Formation Mechanism of Rutile in Sulfate Process

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Abstract. In the sulfate process for the production of TiO₂ white pigments, amorphous metatitanic acid is calcined to microcrystals of the rutile polymorph by experiencing the dehydration, desulfurization, crystallization into anatase and the phase transformation from anatase to rutile (ART). Surface structure and thermal stability of metatitanic acid was characterized by Simultaneous Thermal Analyzer (STA) and FTIR Spectrometer. Powder X-ray diffraction (XRD) and Field Emission Scanning Electron Microscopy (FESEM) were used to describe the changes of phase composition and granule morphology. It was found that Free SO₄²⁻ ions and S=O asymmetric structure existed on the surface of metatitanic acid as well as H₂O with various adsorption state. The calcination intensity has a much stronger impact on crystallinity’s increase than dehydration, desulfurization. The temperature region of phase transform was 900~1000°C. Rutile would not appear until amorphous metatitanic acid has crystallized into anatase completely and the anatase grain was in a slow growth before that. It was also found that particles were mutually merged by means of fusion of grain boundaries.

1. Introduction
Titanium dioxide are observed in three different polymorphs: brookite, anatase and rutile, while only the anatase and rutile can be industrialized [1]-[2]. Anatase is merely produced via sulfate process and rutile can get by sulfate or chloride processes [3]. As anatase has a higher reflectivity to ultraviolet light, this feature makes anatase more suitable as a photocatalyst and has been widely used in air purification, solar exploitation and environment remediation[2][4]. Rutile boasts the highest thermodynamic stability, and excellent pigment properties like nonvolatile, noncombustible, nontoxic compound and high reflective index. It has been recognized as an important inorganic chemical material and been applied in fields like daily life, agriculture, science and technology, even national defense[1]-[5].

In the sulfate process for production of TiO₂, amorphous metatitanic acid (MTA) is calcined to microcrystals of the rutile polymorph by experiencing the dehydration, desulfurization, crystallization into anatase and the phase transformation from anatase to rutile (ART) as well as the crystal grain growth, so the calcination becomes an vital process step of influencing the quality of TiO₂[1],[6]. Aiming at gaining better performance of this material, many experts and researchers have done some researches on factors and parameters in calcination process and the mechanisms of calcining atmosphere[2][7]-[9], residence time[10] and dopants[6][11] on the phase transformation of anatase to rutile have been basically clarified. It is worth noting that there are various preparation methods of raw materials in current studies and different methods can usually lead to differences in polymorph composition of raw materials, ART temperature, even the products’ properties and applications[3][5][13][14].
However, it is hard for us to distinguish the amorphous crystallization process from dehydration and desulfurization for they have a considerable overlap of temperature regions. Moreover, the amorphous crystallization has a direct causality with ART and products’ performance, so further studies on the crystallization from amorphous MTA to anatase and the morphology changes in every stage are very necessary while rare reports have mentioned these.

Characterization and evaluation methods of amorphous crystallization and ART process were established in this paper. Surface structure and thermal stability of MTA was characterized by Simultaneous Thermal Analyzer (STA) and Fourier Transform Infrared Spectrometer (FTIR Spectrometer). the concept of crystallinity which is the evaluation index of the crystallization from amorphous MTA to anatase and rutile conversion rate as ART’s index was introduced to make a division between two steps by Powder X-ray diffraction (XRD) while field emission scanning electron microscopy (FESEM) was used to observe the granule morphology and measure the average particle size. By these means, relationships between the formation of rutile and grain growth were revealed.

2. Experimental

2.1. Samples
Raw material was a paste-like filter cake of metatitanic acid dewatered by vacuum rotary drum filters in Lomon Billions Co. Ltd sulfate process of titanium dioxide. To investigate the dehydration and desulfurization in the calcination process, MTA was programming calcined in a muffle furnace with 1 °C/min heating rate from room temperature to a constant temperature and held for long enough time until the sample got its weight loss limitation. Table 1 shows the experimental layout of temperature and residence time. Furthermore, changes in granule morphology and phase composition were tracked in a series of TiO₂ samples in a continuous calcination experiment. 200g MTA was weighed and divided into 10 equal parts, then calcined in a muffle furnace with 1 °C/min from room temperature to 300, 500, 600, 700, 800, 850, 900, 950, 1000, 1100 °C. As long as the sample arrived the final temperature, took out it and let it cool down naturally.

| Temp/ °C | Resident Time/h |
|----------|-----------------|
| 100      | 3, 6, 10, 21, 26|
| 300      | 3, 6, 18, 24, 30|
| 400      | 3, 5, 18, 22, 27|
| 500      | 3, 6, 12, 16, 26|
| 550      | 3, 6, 12, 16, 27|
| 700      | 3, 6, 12, 18, 27|

2.2. Characterization
Thermogravimetric and differential thermal analysis (TG-DTA) was performed on a simultaneous thermal analyzer (DTG-60, Shimadzu, Japan) from 30 to 1000 °C under an air atmosphere at a constant heating rate of 10 °C/min. Fourier transform infrared spectroscopy (FTIR) spectra of a sample in KBr pellet were recorded on a PerkinElmer Spectrum 100 (The US). the IR spectrum detector was DTGS (deuterated triglycine sulfate). Sulfur content of samples in isothermal calcination experiment was detected by a X-ray Fluorescence Spectrometer (Magix, PANalytical, Netherlands) after mixing and tabletting the sample and methylcellulose with a weight ratio set to 1:1. A Carl Zeiss ULTRA55 field emission scanning electron microscopy (FESEM) operating with a 20 kV accelerating voltage was used for collection of micrographs. Phase composition analysis was carried out on a Powder X-ray diffraction (X’Pert PRO, PANalytical, Netherlands) equipped with a Ni filtered Cu-Kα radiation source and accelerator detector at 40kV/40mA.

Rutile content \((X_R)\) was calculated as Equation $(1)[15]$. \(I_A\) and \(I_R\) represented the integrated intensity of the anatase (101) main peak and the rutile (110) main peak, respectively. \(W_A\) and \(W_R\) were the mass of anatase and rutile.
\[ K = I_x W (I_o W)^{-1} \]  
\[ X_c(\%) = I_x (KI_a + I_o)^{-1} \times 100\% \]

The concept of crystallinity \((X_c)\), the ratio of the crystal content \((g_c)\) in the sample to the total amount \((g_c + g_a)\), was proposed to evaluate the crystallization process from amorphous MTA to anatase.

\[ X_c(\%) = \frac{g_c}{g_c + g_a} \times 100\% \]

3. Results and Discussion

3.1. XRD Pattern Analysis of Metatitanic Acid

The XRD pattern of MTA (Figure 1) shows that MTA was mainly amorphous, with wide and flat diffraction peaks indicating the crystallization was in a low degree. It can also be found that the diffraction peaks were clearly consistent with the standard anatase characteristic peak, so there are small amount of anatase crystallites in MTA. This phenomenon may be related to the hydrolyzation seeds added in the titanyl sulfate solution for the seeds were mostly consisted of anatase crystallites. Swamy[16] found that amorphous MTA would transform into anatase at room temperature when the particle size was extremely small and the seeds added in hydrolyzation were aggregated with large quantities of 4 ~ 6 nm fine grains [17]. Based on their studies, it is reasonable to deduce that fine amorphous grains in the sample have turned into anatase phase and led to wide, flat anatase diffraction peaks’ appearance in examination.

Figure 1. XRD pattern of pure metatitanic acid without nuclei and dopants.

Simultaneously, the amorphous state is metastable in thermodynamics. Structural relaxation would occur and develop into the crystalline state by adjusting atoms’ position under the physical treatment like annealing, high pressure, etc. Thus, it can be speculated from the XRD results that the amorphous structure of MTA was similar to anatase TiO\(_2\) in the short-range ordered range.

3.2. Surface Structure and Thermostability of MTA

In the FTIR spectra (Figure 2), there is a broad medium absorption in 1700~1900 cm\(^{-1}\) range and a weak absorption around 3660 cm\(^{-1}\), both due to adsorbed H\(_2\)O and isolated OH\(^-\) at the particle surface; further, a small absorption at 940 cm\(^{-1}\) indicating the bending vibration peak of O-Ti-O and a sharp absorption band of Ti=O stretching vibration peak at 1009 cm\(^{-1}\) are observed from which reveals that Ti-O group has a rather diverse structure in MTA. Sulfide on the surface of MTA existed in two different forms illustrated in Figure 2, one of which was the free SO\(_4^{2-}\) appearing at 1104 cm\(^{-1}\), another belonging to S=O asymmetric absorption in the region of the 1104 cm\(^{-1}\) on the basis of Sohn’s[18]
research. On top of that, according to the structural formula in CAS (Chemical Abstracts Service), unhydrolyzed titanyl sulfate with T=O group was inferred to be presented in the sample.

M Anpo[19] postulated a structural model of H2O adsorption states on TiO2 surface based on FTIR and DR-NIR and divided H2O molecules into monolayer chemisorbed water, multilayer physisorbed water with hydrogen-bonds and hydrogen-bond-free water on outermost shell. Surface hydroxyl groups stem from desorption of H2O molecules on TiO2[20]. Herman[21]and Henderson[22] classified the hydroxyl groups into two general groups, one of which is terminal hydroxyl, connected to the acidic site on the 5 coordinating Ti4+ while the other is bridge hydroxyl connected to the basic site like O2-. These groups desorb at temperatures above 400 °C[21]. The chemical states of H2O molecules on a TiO2 surface are stabilized by the adsorption as compared to liquid-phase H2O. Free water were found to be easy to desorb around 50 °C resting on Finne’s[20] study.

Figure 2. FTIR spectrum of metatitanic acid.

On the basis of the theories above, surface structure of MTA has a close relationship to the thermal stability and dehydration process. TG-DTA curves in Figure 3 reveals that first endothermic peak around 75 °C was attributed to the loss of hydrogen-bond-free water and the removal rate reached a maximum at 65°C demonstrating from the DTG curve. Then it loses the hydrogen bond H2O and then gradually removes the bridge hydroxyl and the terminal hydroxyl over 400°C. A broad endothermic peak at 546 °C due to the desulfurization process is observed additionally in DTA curve. Based on the inflection point of the weight loss curve, the desulfurization started at about 500 °C and got its fastest rate at about 570°C suggesting from the DTG curve. Also, the DTG curve gives an indication of the desulfurization process ended at 850 °C. The exothermic peak appears at 776 °C caused by the occurrence of phase transition.
It is obvious that the weight has gradually lost as the temperature increasing with total weight loss of 23.23%. According to the temperature region in researches mentioned, the content of free water is calculated to be 7.08% of the total mass of the sample, and hydrogen bond water accounts for about 7.58%. Content of S in MTA was determined by XRF to be 2.7656%. Assuming SO₂ as the main emission gas, which occupied 5.507%, the total moisture in the metatitanic acid (containing surface hydroxyl groups) was about 17.723%

3.3. Weight-Loss Limitation Experiments
The curves of weight loss rate against resident time under isothermal calcination are illustrated in Figure 4 and sulfur content changes of samples detected by XRF are provided in Figure 5. The weight loss has occurred below 100 °C, consistent with the TG-DTA results. It was also found that with the calcination temperature enhancing, the values of weight loss continuously increased. Before temperature reached 400 °C, all the losing weight was owing to H₂O molecules’ emission for the sulfur content in samples remained as initial. Content of S element in samples gradually decreased at 400 °C as calcination time prolonged, accompanied by the removal of multi-layered adsorbed water and hydroxyl groups.

![Figure 3. TG-DTA curves of metatitanic acid.](image)

**Figure 3.** TG-DTA curves of metatitanic acid.

![Figure 4. Weight loss curves and Changes in sulfur content of metatitanic acid.](image)

**Figure 4.** Weight loss curves and Changes in sulfur content of metatitanic acid.

![Figure 5. Changes in sulfur content of metatitanic acid.](image)

**Figure 5.** Changes in sulfur content of metatitanic acid.
The initial sulfur content of samples at 400 and 500 °C are almost the same. But it can be clearly noted that the weight loss rate curves and the plots of S content in the samples calcinated around 500 °C has a more obvious tendency than that at 400°C. These enable us to conclude that desulfuration process starts at 500°C. Further, the sulfur content reduced from 0.2016% to 0.054% after calcinating for 27h at 700 °C, so 500~700 °C maybe the main range of desulfuration accompanied with dehydration process. Final weight loss of the sample calcinated at 700 °C for 27h was 23.93%, raising only 1% compared with the initial weight loss rate (22.87%). Considering the total mass loss in TG curve, it can be inferred that moisture in the sample has completely removed.

3.4. Compositional Analysis of the Calcined TiO₂

Powder X-ray diffraction was conducted to analyze phase composition in TiO₂ calcinated from room temperature to various terminal temperatures viz., 500, 700, 800, 850, 900, 950, 1000 and 1100 °C separately. The results are presented in Figure 6.

A broad 'hump' in the 2θ region of the anatase (101) peak(2θ=25.4°) can be observed in XRD pattern of TiO₂ calcined at 500 °C, indicating that anatase crystallites had existed in the amorphous sample. It got narrowed and sharpened as the temperature went up suggesting a rise in the crystallinity and crystallite size. As there were no other phases before 950 °C, it reveals that amorphous MTA crystallized to anatase TiO₂ during this period. The phase transition temperature for anatase transferring to rutile was found between 900 and 1000 °C. And a single phase of rutile appeared when it up to 1000 °C.

Figure 7 shows plots of the variation of crystallinity, rutile fraction and grain size with temperature in the continuous calcination experiment. In the low temperature range under 300 °C, crystallinity of the sample is improved with the continuous removal of H₂O in MTA, which proves that dehydration is the key of leading to the destruction or modification of MTA structure and resulting in the reconstruction of anatase lattice. When it comes to the desulfuration, crystallinity growth slows down owing to the energy supplied was used to remove sulfur element as well as the existence of SO₄²⁻, as a bidentate ligand, blocked the rearrangement of Ti-O octahedra in metatitanic acid. After 700 °C, sulfur element has basically removed and a dramatic increase in crystallinity appeared, linearly with calcination temperature.

In all, calcination temperature is a significant factor to crystallinity growth which has a stronger influence than dehydration and desulfurization process. This leads us to a conjecture that higher temperature provides more energy for structural relaxation of MTA while dehydration and desulfurization bring about structure destruction. Furthermore, a comparation between crystallinity and rutile fraction shows that crystallization from amorphous MTA to anatase is separated from ART
process in a continuous calcination of pure MTA (without addition of rutile seeds and dopants), so that ART occurs on the condition that the MTA has completely converted into anatase phase.

Anatase grains grow extremely slow before desulfurization. After sulfur removal, it displays a rather rapid growth. But one cannot ignore a noticeable trend that the grain size springs up once the rutile phase appears. Li[23] proposed that the growth rate of anatase grain tends to be stable after 800°C. It’s the rutile grains that ascend rapidly after rutile nucleation whereas anatase grain size unchanged, alike the case mentioned in Banfield’s[13] study.

3.5. Granule Morphology Analysis of Calcined TiO₂
Changes in granule morphology were observed by FESEM with a magnification of 120,000 times, as shown in Figure 8. It can be seen from the graph that the metatitanic acid was some kind of secondary agglomerates (0.3~4 μm) adhered by primary agglomerates of 30 to 60 nm in size with Van Der Waals’ force and hydrogen bonds. Simultaneously, primary agglomerates were consisted of 10 nm primary grains in laminar deposition. Sample obtained at a terminal calcination temperature of 300 °C was also a kind of sheet-like stacked agglomerate. The primary grains grew slowly (12 nm) with the increase of calcination temperature, and their outline became clearer than MTA due to the removal of H₂O. At this time, desulfurization has not yet occurred. Samples obtained was low in crystallinity and in an amorphous state with agglomerates strongly related to each other as a whole.

When the calcination temperature reached 500 °C, water in MTA has been mostly removed and desulfurization has begun combined with the results Figure 4. As the forces of chemical bonds been weakened with the removal process, ties in primary grains were broken up and the agglomerates were microscopically dispersed in a spherical shape. Average sizes of primary particles at this moment was 16 nm, showing a smoothly growth. At 600 °C, the van der Waals force established by the sulfate ion (SO₄²⁻) was destroyed leading to a disintegration of secondary agglomerates. Primary grains grew appreciably in spherical or elliptical column, up to 39 nm.

At the point of 700°C, there is no sign of primary agglomerates’ existence. The average size of primary grains is calculated to be 50nm. The grains are gradually rounded in morphology and uniform in size distribution. Further, the crystallinity was up to 40.28%, indicating that anatase crystallite accounted for 40.28% of the sample and the remaining was amorphous. When the sample calcined to 800 °C, the crystallinity reached 55.02%. In terms of the granule morphology, the grains were similar to a cube with obvious crystal edges and corners. In the meantime, boundary fusion was found on some particles’ crystallographic plane. As the temperature rose up to 850 °C, the crystallinity was greatly enhanced to 68.62%. Under this condition, planes and edges of the anatase crystallites can be clearly viewed while grain size distribution was not ideal and crystallites were fused severely. Phase composition of the sample calcined at 900 °C was nearly pure anatase, accounting for 98.16%. Grains emerged a coarsening trend by fusing and engulfment. Particle boundaries were blurred again and the grain size was in a substantial growth with an uneven distribution. What’s more, the intercrystalline interface and free interface became fewer[24], making it hard for rutile to nucleate.
Additionally, lattice stress of anatase crystal is proportional to the calcination temperature along with the lattice distortion[24]. Thereupon, thermostability was dropped and bulk nucleation of rutile occurred. The content of rutile phase climbed to 48.12% at 950 °C. As the result of fusion and engulfment, there was no distinct grain boundary in sight and particles were disordered simultaneously. When it up to 1000 °C, anatase in sample has completely converted into rutile and the granule morphology in a like manner with that of 950 °C. The rate of grain growth accelerates as the calcination temperature increases. The average particle size of the sample at 1000 °C was calculated to be 274.7 nm, surged towards 486.8 nm at 1100 °C.

Samples with single anatase phase had a slight growth in particle size. Once rutile nucleates, grains’ size shows an apparent rise, in agreement with the plots illustrated in Figure 7. During the growth, anatase grains in smaller size melt with each other, leading to a disappearance of the intergranular interfaces and a shrink in surface area, forming a larger crystal eventually. Over this period, crystal faces with higher surface energy will be preferentially fused[25] and disappeared as a result. Afterwards, the intergranular interface with the second highest surface energy will become the new interface with highest surface energy, following the same rule of oriented growth[25][26].

4. Conclusion
This study established the characterization and evaluation methods of amorphous crystallization and ART process, discovered the relationship between the process of crystal formation and growth, and revealed the mechanism of crystal transformation. Here are some of the conclusions.

From analysis of FTIR spectra, it was found that free SO$_{4}^{2-}$ and asymmetric S=O groups attached to the surface of metatitanic acid; stretching vibration of Ti=O groups and bending vibration of O-Ti-O are the two different forms of Ti-O structures sulfide existed on the surface. Likewise, the adsorption state of H$_2$O molecules is diverse. Over the period from room temperature to 1000 °C, hydrogen-bond-free water was removed before 100 °C, followed by hydrogen-bonded water; and then bridge hydroxyl groups and terminal hydroxyl groups in the sample are gradually removed over 400 °C, depicted from the TG-DTA curves. Besides, the desulfurization process covers the temperature region of 500 to 850 °C, peaking at 550 °C with the sulfide emission rate.

Figure 8. The granule morphology of TiO$_2$ at different calcination temperature
For industrial metatitanic acid without rutile seeds and dopants, 900°C can be regarded as demarcation point between crystallization of MTA to anatase and phase transformation from anatase to rutile. Only when the MTA has completely converted into anatase, can the ART occurs. In other words, phase transition is separated from crystallization during calcination as to pure metatitanic acid. Especially, calcination temperature is the crux of crystallinity’s increase, more effective than dehydration and desulfurization. Theoretically, temperature provides energy for structural relaxation of MTA while dehydration and desulfurization cause the structure destruction.

Broadly speaking, morphology evolution of metatitanic acid and TiO₂ is a process obeying Gibbs-Curie-Wulff theories of crystal growth and oriented growth[27]. The specific surface area and free energy of the system are continuously diminished by boundaries’ fusion, resulting in particles’ engulfment. In addition, single phase primary crystallites are rotated with certain lattice planes, rearranging to uniformize the grain orientation and aggregating to grow bigger by fusion.

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6. References
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