straight lines of Fig. 7 and plotted according to the Arrhenius equation as shown in Fig. 8. The apparent activation energy of reaction (1) was calculated to be 40.8 kJ mol$^{-1}$.

3.3. Phase identification and transformation of the products

To investigate the extraction behavior of titanium in NaOH system, titanium slag and the products at different reaction time in the decomposition process were detected by both SEM (JEOL, Japan) and XRD, and the results were shown in Figs. 9 and 10, respectively. The SEM images shown in Fig. 9 indicate that the contact surface of slag (Fig. 9a) was stepwise eroded by molten NaOH and finally formed a porous surface after being decomposed at 450 °C for 80 min (Fig. 9d). According to the report (Duan and Qiao, 1990), molten sodium hydroxide is considered as an ionized solvent at high temperature of above 350 °C, in which titanium dioxide has a high solubility. Thus, it can be detected that the decomposition of titanium slag in NaOH system is a coupled process of dissolution and reaction. The corresponding XRD patterns in Fig. 10 indicate that the reaction of titanium slag and NaOH takes place according to reaction (1), and the oxidation occurs during the formation of Na$_2$TiO$_3$. Ti$_2$O$_3$ in titanium slag is oxidized by the oxygen anion (O$^{2-}$) in molten sodium hydroxide system at temperature above 350 °C (Duan and Qiao, 1990) as well as by oxygen from the free access of air. Also, according to the report (Pistorius and Motlhamme, 2006), Ti$_2$O$_3$ can be oxidized by exposure to oxygen or water vapour.

The phase transformation of sodium titanate was carried out by refluxing the titanate in H$_2$SO$_4$ solutions (pH=0.3) at 105 °C for 5 h. The hydrous titanium dioxide obtained was calcined at 450 °C and the corresponding X-ray diffraction pattern and SEM image were shown in Figs. 11 and 12, respectively. The XRD pattern in Fig. 11 indicates the well crystallized anatase TiO$_2$ is obtained. The SEM image in Fig. 12 shows that the average size of the elementary particles is 0.5–1.0 μm. The chemical composition of product is TiO$_2$ 99.3%, $\Sigma$Fe 0.060%, MnO 0.038%, Al$_2$O$_3$ 0.049% and SiO$_2$ 0.068%. It could be used as pigment after further treatment.

4. Conclusions

The experimental results on the decomposition of titanium slag in NaOH system indicate that the temperature and particle size have significant influence on the titanium extraction. Approximately 95–98% titanium in the titanium slag could be extracted in the optimal conditions of temperature 475 °C, NaOH-to-slag mass ratio 1.5:1 and 48–58 μm size fraction of slag. The results also indicate that the shrinking core model is applicable and the decomposition process is controlled by chemical reaction with the apparent activation energy of 40.8 kJ mol$^{-1}$. The content of TiO$_2$ obtained in the product is up to 99.3%.

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