Kinetic study on the effect of iron on the grain growth of rutile-type TiO$_2$ under in situ conditions

Xin Xue$^1$, Xian Luo$^1$, Yongfu Long$^1$, Lu Zhang$^1$, Yue Yin$^1$ and Benjun Xu$^{1,2}$

$^1$ College of Materials and Metallurgy, Guizhou University, Guiyang 550025, People’s Republic of China
$^2$ Guizhou Province Key Laboratory of Metallurgical Engineering and Process Energy Saving, Guiyang 550025, People’s Republic of China
E-mail: bjxu@gzu.edu.cn

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Abstract

There have been many studies on the growth kinetics of titanium dioxide and doped titanium dioxide. However, most have calculated the grain size after isothermal treatment and cooling to room temperature; thus, the real grain size of titanium dioxide at the real-time temperature during heat treatment could not be obtained. This study thus aimed to obtain accurate grain information during the heat treatment process. In this study, titanium oxy sulfite (TiOSO$_4$) and ferric chloride (FeCl$_3$·6H$_2$O) were used to hydrolyze and precipitate TiO$_2$ precursors containing impurity iron. Then, the sample was subjected to high-temperature in situ x-ray diffraction. Using the Williamson–Hall mapping method to process the x-ray diffraction information, the grain size could be used to characterize changes in the grain size, and the change law of TiO$_2$ during the heat treatment process was studied. Furthermore, the effect of Fe doping on the growth of TiO$_2$ crystals was examined through the crystal growth kinetics. The results revealed that when the Fe doping amount reached a certain level, it affected the growth mechanism of the rutile type titanium dioxide grains, thereby causing a change in the growth order. Specifically, an increase in the Fe doping amount increased the growth activation energy; that is, it inhibited the growth of rutile-type titanium dioxide grains.

1. Introduction

TiO$_2$ occurs in three distinct crystallographic phases: rutile, anatase, and brookite [1]. TiO$_2$ of various forms has found many important technological applications in the industry [2–8], because of its high chemical stability, nontoxicity, and excel-lent physical and chemical properties. These properties are strongly dependent on the particle size, and kinetic of the size in TiO$_2$ crystals appears to be very important [9, 10]. During heat treatment, anatase-type titanium dioxide gradually grows with an increase in temperature and time. When a certain temperature and time are reached, the phase gradually transforms into rutile type titanium dioxide, and rutile type titanium dioxide grains also follow the heat treatment [11, 12]. With the increase in temperature and time, the change in rutile type titanium dioxide grain size has a greater influence on the crystal form transformation [13, 14]. There have been a number of studies on the growth kinetics of doped and undoped rutile titanium dioxide, particularly on the influence of iron doping on the growth kinetics of rutile titanium dioxide, which is an important physical chemical basis for the industrial application of the heat treatment process [15–18]. However, most current research methods calculate and analyze the grain size after cooling at a certain temperature during the heat treatment process, which does not accurately reflect the actual size of the grains at the real-time temperature during the heating process [19–25].

In this study, the prepared iron-doped TiO$_2$ precursor was tested by in situ high-temperature XRD, and the XRD data were processed by the Williamson–Hall mapping method to obtain the grain size at the real-time temperature [26–29]. The kinetics of grain growth and the effect of iron on the grain growth of rutile titanium dioxide at the real-time temperature were then discussed. High-temperature in situ x-ray diffraction (XRD) can
obtain the parameters of the crystal grains during heat treatment. The data are the true crystal state of titanium dioxide during the heat treatment process. The data were then used to study the rutile crystals during the heat treatment process.

2. Experiment

Titanium oxysulfate (TiOSO₄) and ferric chloride (FeCl₃·6H₂O) were hydrolyzed and precipitated by mass ratio to prepare an iron-containing TiO₂ precursor. A certain amount of FeCl₃·6H₂O was added to the TiOSO₄ solution and stirred, and a saturated NaOH solution was used to adjust the pH to 6 to form a solid precipitate. The formed precipitate was washed several times with distilled water until SO₂ solution and stirred, and a saturated NaOH solution was used to adjust the pH to 6 to form a solid precipitate. Then, the washed precipitate was dried in an electric heated blast drying box at 80 °C for 24 h. By controlling the amount of FeCl₃·6H₂O added, a precursor with a large concentration gradient of Fe impurity content in the TiO₂ precursor (at%: 1%, 2%, 4%, 7%, and 10%) was obtained.

An x-ray diffractometer (PANalytical X’Pert PRO MRD) was used to perform a high-temperature in situ XRD study on the sample. The target material was a Cu target, λKα1 = 1.5406 nm, voltage 40 kV, current 40 mA. The scan range was 2θ = 10°–90°, the step size was 0.026°, and the scan time was 10 min. The obtained diffraction pattern was refined using the HighScore Plus 4.8 software, and the Williamson–Hall mapping method was used to obtain the accurate crystal size of the sample particles. In this study, using HighScore Plus 4.8, the Pearson VII function was selected as the peak shape fitting function in the calculation, and the Caglioti equation was selected as the half-peak width (FWHM) equation. The peak position and area were refined during fitting, and the obtained XRD data were calculated by the Williamson–Hall mapping method.

3. Results and discussion

3.1. XRD analysis of TiO₂ crystals

Samples with different Fe content were heated in a high-temperature in situ x-ray diffractometer. The heating rate was 10 °C min⁻¹, and the test temperature range was 300 °C–1,000 °C. The test was performed every 25 °C, and the residence test time was 10 min. The high-temperature in situ XRD pattern of titanium dioxide with different Fe doping amounts reveals that there were characteristics of the anatase-type titanium dioxide phase and rutile-type titanium dioxide phase.

At temperatures lower than 600 °C, the samples underwent only the growth of anatase type titanium dioxide, as displayed in figure 1, and no other crystalline transformation. As the temperature increased, rutile type titanium dioxide began to appear. Because the peak of the rutile type titanium dioxide that just appeared was relatively low, the size of rutile type titanium dioxide at the beginning of the transformation from anatase type titanium dioxide to rutile type titanium dioxide could not be calculated.

Table S1 (available online at stacks.iop.org/MRX/9/055008/mmedia) presents the grain size of titanium dioxide samples with different Fe content calculated by the Williamson–Hall mapping method for the XRD diffraction spectrum in figure 1 during the continuous heating process, as well as the statistics of the goodness of fit in the data calculation process. According to the data in table 1 s, the columnar diagram of TiO₂ grain size corresponding to different parameters is drawn, as shown in figure 2. It can be clearly seen in the diagram that the grain size of rutile titanium dioxide is different with different Fe doping amount. Fe doping causes the mechanism of grain growth, so it leads to different grain sizes. When the doping amount is small, the grain growth mechanism is not changed, and the doping only increases the grain size. But when the doping amount increases, the growth mechanism changes and the grain size decreases obviously. More detailed discussion is analyzed in the grain growth kinetics part.

Samples with different Fe content were examined with high-temperature in situ XRD for a holding time to evaluate the effect of time on the grain size of rutile TiO₂ at the same temperature. From room temperature to 700 °C, heating rate is 10 °C min⁻¹. The sample was incubated at 700 °C and tested every 10 min from the time the temperature reached the target temperature. The test time was 10 min for a total of 5 h. The obtained in situ XRD patterns are presented in figure 3, and the crystal grain size was calculated by the Williamson–Hall mapping method. The XRD pattern of titanium dioxide at various temperatures indicates that there are characteristics of the anatase type titanium dioxide phase and rutile type titanium dioxide phase. The red symbol represents the peak of the rutile type titanium dioxide phase (ICDD: 01-076-0323). The black symbol represents the peak of the anatase type titanium dioxide phase (ICDD: 01-071-1169). It can be seen in the figure that all samples changed from the anatase type titanium dioxide to the rutile type titanium dioxide with the increase of time. The influence of different Fe doping amounts leads to the difference in the phase transformation process. By observing with the increase of Fe doping amount, the phase transition speed is accelerated.
Table S2 presents the grain size of TiO₂ samples with different Fe content calculated by the Williamson–Hall mapping method from the XRD diffraction spectrum in figure 3 at 700 °C, as well as the statistics of the goodness of fit in the calculation process. According to the data in table 2, the column diagram of TiO₂ grain size corresponding to different parameters is drawn, as shown in figure 4. It can be clearly seen in the diagram that the grain size of rutile titanium dioxide is different with different Fe doping amount. When the doping amount is 1%, the doping amount is small, and the effect on grain size is not obvious. When the doping amount was 2%, the grain growth mechanism was not changed, but it was hindered at the growth interface, so the grain size was large. But when the doping amount increases gradually, the grain growth mechanism changes, so the grain becomes smaller. More detailed discussion is analyzed in the grain growth kinetics part.

3.2. Grain growth kinetics of rutile

3.2.1. Rutile type TiO₂ grain growth kinetic index

The grain growth of titanium dioxide during heat treatment satisfies the following kinetic equation: [30]

\[
D_t^n - D_0^n = K_0 t \exp (-E/RT)
\]

(1)

Where \(D_t\) is the average grain size (nm) of the particles at time \(t\), \(n\) is the kinetic index of grain growth, \(D_0\) is the initial grain size (nm), \(K_0\) is the property constant, \(t\) is the processing time (s), \(E\) is growth apparent activation energy (J mol⁻¹), \(R\) is the gas constant, and \(T\) is the reaction temperature (K).

For a fixed reaction time, at the initial stage of particle preparation, the grain size is very small. After a certain period of time, \(D_t^n \gg D_0^n\), i.e., \(D_0 \approx 0\) [31, 32].

\[
D_t^n = K_0 t \exp (-E/RT)
\]

(2)
Figure 2. Grain size during heating.

Figure 3. In situ x-ray diffraction pattern of each sample kept at 700 °C. The doping amount of Fe: (a) 1%, (b) 2%, (c) 4%, (d) 7%, (e) 10%.
The logarithm is as follows:

\[
\ln D_t = \frac{1}{n} \ln t + \frac{1}{n} \left( \ln K_0 - \frac{E}{RT} \right)
\]

Figure 4. Grain size of each sample at 700 °C.

The above equation demonstrates that the grain growth kinetic index \( n \) of rutile titanium dioxide can be obtained from the slope of \( \ln D_t \) - \( \ln t \).

The data in table S2 are substituted into the formula, and figure 5 displays \( \ln t \) as the \( x \)-axis and \( \ln D_t \) as the \( y \)-axis. After fitting, the slope is obtained, i.e., the grain growth kinetic index for each doping amount. Table 1 displays the kinetic index, which is rounded.

The grain growth index, or \( n \), is a number that is directly linked to the grain growth process. Various indexes ranging from 2 to 6, and even up to 10, have been observed, despite the traditional theory only indicating that the index is 2 [33–35]. According to Eastman’s particle growth theory [36], in the absence of doping, the grain growth kinetic index of rutile type titanium dioxide is \( n = 2 \). The fitting data indicate that when the amount of iron doping was 1% or 2%, the grain growth kinetic index was approximately 2, which is the same as for the case of no doping. When the amount of iron doping was small, the rutile grain growth mode of titanium dioxide was almost unaffected. After calculation, when the doping amount reached 4%, the grain growth kinetic index began to change. The grain growth index reflects the mass transfer mechanism and nucleation growth mechanism of the grain growth process to a certain extent, and different growth indices correspond to different grain growth mechanisms. When \( n = 2 \) indicates that grain development is primarily controlled by the curvature of the grain boundary, \( n = 3 \) shows that grain growth is primarily controlled by volume diffusion, and \( n = 4 \) indicates that grain growth is primarily controlled by atoms crossing the grain border randomly. When \( n > 4 \), the growth control is very complex, which is the common control of the first several mechanisms [37–39]. The growth control was different for different Fe doping amounts; that is, when the Fe doping amount reached a certain level, it affected the growth mechanism of gold-red titanium dioxide grains.

The analysis of the nucleation growth mechanism of rutile-type TiO\(_2\) demonstrated that the nucleation of rutile-type TiO\(_2\) occurred at the interface of anatase-type TiO\(_2\) and the growth extended to the inside of the crystal grains. Therefore, the growth of rutile-type TiO\(_2\) grains mainly occurred by the merger and fusion of the two anatase-type TiO\(_2\) particles with a larger initial particle size. Moreover, the formed rutile-type TiO\(_2\) grains may have grown through surface diffusion and a more complex mixing mechanism was involved during the growth process. When the degree of crystal transformation increased with time, the number of anatase-type TiO\(_2\) particles decreased and the probability of contact and fusion decreased. Additionally, the rutile-type TiO\(_2\) crystal lattice gradually developed.

Therefore, when the doping amount was 0%, 1% and 2%, \( n = 2 \), the growth mechanism did not change. It was still that the nucleation of rutile-type TiO\(_2\) occurred at the interface of anatase-type TiO\(_2\), and the growth
extended to the interior of the grain. The grain development was mainly controlled by the grain boundary curvature. The doping of Fe only increases the grain size. When the doping amount increased to 4%, $n = 3$, Fe doping provides rutile-type TiO$_2$ grain growth process contact and swallowed particles, grain growth is mainly controlled by volume diffusion. When the doping amount reaches 7%, $n = 6$, the amount of particles that can be contacted and swallowed during the grain growth of rutile-type TiO$_2$ provided by Fe doping decreases. Part of the nucleation process occurs at the interface of anatase-type TiO$_2$, and part of the nucleation barrier increases, which is controlled by the atoms randomly crossing the grain boundary, so it is jointly controlled by several

**Figure 5.** Linear fitting graph of $\ln D_1 - \text{Int.}$ The doping amount of Fe: (a) 1%, (b) 2%, (c) 4%, (d) 7%, (e) 10%.

**Table 1.** Kinetic index of rutile type titanium dioxide grains at 700 $^\circ$C with different Fe doping levels.

| Fe   | 1%      | 2%      | 4%      | 7%      | 10%    |
|------|---------|---------|---------|---------|--------|
| Growth progression | 2.040317(2) | 1.828688(2) | 3.163456(3) | 5.968724(6) | 4.342351(4) |
mechanisms. When the doping amount increased to 10%, \( n = 4 \), Fe doping seriously hindered the nucleation of rutile-type TiO\(_2\), which can neither occur at the interface of anatase-type TiO\(_2\) nor swallow the particle nucleation. The rutile-type TiO\(_2\) is controlled by atoms that randomly cross the grain boundary.

### 3.2.2. Growth kinetic activation energy of rutile-type TiO\(_2\)

The growth activation energy of rutile titanium dioxide grains reflects the driving energy required for the growth of rutile type TiO\(_2\). At a temperature of 600 °C–800 °C, rutile type TiO\(_2\) grains have obvious growth. The apparent growth activation energy can be calculated from the change in particle size with heat treatment.

The logarithm of equation (2) is as follows:

\[
\ln nD_t = \ln t + \ln K_0 - \frac{E}{RT} \tag{4}
\]

For each doping amount, the value of \( n \) is calculated according to table 1, and the formula can be simplified as
Using the data in table S1, as illustrated in figure 6, plot $\ln D_t$ as the $y$-axis and $1/RT$ as the $x$-axis. After linear fitting, the obtained slope is $-E$, and the growth activation energy $E$ for each doping amount can be obtained.

Table 2 indicates that with the increase of Fe doping, the activation energy of grain growth gradually increases, and the grain growth requires more energy; that is, Fe doping suppresses the growth of rutile titanium dioxide crystal grains. In addition, the larger the amount of Fe doping, the more it can suppress the growth of rutile type titanium dioxide crystal grains.

4. Conclusions

This study demonstrated that changes in the amount of Fe doping lead to changes in the grain growth index of rutile type titanium dioxide. When the Fe doping amount was only 1% or 2%, the grains nucleated and grew normally. The mechanism did not have significant impact, and the growth index did not change. However, when the Fe doping amount was 4%, 7% and 10%, the mechanism of grain nucleation and growth was affected. Therefore, the growth index was higher than in the case of no doping.

The growth index was then used to calculate the growth activation energy. The results indicated that with the increase of Fe doping, the growth activation energy increased; that is, Fe doping inhibited the growth of rutile type titanium dioxide crystal grains, and the greater the Fe doping, the stronger the inhibition.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

Benjun Xu https://orcid.org/0000-0002-2446-8420

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Table 2. Activation energy of rutile-type TiO2 grain growth with different Fe doping amounts.

| Fe    | 0% | 1% | 2% | 4% | 7% | 10% |
|-------|----|----|----|----|----|-----|
| E/(kJ·mol$^{-1}$) | 141.699 | 289.537 | 305.194 | 342.335 | 366.467 | 386.69 |

\[
\ln D_t = -\frac{E}{RT} + C
\]
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