A melting-like process and the local structures during the anatase-to-rutile transition

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A B S T R A C T

Phase transition of titanium oxide from anatase to rutile was investigated by using transmitted electron microscope (TEM), scanning electron microscope (SEM) and X-ray diffraction (XRD), in combination with the atomic pair distribution function (PDF) technique. The transition range is about 528–805 °C and the critical size is ~73 nm for the sol-gel samples calcined for 6 h. A melting-like process was evidently observed in the transition samples by SEM and it will speed up the phase transition. PDF reveals that anatase crystallites are packed by neighbouring TiO_6 octahedra in a cis-coordinated way. Anatase crystallites larger than the critical size will be unstable and transform into rutile in a trans-coordinated way by torsion and rotation of part of octahedra and it will rapidly spread the entire crystallites driven by a melting-like process. We suggest the maximum size of anatase will be more technically useful for the description of the phase stability from anatase to rutile because unstable small anatase crystals are consumed during longer calcination process to grow the larger anatase crystals.

1. Introduction

Titania (TiO_2) is considered to be one of the most promising multifunctional materials, it will be applied to water treatment [1,2], air purification [3], self-cleaning coatings [4], nonlinear optics [5], photoluminescence [6,7], as well as photo-catalyst and energy conversion [8–10]. But these excellent properties principally depend on their crystal structures. For instance, the anatase phase (tetragonal, $I4_1/amd$) is suitable for catalyst due to the high surface area [11], while the rutile phase (tetragonal, $P4_2/mnm$) is used for optical and electronic purposes for the high dielectric constant and high refractive index [12].

Therefore, understanding and controlling of phase transition from anatase to rutile ($A \rightarrow R$) are essential for titania. It is well known that anatase crystals undergo a solid-to-solid phase transition [13] to form the rutile phase over a wide range of calcining temperatures, 400–1200 °C. Thermodynamic analysis indicated anatase will transform to rutile when its crystallize size greater than a certain critical size. According to Gribb & Banfield's report [14], this value can be determined by the average crystallite size of anatase for the sample containing the first-detected rutile. Nevertheless, there are large deviations in the reported critical sizes. e.g., 11, 13, 14, and 40 nm for the experimental reports [14–17], but the thermodynamic analysis [18] suggested the critical size will be 40, 29, 48 nm, respectively, for

spherical nanoparticles, cylindrical nanowires, and nanotubes.

Several reports suggested that nucleation of rutile only occurs on the surface of coarse anatase particles, or interface nucleation by $\{112\}_{Anatase}$ twinning [17,19,20]. It is also reported that the anatase to rutile transformation is reconstructive, and which involves the breaking and reforming of bonds [21]. More recently, Satoh [16] proposed a hypothesis that the phase transition from the metastable anatase to the thermal stable rutile could be the existence of a melting-like process. This hypothesis can well explain the large mismatch of the coarsening rate between anatase and rutile, but the transition temperature is far lower than its melting point.

In order to further understand the micro-mechanism of $A \rightarrow R$ transition in titania, it is important to investigate the microstructures of individual phases (anatase & rutile) and the transition phase, especially for the variations of local atomic environments. Typically, the local atomic features can be investigated by the atomic pair distribution function (PDF) technique based on the X-ray or neutron diffraction, and the high-resolution PDF requires a wide range of diffraction (e.g., Q = 30 Å^{-1}) which is far beyond the diffraction limit of the traditional X-ray diffractometers. Here, the local atomic environments were revealed through the atomic pair distribution function based on the powder electron diffraction. Cis- & trans-coordination of TiO_6 octahedra were investigated for anatase and rutile, respectively. A melting-

like process hypothesized by Satoh was evidently observed in the transition sample by SEM. We suggest that the maximum size of anatase determined by the logistic function fitting is more suitable to describe the critical size of A → R transition than the average size of anatase for the sample containing the first-detected rutile.

2. Experimental Methods

2.1. Crystal Growths by the Sol-Gel Method

Titania powders were synthesized through the sol-gel method with tetrabutyl orthotitanate as precursors, absolute ethyl alcohol as the solvent and glacial acetic acid as a chelating agent as described elsewhere in greater details [22]. The obtained sol-gels were dried at 80 °C, then ground and calcined for 6 h at various temperatures (200, 300, …, 1000 °C), and naturally cooled down to the room temperature.

2.2. Powder X-Ray Diffraction Experiments

To record high-quality diffraction data, powder X-ray diffraction (XRD) experiments were carried out on Bruker D8 advance diffractometer by a step-scanning method with a step size of the 3°/min. In order to obtain an accurate quantitative result, Rietveld refinement was involved in to extract the phase fraction of rutile, the crystallite size of anatase, the averaged density and the other crystallographic parameters.

2.3. Microstructural Characterization

The characterization of the microstructural morphology was performed on Hitachi S-4800 scanning electron microscope (SEM). Phase identification based on the selected-area electron diffraction (SAED) was performed on JEOL JEM-2100 with Orius-832 CCD. The typical parameters are that the selected-area aperture is 2# (1 μm), the camera length is 100 mm, and the exposure time is 2.5 s. Before SAED experiments, the camera length was strictly calibrated using a standard specimen of Au.

ePDF tools were employed to extract the atomic pair distribution functions (PDF) from SAED patterns collected from calcined samples (granular particles for samples at 200–700 °C, and blocks for samples at 800–1000 °C): The SAED pattern will be projected as the intensity profile around the transmitted center via the rotation-average method, the diffraction vector $Q = 4\pi sin\theta/\lambda$ is truncated at 16 Å^{-1}. Next, a cubic spline background is removed from the intensity profile to get Ic(Q). And then the structure function S(Q) is obtained by the normalization of Ic(Q),

$$S(Q) = 1 + \frac{N * I_c(Q) - <f_e^2(Q)> + c}{<f_e(Q)>^2} \tag{1}$$

where N is a normalization parameter, c is a constant to keep $S(Q)$ oscillating around 1 at high-Q values, $<f_e^2(Q)>$ and $<f_e(Q)>^2$ are the composition-averaged electron form factors. The reduced atomic pair distribution function, $G(r)$, can be obtained by the sine Fourier transformation method,

$$G(r) = \frac{2}{\pi} \int_{Q_{min}}^{Q_{max}} Q[S(Q) - 1] \sin(Qr) dQ \tag{2}$$

PDF calibration was carried out based on the average material density which was obtained by Rietveld refinement of XRD data.

3. Results and Discussion

Fig. 1a represents a series of experimental XRD patterns of samples calcined at temperatures from 200 to 1000 °C for 6 h. When the sample is calcined at 200 °C, it shows some small broad bumps at about 25, 38,

48, 54 and 63°, suggesting the nature of small crystallites and the poor crystallization. These bumps will become sharp and strong with the increase of calcining temperatures, which denotes anatase crystals were incessantly growing. At T > 500 °C, some rutile peaks located at 27, 36, 41 and 54° spring out and become strengthened as the increase of calcination temperatures, indicating the development of rutile crystals.

3.1. The Critical Size of Anatase Crystallites

Some reports indicated that during the growth of anatase it begins to transform to rutile only after growing to a certain critical size, ~13 nm in diameter. This value, according to Gribb & Banfield's definition [14], is the average crystallite size of anatase for the transition initiation sample containing the first-detected rutile. Hence, parameters of the crystallite size of anatase and the weight fraction of rutile are important to describe A → R transition. Commonly, the weight fraction of rutile can be empirically estimated by the ratio of the rutile (110) peak to the anatase (101) peak [15], and the crystallite size can be deduced by utilizing Scherrer formula. In order to get accurate crystallographic parameters of the obtained samples, Rietveld refinement was involved in this report, which is regarded as the most effective technique for the crystallographic analysis. Details of the extracted parameters are listed in Table 1.

Fig. 1b represents the temperature dependence of the crystallite size of anatase (blue) and the weight fraction of rutile (red), respectively. It indicates that the crystallite size of anatase tends to exponentially develop as the increase of calcining temperatures, and then fluctuates around 73 nm at T > 700 °C. For the weight fraction of rutile, it will dramatically increase only after T > 500 °C. According to the Gribb & Banfield's definition, in this report, the critical size of anatase crystallites should be ~38 nm determined from the first-detected rutile (600 °C, 8.3% rutile), labelled as "Gribb's method" in Fig. 1b.

Apparently, this critical value is seriously overestimated for the reason that anatase crystallites coarsen aggravatingly from ca. 22 to 38 nm within the range of 500–600 °C, i.e., it will be < 38 nm. In order to accurately determine the critical size of anatase from the limited data points, a five-parameter logistic function [23,24], which has been widely used in biology and medicine for investigating the growth of species or tumors, was employed to determine asymptotes.

$$y(x) = A_{min} + \frac{A_{max} - A_{min}}{[1 + (x/x_0)^{-h}]^s} \tag{3}$$

where A_{min} and A_{max} are the lower and upper asymptotes, x0 is x of half y, h is the hill slope (the growth rate) and s is a control factor. Based on the logistic function fitting, the transition initiation temperature is 528 °C assuming 2% rutile can be detected by X-ray diffraction. And then the critical size of anatase is 24 nm for our sol-gel samples calcining for 6 h, labelled as "Fitting method" in Fig. 1b. This critical value is consistent with that of cylindrical nanowires (~29 nm) derived from thermodynamic analysis, but it deviates from Gribb & Banfield report (~13 nm).

Considering the thermodynamic phase stability of anatase mainly depends on the critical size, and it will start to convert to rutile when its size larger than this critical value. So, the maximum size of anatase may be more suitable to describe this thermodynamic stability. The critical size of anatase determined based on the traditional method will be significantly underestimated if the examined samples with non-uniform crystallite size. For instance, the maximum size of anatase in Gribb & Banfield's report [14] approaches to 37 nm, while the determined critical size is ca. 13 nm. Similarly, in Zhang & Banfield's report [15], the critical size is ~11 nm, but anatase crystallites can grow up to ~61 nm at 1023 K.

The maximum size of anatase crystallites can be derived from the experimental data of temperature dependent anatase size with the five-parameter logistic function fitting. In this report, the lower and upper asymptotes are 5.8 and 73 nm, respectively. That means the sol-gel