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Thermodynamic analysis of phase stability of nanocrystalline titania

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The phase stability of nanocrystalline anatase and rutile was analyzed thermodynamically. According to the present analysis, anatase becomes more stable than rutile when the particle size decreases below *ca.* 14 nm. The calculated phase boundary between nanocrystalline anatase and rutile coincides with the experimental data for appearance of rutile during coarsening of nanocrystalline anatase. Both surface free energy and surface stress play important roles in the thermodynamic phase stability, which is a function of particle size.

Titania (TiO_2) is widely used in ceramics, catalysis, electronics and metallurgy. In many cases nanocrystalline titania can enhance material performance or improve industrial processing. For instance, sintering of nanocrystalline titania can be achieved at much lower temperatures. A good understanding of the thermodynamic phase stability of nanocrystalline titania is helpful to the control of the processes of nucleation, grain growth, and the phase transformation of nanocrystalline titania, and thus is fundamental to its applications.

At standard pressure (1 bar) and normal temperatures, rutile is more stable than anatase thermodynamically. Nevertheless it is known that anatase is a majority product of industrial, sol–gel, and aerosol syntheses of titania.[1] Experiments in our research group (Gribb and Banfield [1]) revealed that, in the synthesis of ultrafine titania by the sol–gel method, the prepared titania always exists in the form of nanocrystalline anatase or brookite (brookite is a minority product of most syntheses). During coarsening of the nanocrystalline anatase, anatase transforms to rutile only after growing to a certain size (*ca.* 14 nm in diameter), and once rutile is formed, rutile coarsens much faster than anatase.[1] These experimental facts suggest that anatase may be more stable than rutile when crystals are only a few nanometers in diameter. The relative phase stability of graphite and diamond,[2,3] and that of polymorphs of some other oxides, such as zirconia (ZrO_2)[4] and alumina (Al_2O_3),[5] were found to be reversed at very fine particle sizes due to the contribution of surface free energy. The purpose of the present work is to analyze the thermodynamic stability of nanocrystalline titania in order to elucidate the phase stability of anatase at ultrafine sizes.

Thermodynamic principle

Surface free energy constitutes a large part of the total free energy of substances of ultrafine particle sizes. The reversible work per unit area involved in forming a new surface of a substance (for instance by cleavage) is defined as the specific surface free energy (or simply called the surface free energy), while the reversible work per unit area required to elastically stretch a surface is the surface stress.[6] For liquids, the configuration of a surface produced either by cleavage or by stretching is the same, because the mobility of liquid molecules is high and the surface takes the equilibrium configuration of minimum energy. Thus the work required for cleavage or surface stretching is the same, and surface free energy equals surface stress. For this reason, surface free energy is also called surface tension. However, for solids, the atoms (or ions) are relatively immobile, the work needed in cleavage and surface deformation (like stretching) is not the same, hence usually surface stress does not equal surface free energy in value.[6,7] Meanings of different terms should be clarified when dealing with solid surfaces. In this paper, surface tension and surface free energy are defined the same (as in ref. 7), but they are different from surface stress.

1 Conventional formalism

For the transformation of nanocrystalline anatase to rutile

$$\text{Anatase} = \text{Rutile} \tag{1}$$

the change of standard free energy ($J\ mol^{-1}$) is

$$\Delta G^0 = \Delta_f G^0(T, \text{rutile}) - \Delta_f G^0(T, \text{anatase}) + A_R\gamma_R - A_A\gamma_A \tag{2}$$

where $\Delta_f G^0$ is the standard free energy of formation, A and γ represent, respectively, the molar surface area and the surface free energy of particles of titania; and the subscripts R and A represent, respectively, rutile and anatase. Suppose the particles are spherical, and the expansion or contraction in volume when particle size changes can be neglected in the calculation of A, then

$$A = 3\frac{V_m}{r} = 3\frac{M}{\rho r} \tag{3}$$

where V_m is the molar volume, r the radius of the particles, M the molecular weight, and ρ the density. Upon substituting eqn. (3) into eqn. (2), one obtains

$$\Delta G^0 = \Delta_f G^0(T, \text{rutile}) - \Delta_f G^0(T, \text{anatase}) + \frac{3M}{r}\left(\frac{\gamma_R}{\rho_R} - \frac{\gamma_A}{\rho_A}\right) \tag{4}$$

If, $\Delta G^0 = 0$, nanocrystalline anatase is in equilibrium with rutile at a certain temperature and particle size.

2 Effect of surface stress

Eqn. (4) does not take into account the effect of surface stress on free energy. In fact, the particles are subject to an excess pressure (ΔP) caused by the surface stress (f), which is not negligible on the nanometer scale:[7]

$$\Delta P = 2f/r \tag{5}$$

The surface stress is related to the surface free energy *via*[7]

$$f = \gamma + \frac{\partial \gamma}{\partial \varepsilon} \tag{6}$$

where ε is the surface strain. The explicit relationship between

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surface free energy and surface stress is not known for titania. For metals, surface stress is about one to two times surface free energy.[6] Thus, it is reasonable to assume that surface stress is t times the surface free energy, *i.e.*, $f=t\gamma$. Under such consideration, eqn. (4) can be modified by adding the contribution from the excess pressure:

$$\begin{aligned}\Delta G^0 &= \Delta_f G^0(T, \text{rutile}) - \Delta_f G^0(T, \text{anatase}) + \frac{3M}{r}\left(\frac{\gamma_R}{\rho_R} - \frac{\gamma_A}{\rho_A}\right) \\ &\quad + \Delta P_R V_{m,R} - \Delta P_A V_{m,A} = \Delta_f G^0(T, \text{rutile}) \\ &\quad - \Delta_f G^0(T, \text{anatase}) + (2t+3)\frac{M}{r}\left(\frac{\gamma_R}{\rho_R} - \frac{\gamma_A}{\rho_A}\right) \qquad (7)\end{aligned}$$

Thermodynamic data

1 Literature data

Data for the standard free energy of formation of rutile and anatase are taken from the JANAF tables.[8] Eqn. (8) and (9), in a form widely used in phase diagram calculations (*e.g.* ref. 9), are the regression representation of the values in the range 298–1000 K (in J mol^{-1}). In this temperature range the data reproduced by the equations are identical to data in the JANAF tables.

$$\begin{aligned}\Delta_f G^0(T, \text{rutile}) = &-9.539962\times10^5 + 3.040222 \\ &\times 10^2 T - 1.683551\times 10 T\ln T + 3.166423 \\ &\times 10^{-3} T^2 + 6.748623\times10^5 T^{-1} \qquad (8)\end{aligned}$$

$$\begin{aligned}\Delta_f G^0(T, \text{anatase}) = &-9.491471\times10^5 + 3.211113 \\ &\times 10^2 T - 1.927547\times 10 T\ln T + 4.039531 \\ &\times 10^{-3} T^2 + 7.533409\times10^5 T^{-1} \qquad (9)\end{aligned}$$

2 Surface enthalpies of rutile and anatase

Experimental data of surface energy or surface free energy of rutile and anatase are not available. Values from theoretical calculations are used.

By atomistic simulation[10] surface energies of rutile {011}, {110}, {100} and {221} faces are 1.85, 1.78, 2.08 and 2.02 J m^{-2}, respectively; surface energies of anatase {011} and {001} (relaxed) faces are 1.40 and 1.28 J m^{-2}, respectively. The predicted equilibrium forms of titania with these values are in good agreement with experimental morphologies of rutile and anatase.[10] In this work, we take the mean of the values as the average surface enthalpy at 0 K, because in the atomistic simulation, kinetic energy was not taken into account. So,

surface enthalpy of rutile h_R (0 K) = 1.93 J m^{-2},
surface enthalpy of anatase h_A (0 K) = 1.34 J m^{-2}

It is seen that the surface anthalpy of rutile is greater than that of anatase. This can further be justified by employing the semi-empirical estimation of surface tension:[7]

$$\gamma = \frac{2E}{d_0}\left(\frac{a}{\pi}\right)^2 \qquad (10)$$

where E is the Young modulus of a solid, d_0 the equilibrium interplanar spacing normal to a surface of the solid. a is a parameter which can take the mean atomic or ionic radius of atoms or ions on the surface. Assuming a is the same for rutile and anatase, and $d_{0,A}/d_{0,R} \approx (\rho_R/\rho_A)^{1/3}$, then

$$\frac{\gamma_R}{\gamma_A} \approx \frac{E_R}{E_A}\left(\frac{\rho_R}{\rho_A}\right)^{1/3} \approx \frac{B_R}{B_A}\left(\frac{\rho_R}{\rho_A}\right)^{1/3} = \frac{0.23}{0.21}\left(\frac{4.249}{3.893}\right)^{1/3} = 1.13 \qquad (11)$$

where B, the bulk modulus (TPa), and density data (g cm^{-3}) are taken from ref. 11. Eqn. (11) also proves that rutile has higher surface tension.

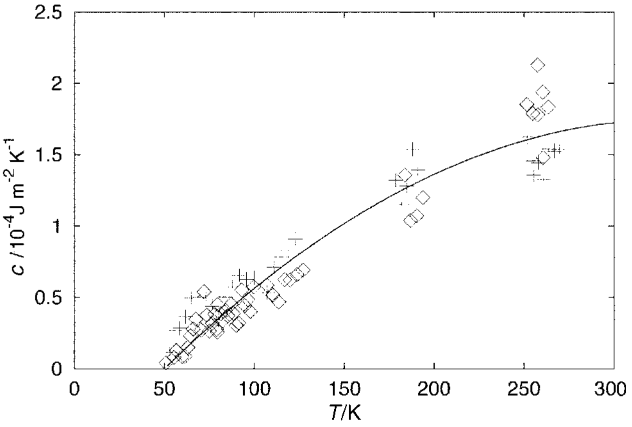

Fig. 1 Surface heat capacity of rutile: (◇) 100 m^2 g^{-1} sample,[12] (+) 55 m^2 g^{-1} sample,[12] (—) regression

3 Surface heat capacity

Ultrafine samples of rutile (100 and 55 m^2 g^{-1}, respectively) have higher heat capacities compared to polycrystalline rutile, as revealed by calorimetry over the range 12–270 K.[12] The enhancement in heat capacity is attributed to the atoms or ions on the surface, and thus is the surface heat capacity (c) (Fig. 1).

Experimental data of surface heat capacity of anatase are not available. Based on the fact that heat capacity of anatase is very close to that of rutile (*e.g.*, in J mol^{-1} K^{-1}, 41.865 *vs.* 42.012 at 200 K, 55.271 *vs.* 55.103 at 298 K [8]), the surface heat capacity of anatase is assumed the same as that of rutile in the range 0–300 K.

Calculation

1 Surface free energies of rutile and anatase

Below 50 K, the surface heat capacity of rutile is considered zero (Fig. 1). At 50–270 K, surface heat capacity data of rutile are represented by the regression equation (Fig. 1)

$$\begin{aligned}c(\times10^{-4}\ \text{J m}^{-2}\ \text{K}^{-1}) = &(1.24\pm0.06)\times10^{-2}(T-50) \qquad (12) \\ &-(2.18\pm0.31)\times10^{-5}(T-50)^2\end{aligned}$$

The surface heat capacity of anatase is the same as that of rutile, as assumed before. Thus, the surface enthalpy and surface entropy of titania can be calculated from eqn. (13) and (14), respectively:

$$h(T) = h(0\ \text{K}) + \int_0^T c\,\mathrm{d}T \qquad (13)$$

$$s(T) = \int_0^T \frac{c}{T}\mathrm{d}T \qquad (14)$$

and the surface free energy

$$\gamma(T) = h(T) - Ts(T) \qquad (15)$$

Inserting surface heat capacity and h(0 K) of titania into eqn. (13)–(15), and extrapolating the results up to 298 K, we obtain:

$$\gamma_R(298\ \text{K}) = 1.91\ \text{J m}^{-2}$$

$$\gamma_A(298\ \text{K}) = 1.32\ \text{J m}^{-2}\ \text{and}$$

$$(\partial\gamma_R/\partial T)_{298\ \text{K}} = (\partial\gamma_A/\partial T)_{298\ \text{K}} = -1.48\times10^{-4}\ \text{J m}^{-2}\ \text{K}^{-1}$$

The magnitude of the temperature coefficient of surface free energy of titania is comparable to but less than those of metals (*e.g.*, -5×10^{-4} J m^{-2} K^{-1} for Cu according to Fig. 1.2 of ref. 7, -8×10^{-4} J m^{-2} K^{-1} for Ni and -13×10^{-4} J m^{-2} K^{-1} for stainless steel according to Fig. 6 of ref. 13). Suppose the

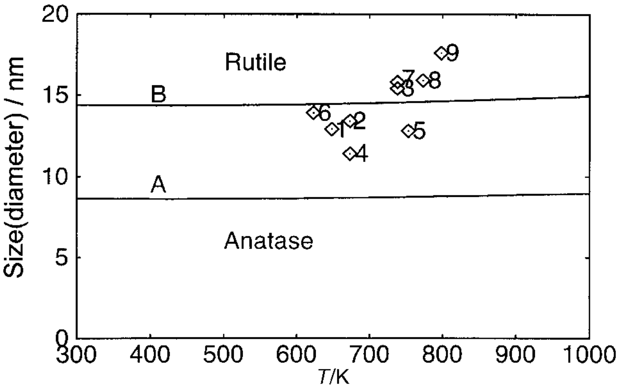

Fig. 2 Phase boundary between nanocrystalline anatase and rutile. Line A: calculated without consideration of surface stress [eqn. (4)]; line B: calculated with consideration of surface stress [eqn. (7), assuming surface stress takes the value of surface free energy, or $t = 1$]. Points: experimental data from ref. 1 (see Table 1).

coefficient is constant at $T > 298$ K, then the surface free energies (J m^{-2}) for rutile and anatase are, respectively,

$$\gamma_R = 1.91 - 1.48 \times 10^{-4} (T - 298) \quad (16)$$

$$\gamma_A = 1.32 - 1.48 \times 10^{-4} (T - 298) \quad (17)$$

2 Phase boundary between nanocrystalline anatase and rutile

Inserting the surface free energies of rutile and anatase [eqn. (16) and (17)] into eqn. (4) and (7), and letting $\Delta G^0 = 0$, the phase boundary between nanocrystalline anatase and rutile can be calculated (Fig. 2).

Data points on Fig. 2 are the particle sizes of anatase when rutile was first detected during the coarsening of nanocrystalline anatase powders at different temperatures (Gribb and Banfield [1]) (Table 1).

Discussion

Under standard pressure within the range 300–1000 K, $\Delta_f G^0(T, \text{rutile}) - \Delta_f G^0(T, \text{anatase}) < 0$, which demonstrates that anatase is unstable relative to rutile. According to the calculated results (Fig. 2), this relative phase stability reverses when the particle size decreases to a certain value: about 8 nm when the effect of surface stress is not considered, or about 14 nm when we assume that the surface stress equals the surface free energy in value. These two sizes are evidently different, which shows that the effect of surface stress on phase stability can not be neglected. The calculated particle size on the phase boundary (line A or line B) only increases slightly with increase in temperature.

The particle size of anatase when rutile was first detected (Table 1) was obtained by X-ray diffraction examination of the reacting samples after reaction for a certain time.[1] However, at higher temperatures the increased transformation rate led to difficulty in arresting the reaction at the point where rutile first becomes detectable by XRD (*ca.* 2%). The particle coarsening rate was proportional to the rate of transformation[1] and higher temperature runs contain up to almost 10% rutile (Table 1). Thus, it is clear that the high temperature results overstate the anatase size when rutile first formed. Given this consideration, anatase size data in Table 1 consistently indicate the critical size at which anatase starts to transform to rutile is around 14 nm. The critical size of anatase may arise from kinetic effects or thermodynamic constraint. If it is due to kinetic effects, *i.e.* the activation energy of the transformation [eqn. (1)] is related to the particle size in some way, it is expected that this size varies greatly with temperature, because a change in temperature can significantly change the kinetic energy of atoms in the nanocrystalline anatase. Such a kinetic effect can be estimated according to the kinetic data of ref. 1 (Fig. 3 and 4): the temperature dependence of the anatase size is 0.2–0.6 nm K^{-1} at reaction time = 50 h and 0.1–0.3 nm K^{-1} at reaction time = 100–200 h. Extrapolating these data to shorter reaction time when rutile is just about to form, the temperature dependence of the anatase size is even more than 0.2–0.6 nm K^{-1}. However, the maximum temperature dependence of anatase size in Table 1 is (17.6–11.4)/(798–623) = 0.035 nm K^{-1}, which is far less than it could be if it were due to the kinetic effect (>0.2–0.6 nm K^{-1}). The real temperature dependence of the critical size must be even less than 0.035 nm K^{-1}, because this value was calculated without con-

Table 1 Particle size of anatase when rutile was first detected (ref. 1)

no.	T/K	% transformation to rutile	average size of anatase/nm	time/hour
1	648	<2	12.9	450
2	673	<2	13.4	200
3	738	<2	15.4	90
4	673	2.0	11.4	15
5	753	2.2	12.8	2.2
6	623	3.1	13.9	115
7	738	6.1	15.8	15
8	773	6.6	15.9	2.5
9	798	9.6	17.6	1.2
average			14.3 ± 2.0^a	

[a] Standard deviation.

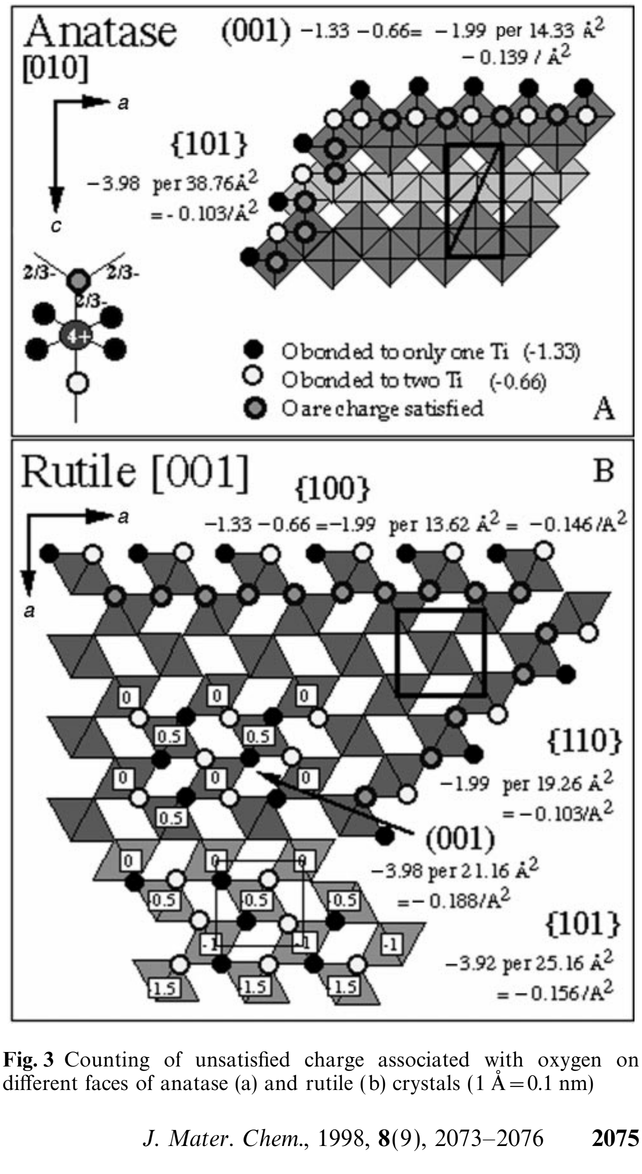

Fig. 3 Counting of unsatisfied charge associated with oxygen on different faces of anatase (a) and rutile (b) crystals (1 Å = 0.1 nm)

Table 2 Unsatisfied charge associated with oxygen on different surfaces of titania crystals

surface	unsatisfied charges/ $\times 10^{-2}$ unit charge nm^{-2}
anatase {101}	0.103
anatase (001)	0.139
rutile {101}	0.156
rutile (001)	0.188
rutile {110}	0.103
rutile {100}	0.146

sideration of the amount of rutile, and thus the coarsening of anatase after rutile was formed. Since kinetic effect cannot reasonably account for the critical size phenomenon, the anatase size in Table 1 can be regarded as the size when nanocrystalline anatase and rutile are about of the same thermodynamic phase stability. The calculation (Fig. 2, line B) coincides with the experimental observation (Table 1 and Fig. 2) fairly well. Consequently, it can be concluded when the particle size is below *ca.* 14 nm anatase is more stable than rutile.

The conclusion of this study is that experimental and theoretical analysis supports a stability field for anatase at small particle size. However, the theoretical prediction depends upon the fact that rutile has higher surface energy than anatase. All lines of estimation support this conclusion. This result is also verified by structure-based analysis of surface energy. Surface free energy is defined as the reversible work done in creating a new unit surface area. Clean metal oxide surfaces are composed of ions of unsatisfied coordination, which means some atoms have unsatisfied electric charges. The more the unsatisfied charges per unit surface area, the greater the work needed for creating the surface, and thus the higher the surface energy and the higher the surface free energy. Considering the structures of anatase and rutile, unsatisfied charges of surfaces of anatase and rutile were counted (Table 2 and Fig. 3). Because a crystal must be bounded by surfaces defining a closed form, both anatase and rutile are terminated by at least two sets of surfaces. Morphology evolution studies of Penn and Banfield (1998)[14] indicate dominance of anatase {101}, with smaller {112} and (001) surfaces. Rutile forms are typically dominated by {110} and {101}, with smaller {100}, {111} and (001). The predominance of higher unsatisfied charge densities of rutile surfaces (Table 2) confirms that rutile has higher surface free energy than anatase.

Conclusion

Thermodynamic, experimental, and structure-based analyses confirm that when particle size decreases to sufficiently low values, the total free energy of rutile (contributed by bulk and surface) is higher than that of anatase, the relative phase stability of anatase and rutile reverses, and anatase becomes the stable phase. The calculated particle size on the phase boundary between nanocrystalline anatase and rutile is *ca.* 14 nm, assuming the surface stress equals the surface free energy in value. This particle size coincides fairly well with the experimentally observed particle sizes of anatase when rutile was first detected during the coarsening of nanocrystalline anatase powders. This analysis explains the predominant experimental synthesis of finely crystalline anatase and the prevalence of anatase at low temperatures in the natural environment.

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