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Exploring the Phase Transformation Mechanism of Titanium Dioxide by High Temperature in Situ Method

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Abstract. In this study, the real-time phase measurement of titanium dioxide under different temperature conditions was tested by real-time measurement of high temperature sample stage and Rietveld refinement method. The real-time phase transformation process of titanium dioxide under high temperature conditions was analyzed. The results show that the (101) crystal plane of anatase titanium dioxide is most stable when the amorphous metatitanic acid is transformed into anatase titanium dioxide during the phase transformation of titanium dioxide, and the growth of anatase has a preferred orientation along the c-axis. In the case of anatase-type titanium dioxide to rutile-type titanium dioxide, the (110) crystal plane of rutile-type titanium dioxide is the most stable, but the rutile type has no preferred orientation.

1. Introduction

TiO₂ has good chemical stability and is widely used in aerospace, aerospace and marine applications. With the continued development of China's economy and the evolution of the international situation, people's needs for TiO₂ in medical, sports and clothing are also increasing. There are three crystal forms of TiO₂, namely: Rutile, Anatase, and Brookite. Among them, the plate titanium type is very unstable in nature, so it is rare in nature. At present, rutile and anatase are the main research objects and applications. Among the three crystal forms, rutile is a thermodynamically stable phase, while anatase is a metastable phase, and the phase transition of anatase to rutile (A→R phase transition) is an irreversible phase transition process [1].

Both the rutile and anatase types belong to the cubic system. The unit cell parameters are: anatase type $a=3.7852\text{\AA}$, $c=9.5139\text{\AA}$; rutile type $a=4.58\text{\AA}$, $c=2.95\text{\AA}$. Under normal conditions, the temperature at which pure anatase titanium dioxide is converted to rutile titanium dioxide is 610 to 915°C [2]. In order to completely convert anatase titanium dioxide into rutile titanium dioxide, the calcination temperature is preferably higher than 1000°C [3]. In the process of grain growth, the order of occurrence of different crystal faces is different, and the activity of each crystal face is different. Some researchers have studied the titanium dioxide dominated by anatase (001) crystal plane [4], a lot of research has been done by scholars at home and abroad on the phase transition of titanium dioxide. For example: D. M. Tebaldi used XRD to study the effect of different sol counterions on the phase transition of titanium dioxide. It was found that Cl⁻ and Br⁻ are more likely to inhibit the A→R transition of titanium dioxide than NO₃⁻ [5]. S. Kalaiarasi and M. Jose used the anatase-type titanium dioxide prepared by hydrolysis to heat-treat the kinetic analysis of the crystal growth of the titanium oxide A→R transition using an



XRD normal temperature sample stage [6]. Jeng-Shin Ma et al. used titanium dioxide prepared by hydrolysis to investigate the effect of hydrolysis of PH on the A→R transition of titanium dioxide. It was found that the phase transition activation energy increased with the increase of pH at the beginning of hydrolysis [7]. In summary, it can be found that most of the titanium dioxide phase change is detected at the normal temperature sample stage. The researchers often use the temperature to rise to the specified temperature and then lower the temperature and measure it on the normal temperature sample stage. At this time, the crystal structure of the sample dropped to normal temperature is not the sample. The type at high temperatures does not reflect the phase transition of titanium dioxide well in real time. In this study, X-ray diffraction high temperature in situ method was used to test the real-time phase of titanium dioxide under high temperature conditions. The actual phase of titanium dioxide under the temperature condition is ensured, and the change of the phase of the phase under high temperature conditions can be accurately determined, and an accurate phase change process is obtained.

The mechanism of crystal growth kinetics mainly includes Ostwald Ripening (OR) and Oriented Attachment (OA). In the crystal growth process, the two mechanisms tend to exist at the same time. The OR maturation mechanism is to consume small crystal grains through large grains, so that the total specific surface area of the crystal is reduced, so that the total interface free energy is reduced, and the driving force for the growth of the crystal grains is provided. The OA orientation adhesion mechanism is mainly the self-assembly of adjacent crystal grains, and the two crystal grains having the same crystal plane orientation are fused to grow in a specific direction [8]. In order to accurately analyze the growth mechanism of crystals during the phase transformation of titanium dioxide, Rietveld's full-spectrum fitting method was used to obtain the crystal parameters of the phase under high temperature conditions.

2. The experimental part

2.1. Instruments and reagents

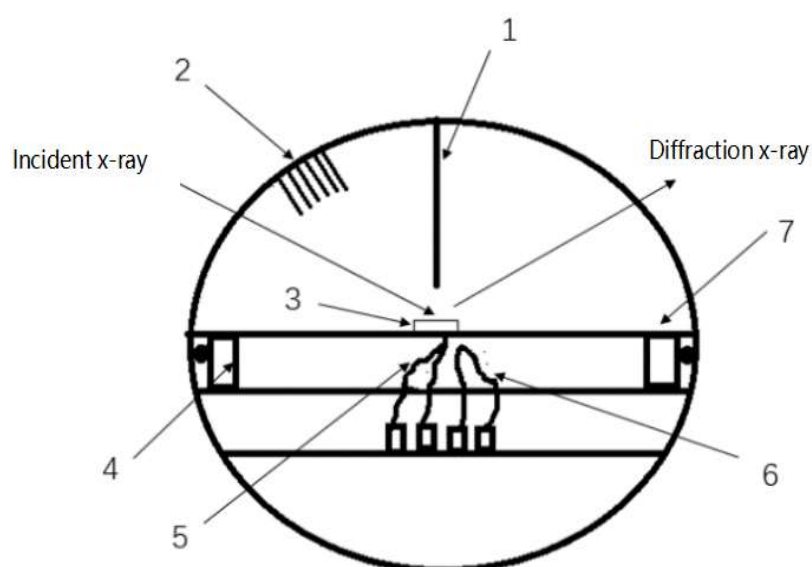
TiCl₄≥99% solution, NaOH≥96% particles, 98%H₂SO₄, 36%HCL, BaCl₂≥99.5% particles, AgNO₃≥99.8% particles, distilled water, ultrasonic cleaner manufactured by Shanghai Kedao Ultrasonic Instrument Co., Ltd., Pana, Netherlands X'pert Pro MPD high temperature X-ray diffractometer, Germany Benzchi STA 409PC synchronous thermal analyzer.

2.2. Synthesis of precursor-amorphous met titanic acid

Take 200ml of TiCl₄ ≥ 99% solution and 100ml of 98% H₂SO₄. The TiCl₄ ≥ 99% solution was slowly added to 100ml of 98% H₂SO₄ in batches to prepare a saturated yellow-green TiOSO₄ solution, and the saturated yellow-green TiOSO₄ solution was heated on an electric furnace until the hydrogen chloride in the yellow-green TiOSO₄ solution volatilized into a nearly colorless TiOSO₄ solution. Leave for 48 hours, the colorless TiOSO₄ solution was added to the beaker and stirred, and a supersaturated NaOH solution prepared by dissolving NaOH ≥ 96% particles in water was added until the TiOSO₄ solution was hydrolyzed to give white colloidal met titanic acid, and PH=6 was measured at this time. The met titanic acid solution was washed several times with an ultrasonic cleaner, and the impurity ions adhering to the met titanic acid were washed into the solution, and then washed by filtration. An appropriate amount of BaCl₂ ≥ 99.5% particles were dissolved in distilled water to prepare a supersaturated BaCl₂ solution, and AgNO₃ ≥ 99.8% particles were dissolved in distilled water to prepare a supersaturated AgNO₃ solution. The filtrate was added to the supersaturated BaCl₂ solution and the supersaturated AgNO₃ solution with a plastic dropper until no white precipitate was observed, which proved that Cl⁻, Na⁻ and SO₄²⁻ had been removed. The white met titanic acid was placed in an oven for 24 hours to dry and grinded into a white powder.

2.3. Methods

The obtained amorphous titanic acid was repeatedly ground with an agate polishing dish. Press the tablet press to a thickness of about 1 mm, and place the pressed sample in a STA 409PC type synchronous thermal analyzer for differential scanning. The temperature range is 26°C to 1100°C, and the heating rate is 10°C/min. Export the dsc map. In addition, the sample was placed on a X'pert Pro MPD high-temperature X-ray diffractometer for high-temperature in-situ testing, using continuous scanning, Cu target, voltage 40kV, current 40mA, step size: 0.026°, starting angle 5°, end Angle: 90°, each step time: 49s. Finally, a high temperature in situ diffraction spectrum is derived. Figure 1 is an X-ray diffraction high temperature sample stage. In the figure, 7 is a platinum piece for heating the sample, the platinum piece was heated by an external power supply of 4, and the temperature of the platinum piece was measured by thermocouples 5 and 6, and regulated in real time by a computer. In this way, the X-ray diffractometer can perform real-time scanning during the heating process. Loss of information after the sample has cooled down is avoided. The diffraction pattern was refined by Rietveld using HighScore Pluse software to obtain the lattice parameters of different crystal forms, and the mapping analysis was performed.



1. Beam blade; 2. Heating restressing measurement table; 3. Sample; 4. Heating sample station power connector; 5. Measuring sample temperature thermocouple; 6. Measuring air thermocouple; 7. Heating sample stage

Figure 1. Schematic diagram of the high temperature sample stage.

3. Results and discussion

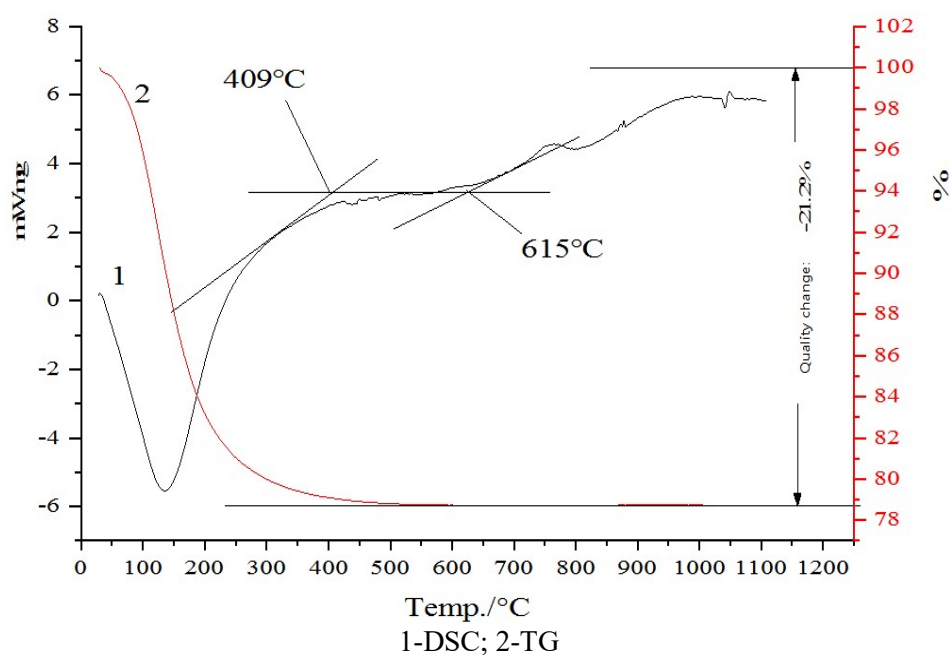


Figure 2. TG-DSC diagram

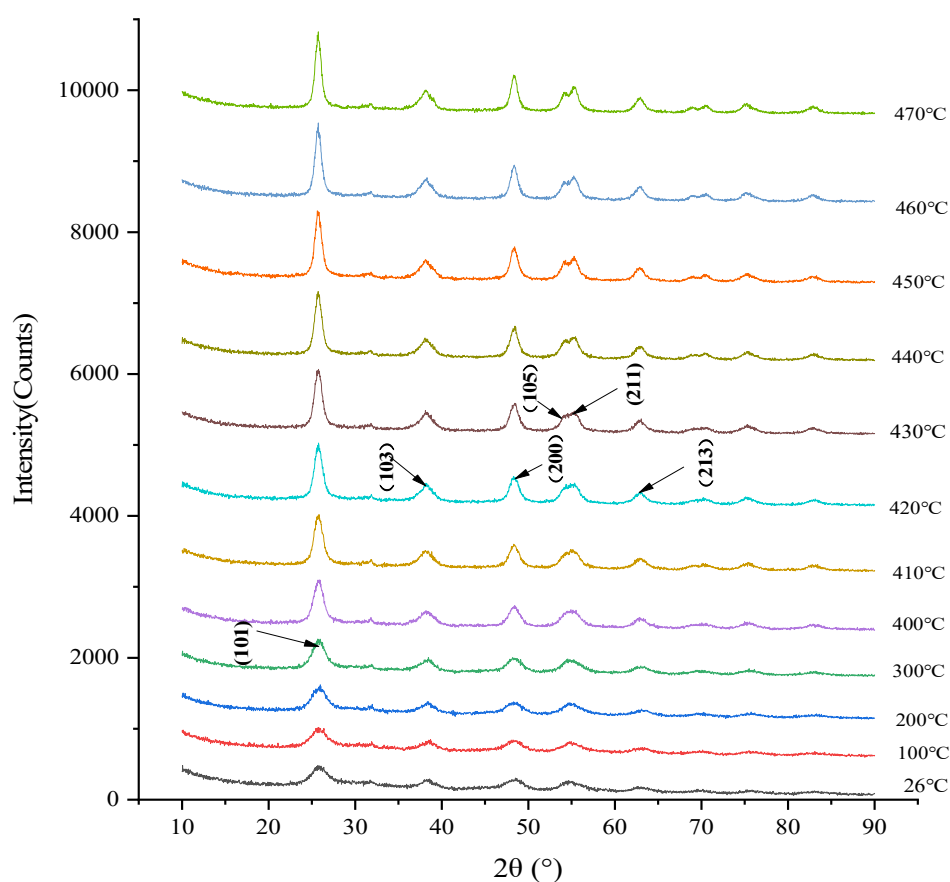


Figure 3. Anatase titanium dioxide phase change diffraction pattern

The obtained metatitanic acid was placed in an X'pert Pro MPD type high-temperature X-ray diffractometer, and heated from 26°C to 700°C at a heating rate of 10°C/min. Continuous scanning, Cu target, voltage 40kV, current 40mA, step size: 0.026°, starting angle 5°, ending angle: 90°, residence time per step: 49s. The high temperature in-situ XRD diffraction pattern of amorphous titanium dioxide converted to anatase titanium dioxide is shown in Figure 3. As can be seen from Figure 3, the diffraction peaks at 26°C are all low Shantou peaks, indicating that the sample is better. Amorphous titanium dioxide, the peak height of the diffraction peak increases continuously from 26°C to 420°C, because the amorphous type changes to anatase, and the crystal planes of the anatase type are sequentially formed, but the intact anatase type has not yet appeared. It is in the transition zone from amorphous to anatase. When heated to 300°C, the diffraction peak of the anatase (101) crystal plane begins to appear. Generally, we believe that the lower the energy, the more stable it is. Therefore, the (101) crystal plane has the lowest energy and the best stability. When heated to 420°C, the (103) crystal plane, the (200) crystal plane and the (213) crystal plane appear almost simultaneously, indicating that the (103) crystal plane, the (200) crystal plane and the (213) crystal plane are substantially equal in stability. When heated to 430°C, diffraction peaks of about 55° diffraction angle began to appear as two anatase diffraction peaks. They are (105) crystal plane and (211) crystal plane, respectively. It is indicated that the (105) crystal plane and the (211) crystal plane are substantially the same. At this time, all the diffraction peaks of the anatase type have appeared substantially, and thereafter, the diffraction peaks of the respective anatase types are continuously increased, and the anatase type titanium dioxide is continuously grown. Therefore, 430°C is an anatase phase transition point. This is basically consistent with the phase change point of 409°C measured by DSC in Figure 2. In addition, we can see that the diffraction peak of the (101) crystal plane is significantly higher than that of other crystal planes, indicating that the anatase type mainly exists in the form of a stable (101) crystal plane. It can also be seen from Figure 3 that the transition from amorphous to anatase is a gradual process. The order of occurrence of different crystal faces is different. Therefore, the stability of different crystal faces of anatase is different.

Table 1. Rietveld refined anatase lattice constant

Anatase	Lattice constants after refinement						Index parameter	
T/°C	a/Å	b/Å	c/Å	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$	Rp	GOF
200	3.799966	3.799966	9.507957	90	90	90	7.21579	1.4484
300	3.797119	3.797119	9.53502	90	90	90	7.15089	1.38809
400	3.797959	3.797959	9.546454	90	90	90	7.56857	1.53017
410	3.796612	3.796612	9.552286	90	90	90	7.93929	1.68851
420	3.799367	3.799367	9.552837	90	90	90	8.12374	1.74038
430	3.799053	3.799053	9.55575	90	90	90	8.18964	1.7464
440	3.798836	3.798836	9.554988	90	90	90	8.69047	1.92745
450	3.80121	3.80121	9.566093	90	90	90	8.8585	2.04749
460	3.80132	3.80132	9.553848	90	90	90	7.77964	1.65592
470	3.801778	3.801778	9.564708	90	90	90	8.17689	1.88148

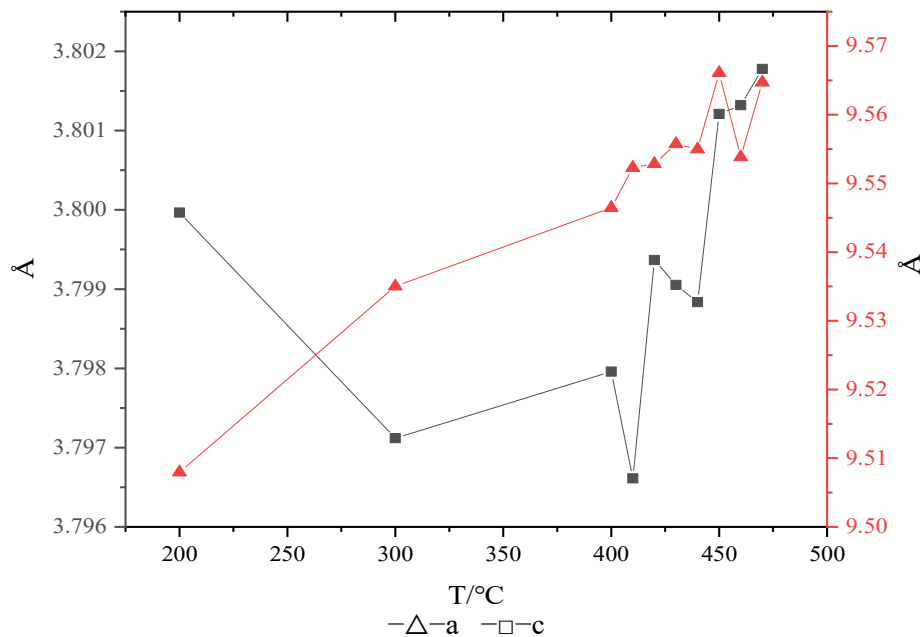


Figure 4. Refined anatase lattice constant after finishing.

Rietveld full-spectrum fitting was performed on the diffraction spectrum of 200°C to 470°C anatase by HighScore Pluse software. The lattice parameters obtained by Rietveld full-spectrum fitting method for refining the crystal are shown in Table 1. From Table 1, $R_p \leq 10$, $GOF \leq 5$, indicating that the finishing result is better and the lattice parameters are credible. Make a picture of Table 1, and get Figure 4, anatase type titanium dioxide belongs to tetragonal system, anatase type titanium dioxide is composed of four TiO_2 molecules per unit cell, and each unit cell of rutile type is composed of two TiO_2 molecules [10]. It can be seen from Fig. 4 that the overall trend of the lattice parameters a and c is increased in the temperature range where the anatase crystal form is gradually improved from 200°C to 450°C, it embodies the process in which the anatase type in Figure 3 is gradually growing. However, we can clearly see that although the overall trend of a value is increased, it is reduced at 410°C, 430°C, and 440°C. Conversely, looking at the value of c has been increasing. In this respect, the crystal growth of anatase titanium dioxide is similar to the growth mode of the dendritic preferred orientation (OA orientation adhesion mechanism). That is, the anatase type is mainly elongated along the direction of the crystal axis c , and the growth of each unit cell is equivalent to the superposition of TiO_2 molecules from the disordered amorphous state to the ordered anatase type continuously toward the crystal axis c . Until each anatase type unit cell contains 4 TiO_2 molecules, a complete rectangular anatase-type tetragonal system is gradually formed. The values of a and c in the range of 450°C to 470°C did not change much, because a complete anatase type titanium dioxide unit cell was formed at this time, and only the growth process of the crystal grains was left. On the other hand, the value of a increases and decreases, and the value of c increases all the time, indicating that not all crystal faces appear at the same time during the growth of anatase, and the order of occurrence of the crystal faces is first and foremost, if all crystal faces appear at the same time, then a and c should be increased at the same time, there will be no increase or decrease in the value of a .

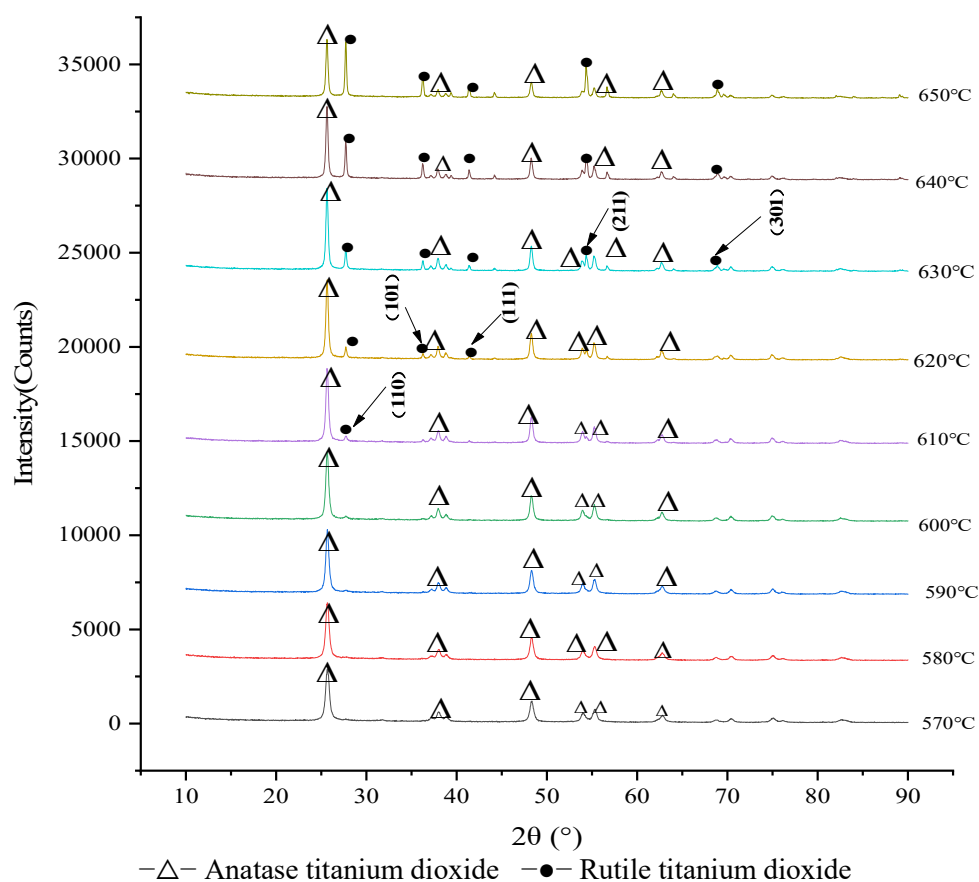


Figure 5. Rutile-type titanium dioxide phase change diffraction pattern.

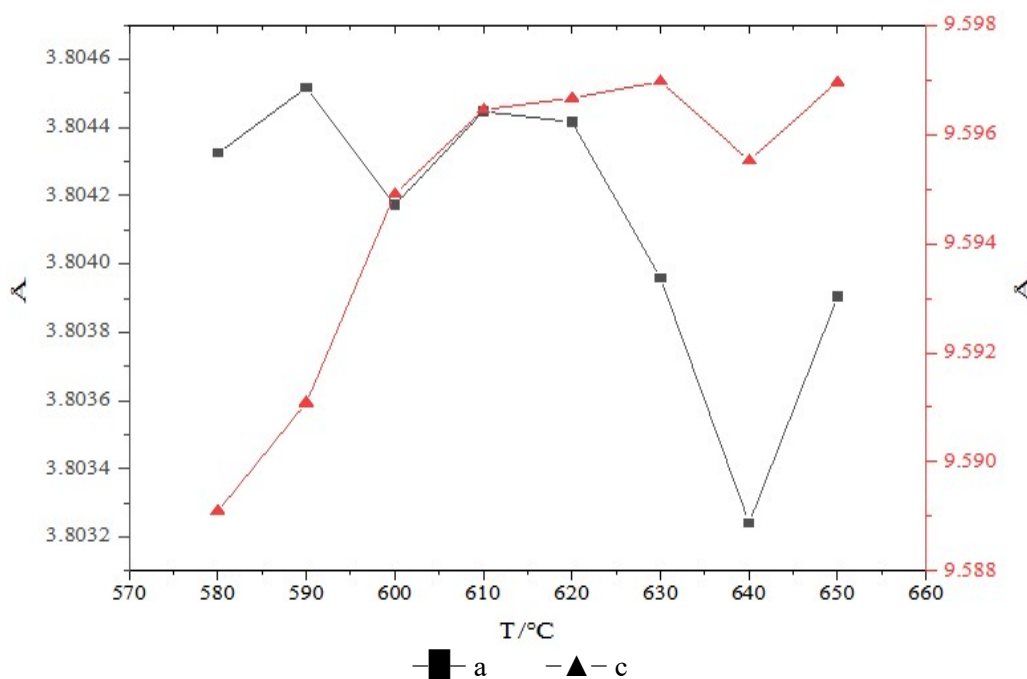
The obtained met titanamic acid was placed in an X'pert Pro MPD type high-temperature X-ray diffractometer, and heated from 26°C to 700°C at a heating rate of 10°C/min. Continuous scanning, Cu target, voltage 40kV, current 40mA, step size: 0.026°, starting angle 5°, ending angle: 90°, residence time per step: 49s. The high temperature in-situ XRD diffraction pattern of the anatase-to-rutile transition is shown in Figure 5. As can be seen from Figure 5, the process of the anatase-type rutile transformation is similar to the amorphous to anatase transformation. It is gradual. First, a rutile crystal face is formed, and then other crystal faces are gradually formed. Finally, a complete rutile type is formed. At 610°C, the (110) crystal plane of the rutile type begins to form, and this can be considered as the phase transition point of the anatase-type rutile type transition. The dsc of Figure 2 is basically consistent. At the same time, it can be known that the rutile type (110) crystal plane has the lowest energy and the best stability. Then, the (101) crystal plane and the (111) crystal plane of the rutile type appear almost simultaneously at 620°C, and the (211) crystal plane and the (301) crystal plane of the rutile type also appear simultaneously at 630°C. At this time, the main crystal face of the rutile type has been completely crystallized, and the crystal form of the rutile type has been basically formed. Similarly, we can find that the (110) crystal plane has the highest diffraction peak, so the rutile type mainly exists in the form of a stable (110) crystal plane.

Table 2. Refined anatase lattice constant after finishing.

Anatase	Refined lattice constant						Wt%	index parameter	
T/°C	a/Å	b/Å	c/Å	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$		Rp	GOF
580	3.804325	3.804325	9.589101	90	90	90	100	9.0112	2.21391
590	3.804517	3.804517	9.591088	90	90	90	100	8.9006	2.20326
600	3.804174	3.804174	9.594913	90	90	90	100	7.85277	1.68966
610	3.804447	3.804447	9.596449	90	90	90	90.1	8.13709	1.7721
620	3.804416	3.804416	9.596667	90	90	90	85.4	7.61506	1.65773
630	3.803959	3.803959	9.596966	90	90	90	76.5	7.50236	1.67974
640	3.803241	3.803241	9.595524	90	90	90	60.8	7.86583	1.79994
650	3.803905	3.803905	9.596961	90	90	90	53.7	7.72385	1.7478

Table 3. Refined rutile lattice constant after finishing.

Rutile type	Refined lattice constant						Wt%	index parameter	
T/°C	a/Å	b/Å	c/Å	$\alpha/^\circ$	$\beta/^\circ$	$\gamma/^\circ$		Rp	GOF
610	4.627069	4.627069	2.983311	90	90	90	9.9	8.13709	1.7721
620	4.625633	4.625633	2.983738	90	90	90	14.6	7.61506	1.65773
630	4.625197	4.625197	2.983706	90	90	90	23.5	7.50236	1.67974
640	4.624257	4.624257	2.983694	90	90	90	39.2	7.86583	1.79994
650	4.625226	4.625226	2.984386	90	90	90	46.3	7.72385	1.7478

**Figure 6.** Refined anatase lattice constant after finishing.

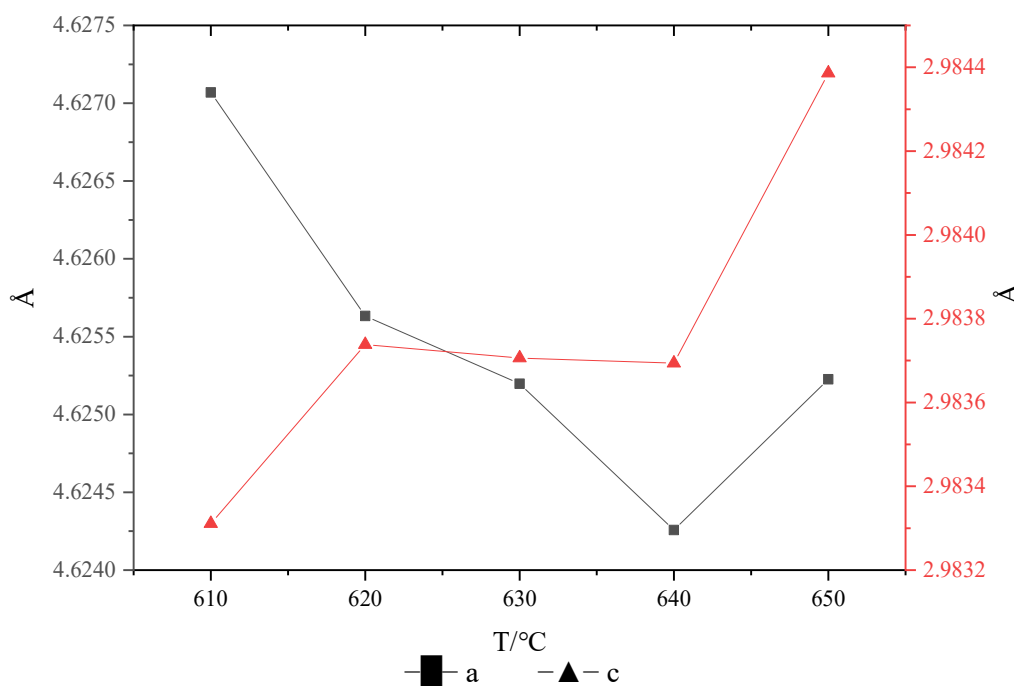


Figure 7. Refined rutile lattice constant.

A Rietveld full-spectrum fit was performed on the diffraction pattern from 580°C to 650°C using HighScore Plus software. The lattice parameters obtained by the Rietveld full-spectrum fitting method for refining the crystal are shown in Table 2 and Table 3. Table 2 shows the lattice parameters of the anatase type, and Table 3 shows the lattice parameters of the rutile type. $R_p \leq 10$, $GOF \leq 5$, indicating that the refinement results are better and the lattice parameters are credible. Tables 2 and 3 are plotted separately, and Figures 6 and 7 can be obtained. It can be seen from Figure 6 that after the phase transition point of the anatase-type rutile transition is 610°C, the lattice parameter *a* of the anatase type is basically unchanged, while *c* shows a downward trend, anatase and The rutile type belongs to the tetragonal system, the anatase type $a=b=3.7852\text{Å}$, $c=9.5139\text{Å}$; the rutile type $a=b=4.58\text{Å}$, $c=2.95\text{Å}$. This indicates that during the anatase-type rutile transformation, the Ti-O bond on the anatase-type *c*-crystal axis may preferentially break and then form a rutile type. From the lattice parameters of the rutile type in Figure 7, it can be found that during the growth of the rutile type after the phase transition at 610°C, the *a* and *c* values are not as large as the anatase growth mechanism, and the total *a* and *c* are increased. Instead, *a* decreases and *b* increases. It shows that the rutile type does not show signs of preferential growth like the anatase type, but grows in all directions.

4. Conclusion

1) The temperature at which titanium dioxide is transformed from an amorphous phase anatase is 300°C, and the transition is gradual. The (101) crystal plane of the anatase type appears first, and the other crystal planes appear in order, so the anatase type (101) The crystal face has the smallest energy and is the most stable. And the anatase type mainly exists in the form of a (101) crystal plane. The phase transition temperature of the anatase-type rutile type transition is 610°C. The (110) crystal plane of the rutile type appears first, and the other crystal planes appear in order, so the rutile type (110) crystal plane has the smallest energy and is the most stable. And the rutile type mainly exists in the form of (110) crystal faces.

2) The growth mechanism of titanium dioxide transformed from amorphous phase anatase is oriented, which grows faster toward the crystal axis *c*, while the anatase to rutile transition has no directionality and only grows around.

Acknowledgments

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