

## Particle size effects on transformation kinetics and phase stability in nanocrystalline TiO<sub>2</sub>

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### ABSTRACT

Kinetic studies conducted primarily between 465 and 525 °C demonstrate that the rate of the polymorphic anatase to rutile transformation increases dramatically when the reacting anatase is very finely crystalline. Coarsening of the reactant anatase and product rutile crystallites occurs simultaneously with the transformation. Kinetic behavior and quantification of transformation rate as a function of average crystallite size indicate that the increase in favorable nucleation sites is a likely cause of increase in transformation rate at small crystallite sizes. Additionally, experimental evidence supports the reversal of stabilities of anatase and rutile at small crystallite sizes. It is proposed that the reversal of stabilities is the result of rutile having a higher surface energy than the anatase phase. Data for coarsening kinetics of anatase and rutile supports the prediction that the surface energy of rutile is significantly larger than that of anatase. Thermodynamic data and theoretical estimates are used to show that a 15% greater surface energy for rutile causes the total free energy of rutile to be greater (less negative) than anatase at crystallite diameters in the few nanometer range. Given the fact that anatase and rutile structures have no polymerized octahedral fragments in common, this may be significant in determining the nature of the nucleated phase.

### INTRODUCTION

Research concerning the effect of very small crystallite size on fundamental properties and behaviors has relevance to both geology and materials science. Nanocrystalline materials are commonplace in geologic environments such as soils and sediments at the Earth's surface. Crystals as small as 2–3 nm in diameter are frequently produced by weathering of aluminum and ferromagnesian silicates (hematite, goethite, ferrihydrite, gibbsite, anatase, clays, and others), form in diagenetic reactions (e.g., iron sulfides, iron and manganese oxyhydroxides, titanium oxides, clay minerals), and are precipitated in microbially mediated redox reactions (e.g., magnetite, greigite, and others). In addition to their presence as dispersed materials and colloidal aggregates, these finely crystalline phases form reactive coatings on mineral grains and fracture surfaces and have tremendous potential to control the exchange of constituents between solids and fluids near the surface of the Earth, and thus to control the distribution of natural and anthropogenic inorganic and organic chemicals.

Finely crystalline minerals form in numerous other geological processes and may control important physical behavior. For example, nanocrystals of oxides that nucleate in volcanic glass may control the rock magnetic properties in ways that depend directly on their particle size

(Tarling 1983). Particle size is also an important factor in controlling clay mineral behavior and affects the andalusite-fibrous sillimanite (fibrolite) equilibria of the widely used aluminosilicate geothermometer-geobarometer. For example, a modeling study using particle size distribution and grain boundary structural information has recently shown that surface energy may shift the andalusite-fibrolite metastable equilibria by at least 140 °C (Penn et al. 1994; in review).

The unique properties and behaviors of finely crystalline materials are also the subject of materials science research. For example, Tolbert and Alivisatos (1994) investigated the pressure-induced phase transformation of CdSe from the wurtzite to rock salt structure and found a qualitative difference in transformation kinetics for bulk and nanocrystalline CdSe. A dramatic decrease in the equilibrium melting temperature was found for nanocrystalline gold (Buffat and Borel 1976) and nanocrystalline CdSe (Goldstein et al. 1991). Studies of nanocrystalline CdS and CdSe (Zhao et al. 1992; Haase and Alivisatos 1992; Tolbert and Alivisatos 1994) have found experimental evidence for changes in solid-solid phase stability fields with small particle size.

The unique properties of nanocrystalline materials may be exploited for numerous materials applications. Examples of applications currently being investigated include catalytic materials (Aguado and Anderson 1993; Zeltner et al. 1993), sensors (Sakohara et al. 1992), thin-film batteries and capacitors for electrical storage, and ceramic

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membranes for gas and liquid phase separation processes (Anderson et al. 1990). In the domain of environmental remediation, TiO<sub>2</sub> has proved to be the most active photocatalyst for the purpose of semiconductor-mediated photooxidative degradation for the treatment of toxic and biologically persistent compounds, with the anatase polymorph showing higher activity than rutile (Fox and Dulay 1993). Because the photocatalytic reactions of interest occur at surfaces, small crystal size is desirable to maximize surface area. Additionally, because the anatase polymorph was shown to have higher activity than rutile, phase stability as a function of particle size is relevant.

TiO<sub>2</sub> has great potential as an advanced high-level nuclear waste form, as discussed by Adelhelm et al. (1988). The sintering of powdered TiO<sub>2</sub>, which is a critical process for the formation of the waste form, is strongly enhanced by the phase transformation and by small crystal sizes, and thus studies of transformation kinetics and phase stability as a function of particle size are again useful.

By far the largest industrial use of TiO<sub>2</sub> is as a white pigment, and for this application, the production of finely crystalline rutile is desirable. Rutile has historically been produced from anatase (the majority product of the industrial synthesis of TiO<sub>2</sub>). The coarsening of the crystallites that occurs at the high temperatures necessary to induce the transformation of anatase to rutile is an undesirable side effect of the transformation process. Investigation of phase stability at very small sizes may aid in the search for an industrial synthesis procedure that produces the rutile phase directly.

The effect of average crystallite size on anatase to rutile transformation rate was previously investigated (Suzuki and Tukuda 1969; Banfield et al. 1993; Kumar et al. 1993). The rate change can be quite large. For example, coarsely crystalline anatase used in a study by Navrotsky and Kleppa (1967) remained 100% anatase after annealing for 24 h at 700 °C. In contrast, our results show nanocrystalline anatase transformed 80% to rutile after 24 h at 525 °C. Kumar (1995) also discussed the metastable crystallization of anatase and the experimental observation of a difference in average size of anatase and coexisting rutile during the transformation in nanocrystalline TiO<sub>2</sub>.

In this report, we quantify the form of the dependence of the phase transformation rate on the coarsening rate, analyze possible reasons for the correlation, and propose alternate explanations for previously reported phenomena. It is well known that the free energy of an individual phase is increased (made less negative) by the contribution of surface energy (either grain boundary energy for compact materials or the energy of free surfaces for a material composed of separated crystals) to the total free energy. However, the effect that surface energy has on the free energy difference between two phases has been considered much less. We present calculations that show that a small difference in surface energy of anatase and rutile can result in reversal of stability of anatase and

rutile at small crystallite sizes and consider the implications of this reversal to the crystallization of the metastable anatase phase from solution.

## EXPERIMENTAL

### Synthesis of starting materials

TiO<sub>2</sub> used in this study was synthesized using a sol-gel method similar to that described by Bischoff (1992) in which titanium isopropoxide is hydrolyzed under acidic conditions. The procedure used is as follows: 300 mL of MilliQ (Millipore Corp.) water is added to a 500 mL round-bottom flask. A cold-water condenser is attached to the neck of the flask, which sits in a heating mantle covering the lower half of the flask. A moderate rate of stirring of the water is established using a magnetic stir plate and Teflon-coated stir bar and is maintained throughout the remainder of the synthesis process. A 30 mL volume of titanium(IV) isopropoxide (Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, Aldrich, Cat. No. 20,537-3) is transferred slowly to the flask by means of an addition funnel. After the isopropoxide is completely transferred to the round bottom, 2.0 mL of concentrated nitric acid (Fisher Optima Nitric Acid, Cat. No. A467-250) is slowly added to the mixture. Heat is applied and the mixture is refluxed for 72 h. The mixture is allowed to cool in the flask for approximately 2 h. The mixture, or sol, produced by the hydrolysis is then transferred to plastic weighing boats, which are placed in drying boxes containing dehydrating agents. In approximately 22 days, the sol dries to form a thin membrane. The membrane is ground with a mortar and pestle to produce a powder. The powder is composed of 4–6 nm diameter anatase particles (average diameter by XRD). Reproducible coarsening and phase transformation kinetics are obtained if all steps in the synthesis process are kept constant.

### Kinetic experiments

Samples of anatase powder were thermally pretreated at 325 °C for 2 h to remove gelation water and other volatiles that remained from the synthesis procedure. This pretreatment time was determined from thermogravimetric analysis, which indicated that after holding sol-gel-derived anatase powder at a temperature of 340 °C for 1 h, there is negligible (<0.5%) weight loss during the subsequent heating to 800 °C. Additionally, the reproducibility of kinetic experiments under different pretreatment times was tested. For anatase samples heated for 71 h at 465 °C after pretreatments of 0.5, 1, and 5 h at 325 °C, it was found that the standard deviation in the size of anatase, size of rutile, and percent of transformation was 0.3 nm (average size = 26.8 nm), 0.6 nm (average size = 45.1 nm), and 0.5% (average = 19.5%), respectively (average size calculated from X-ray line broadening using the Scherrer equation).

Samples used in kinetic experiments were composed of ~40 mg of anatase powder. TEM observations showed that the powdered material consists of large aggregates of approximately spherical, ~6 nm diameter anatase crys-

tals. Samples were placed in small alumina crucibles (designed for DTA experiments) and inserted in countersunk holes drilled into a stainless steel block equilibrated at the pretreatment temperature. All kinetic studies were carried out in a Thermolyne 47915 furnace (room temperature to 1200 °C), which is heated by two open coil electric resistance heaters and insulated with a ceramic fiber insulation. Temperature was monitored using an Omegalloy-NICROSIL-NISIL (Model No. TJ36-NNIN-116-12), Iconel 1/16"-diameter sheath, rugged transition joint probe thermocouple and controlled using a Digital Eurotherm Model No. 815S controller with a plug in, modular, single phase, solid state, silicon-controlled rectifier (SCR) assembly (Eurotherm Model No. 831). Extensive tests were carried out to characterize the thermal characteristics of the furnace and to verify the accuracy of the electrode inserted into the sample holder block.

After the period of pretreatment, the temperature was ramped to the temperature at which the kinetics experiment was to be run. (The samples remained in the furnace during ramping to prevent readsorption of ambient water). The first sample was removed when the desired temperature was reached, and this sample defined the time = 0 sample for the experiment. The remaining samples were removed at progressively later times. Samples were reacted and quenched in an air atmosphere.

#### X-ray diffraction analysis

X-ray diffraction (XRD) was used to determine the extent of reaction of anatase to rutile and the average particle size for anatase and rutile. Diffraction patterns were recorded using CuK $\alpha$  radiation from 19 to 36° 2 $\theta$  in steps of 0.01° with a collection time of 10s per step.

The extent of reaction,  $\alpha$ , was calculated using the ratios of areas under background-subtracted 101 anatase and 110 rutile peaks ( $K\alpha_2$  peaks removed). The peak areas were corrected to determine the extent of transformation, using  $\alpha = 1/[1 + 0.884(\text{area anatase}/\text{area rutile})]$ . The correction factor of 0.884 was measured using known mixtures of pure, finely crystalline anatase and rutile.

Average crystallite size data was determined from X-ray line broadening using Warren-Averbach analysis (Matyi et al. 1987). This analysis was found to give a more accurate measurement of average crystallite diameter than the more frequently used Scherrer equation. The increase in accuracy of Warren-Averbach analysis over the Scherrer equation was confirmed by comparing results for average particle size using the two different methods with average particle size measured from transmission electron microscopy (TEM) images. For a sample of nanocrystalline anatase TiO<sub>2</sub> having a TEM-measured average particle size of 25 nm, Warren-Averbach analysis produced an average particle size of 30 nm, whereas the Scherrer equation resulted in an average particle size of 65 nm. This is consistent with diffraction theory, which predicts that the average particle size calculated using Warren-Averbach analysis will be closer to the actual average size, especially at larger crystallite sizes (Matyi et

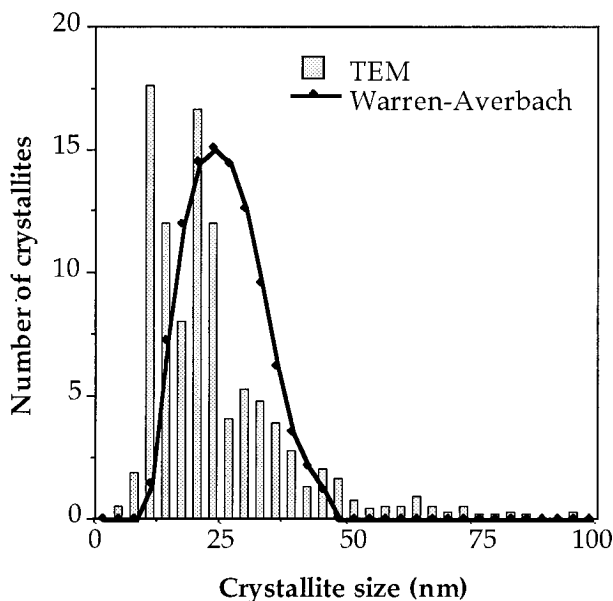


FIGURE 1. Comparison of size distribution of anatase measured from TEM photographs and calculated using Warren-Averbach method.

al. 1987). Particle size distribution information acquired from Warren-Averbach analysis was verified using size distributions measured from TEM images (Fig. 1).

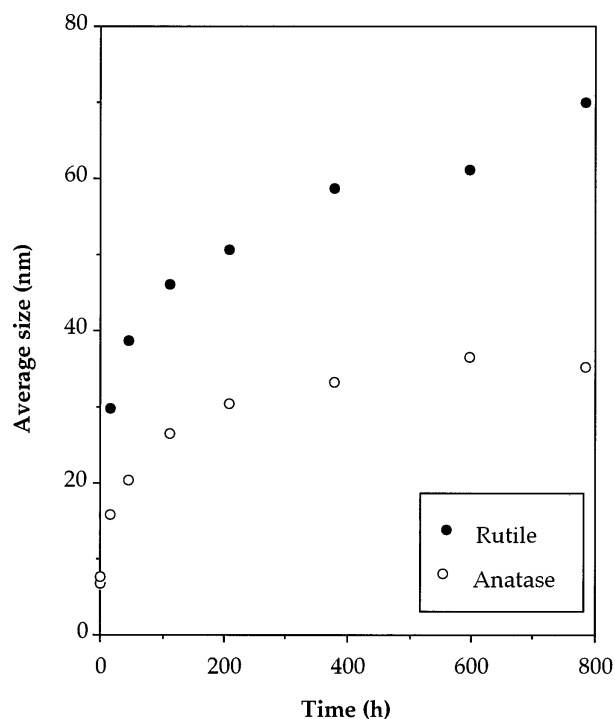
#### TEM analysis

Because of their small size, the crystallites composing the TiO<sub>2</sub> powder used in this study were electron transparent. Samples were prepared for TEM study by dispersing the TiO<sub>2</sub> powder on a holey carbon-coated Formvar® support. TEM analyses were performed using a Philips CM20 UltraTwin Electron Microscope.

### RESULTS

Kinetic experiments were performed at temperatures of 465, 480, 500, and 525 °C. Reproducible kinetic data were obtained from batches of anatase prepared using an identical synthesis procedure. Variation of the synthesis procedure produced materials of variable nanocrystalline anatase packing arrangements (Bischoff 1992) that show systematic differences in both coarsening and transformation rates.

Average size data indicate that grain growth of both anatase and rutile occurred during kinetic experiments. Average size for both anatase and coexisting rutile increased smoothly with time (Fig. 2), and the rate of coarsening of anatase and rutile increased a significant amount with temperature in the range of temperatures investigated in this study (Fig. 3). (For clarity, only anatase coarsening data are included in Figure 3. Coarsening data for rutile show a similar increase in coarsening rate with temperature.) No evidence was found for discontinuous grain growth either in the average size data calculated from XRD or in crystallite morphology observed by TEM.

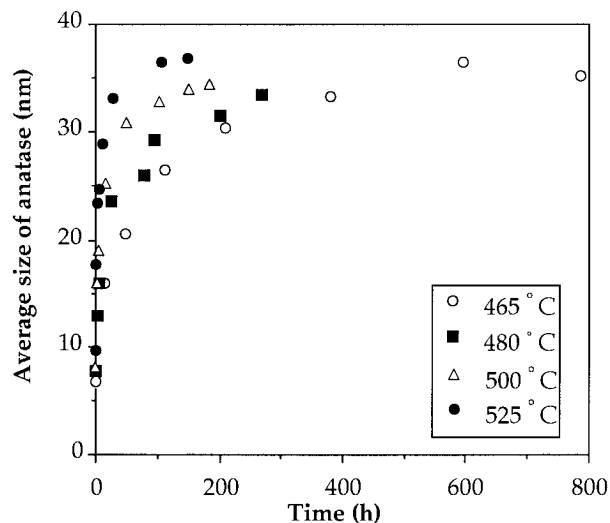


**FIGURE 2.** Average size of anatase and rutile vs. time for kinetic samples heated at 465 °C. Note that average size of rutile is larger than coexisting anatase and that over most of the experiment, rutile coarsens faster than anatase.

Note that rutile has a larger average size than the anatase from which it is transforming (Fig. 2).

Extent of reaction increased smoothly with time (Fig. 4). The rate of reaction increased significantly with temperature in the reported temperature range. A plot of transformation rate vs. coarsening rate of anatase (Fig. 5) reveals a linear correlation between the change in surface-weighted average size per hour and the percent transformation per hour at a given temperature. The larger slope for data collected at higher temperatures indicates that transformation rate has a greater temperature dependence than coarsening rate.

A correlation between coarsening and transformation is also observed in a plot of average size of anatase vs. percent transformation to rutile (Fig. 6). The size axis is intercepted at approximately 13 nm. Figure 7 shows that the average size of anatase in samples containing the first-detected rutile is consistent over a wide range of temperature and time. Note that this plot includes data from the kinetic experiments reported here and also data from similar experiments performed on a Y-doped and other undoped sol-gel-derived anatase. These additional data were included to display the breadth of the trend. Some of the scatter present is due to varying amounts of transformation of the samples (the range of percent transformation represented by data points is < 2 to 9.6%). Samples having undergone a greater percentage of transformation over-represent the average size of anatase containing the



**FIGURE 3.** Average size of anatase vs. time for kinetics experiments conducted at  $T = 465, 480, 500,$  and  $525$  °C.

first-formed rutile because of coarsening occurring simultaneously with the transformation.

Figure 8 shows the relationship between surface area and volume of the sample (assumed to be approximately proportional to the number of favorable nucleation sites for surface nucleation) and transformation rate for anatase crystallites having average diameters between 10 and 30 nm. At a given temperature, the trend for small, rapidly reacting particles is approximately linear.

Figure 9 shows coarsening rate of anatase and rutile vs. total surface area. Note that for a sample with any given total surface area, the coarsening rate for rutile is significantly greater than that of anatase.

Figure 10 compares anatase and rutile crystallite size distributions calculated using Warren-Averbach analysis for a kinetic sample reacted at 525 °C for 1.2 h that contained 9.6% rutile. Areas under the distribution curves were adjusted to reflect the relative amounts of anatase and rutile in the sample.

For comparison, kinetic experiments were performed on a commercial sample of coarsely crystalline anatase (average crystallite diameter 0.15  $\mu\text{m}$  by TEM). A sample of this material heated at 885 °C for 3.5 h underwent no detectable transformation to rutile. A sample of the same material heated to 1000 °C for 4.5 h transformed 97% to rutile.

## DISCUSSION

### Analysis and discussion of kinetic data

Conventional kinetic analysis entails identifying a rate law that accurately models the experimentally determined transformation vs. time curve. Standard rate laws differ in mathematical form depending on the reaction mechanism on which they are based. Ideally, the rate law that is found to accurately model the experimental kinetic data

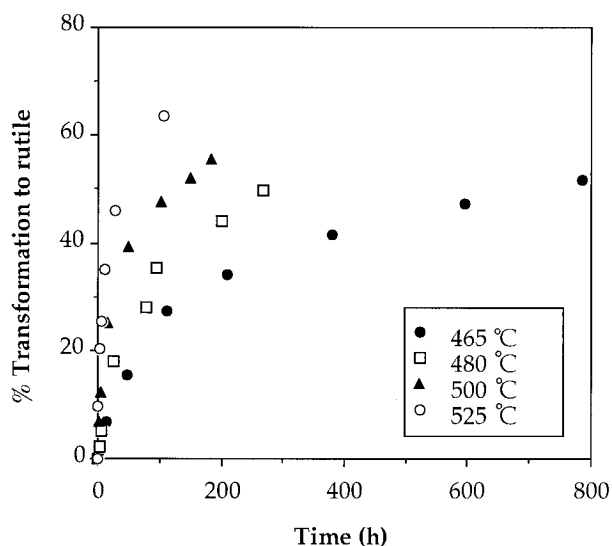


FIGURE 4. Percent transformation to rutile vs. time for kinetics experiments conducted at  $T = 465, 480, 500,$  and  $525$  °C.

is representative of the mechanism operating in the reaction being investigated.

Because standard rate laws do not take into account particle-size effects and because our experimental data indicate that there exists a significant particle-size effect on the transformation rate for nanocrystalline TiO<sub>2</sub>, it was expected that standard rate laws would be unable to model accurately the observed reaction kinetics for nanocrystalline TiO<sub>2</sub>.

To verify this inference, an attempt was made to model the reaction kinetics reported here for nanocrystalline TiO<sub>2</sub> with a rate law consistent with the reaction mechanism. To determine reaction mechanism, a TEM examination of partly transformed samples was conducted. Individual crystallites were found to be either entirely anatase or entirely rutile, and no partially reacted crystals were found. This observation suggests that once the transformation is initiated in an individual anatase crystallite, it proceeds rapidly through the entire crystallite. A rate law consistent with the transformation mechanism inferred from TEM observations, i.e., random nucleation of particles and rapid growth of nucleated particles, is given by  $\ln(1 - \alpha) = kt + C$ , in which  $\alpha$  = the fraction of transformation completed,  $k$  = the rate constant,  $t$  = time,  $C$  = a constant of integration (Jacobs and Thomkins 1955). Experimental data for nanocrystalline TiO<sub>2</sub> did not fit this rate law.

Further support for the conclusion that standard rate laws cannot be used to model reaction kinetics for nanocrystalline TiO<sub>2</sub> was provided by the failure of rate laws previously reported to model reaction kinetics accurately in coarsely crystalline TiO<sub>2</sub> (Czanderna et al. 1958; Rao 1961; Shannon and Pask 1965; Suzuki and Tukuda 1969) to fit the experimental data reported here for nanocrystalline TiO<sub>2</sub>.

We believe that conventional kinetic analysis fails in

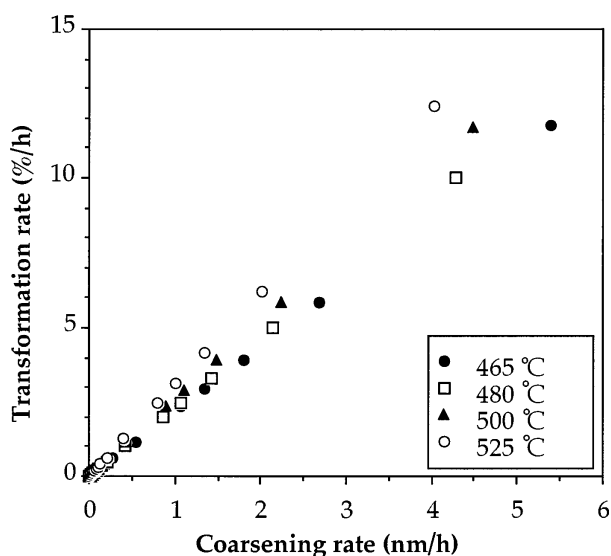
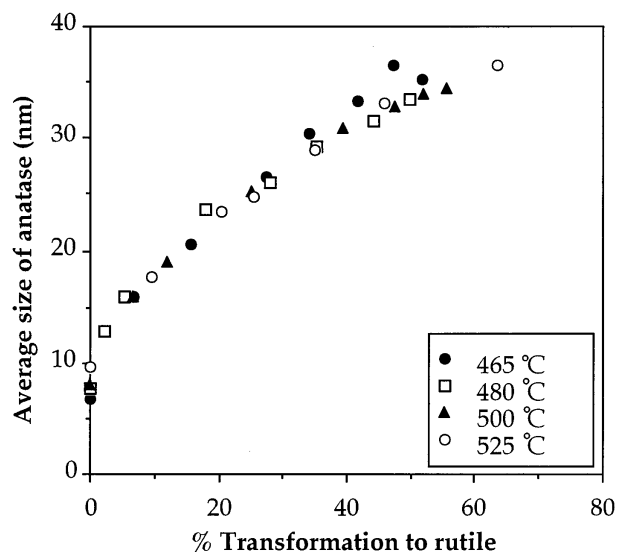


FIGURE 5. Plot showing the linear correlation between transformation rate and coarsening rate of anatase for kinetics experiments run at  $T = 465, 480, 500,$  and  $525$  °C.

the case of the anatase to rutile transformation in nanocrystalline TiO<sub>2</sub> because standard rate laws do not take into account particle-size effects. Before standard rate laws can be modified to account for a particle-size effect, the nature of the particle-size effect must be identified. We now pursue a qualitative investigation of the particle-size effect with the intent of identifying the size-related variable that is responsible for the increase in transformation rate in nanocrystalline TiO<sub>2</sub>. Fundamental factors controlling transformation rate will be identified, and of this group, those that are altered by small crystallite size will be further considered to determine if the affect of the size dependence is consistent with the experimentally observed increase in transformation rate with decrease in crystallite size.

To identify fundamental rate-controlling factors, the reaction mechanism must be known. In coarsely crystalline TiO<sub>2</sub>, the anatase to rutile transformation is a nucleation and growth process (Shannon and Pask 1964). This is consistent with the lack of common structural slabs (Banfield and Veblen 1992) and consequent significant structural changes necessary for the transformation. It is also likely that the transformation mechanism for finely crystalline materials is nucleation and growth.

The overall reaction rate for a nucleation and growth transformation is given by the product of the nucleation rate and the growth rate. In simplified terms, nucleation rate is equal to the product of a frequency term, a term related to the energy to form a thermodynamically stable nucleus, and the number of potential nucleation sites. The energy to form a thermodynamically stable nucleus may be further broken down into terms depending on the free energy change for the reaction, the energy to create an interface between the nucleus and the matrix, and the



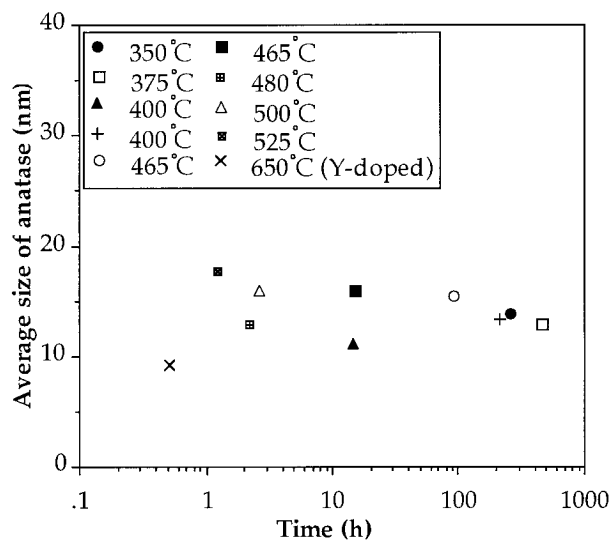
**FIGURE 6.** Average size of anatase vs. percent transformation to rutile for kinetics experiments conducted at  $T = 465, 480, 500,$  and  $525$  °C.

strain energy involved in the formation of a nucleus (this factor is important for solid-solid reactions such as the conversion of anatase to rutile, where a large volume change accompanies the transformation). The growth rate is equal to the product of a frequency term, the driving force for the reaction (free energy change for the reaction), and the energy for movement of atoms across the reaction interface. In summary, the fundamental factors determining rate for transformation of phase  $\alpha$  to phase  $\beta$  by a nucleation and growth mechanism are  $N_n$ , which is the number of potential nucleation sites;  $\Delta G_{\alpha \rightarrow \beta}$ , which is the difference in free energy between  $\alpha$  and  $\beta$  phase (driving force);  $\Delta G_i$ , which is the free energy to form an interface between nucleus of  $\beta$  and the  $\alpha$  matrix and  $\Delta G_{\text{strain}}$ , which is the strain energy associated with nucleus formation.  $\Delta G_d$  is the energy for atoms to cross the reaction interface. In general, one or more of these factors will limit overall reaction rate.

In the case of the anatase to rutile transformation, the observed size dependence of reaction rate indicates that the rate-limiting factor or factors are size dependent. Of the factors listed above, the number of potential nucleation sites (for reactions that are surface nucleated), the free energy change for the reaction, and the strain energy associated with nucleus formation are size dependent.

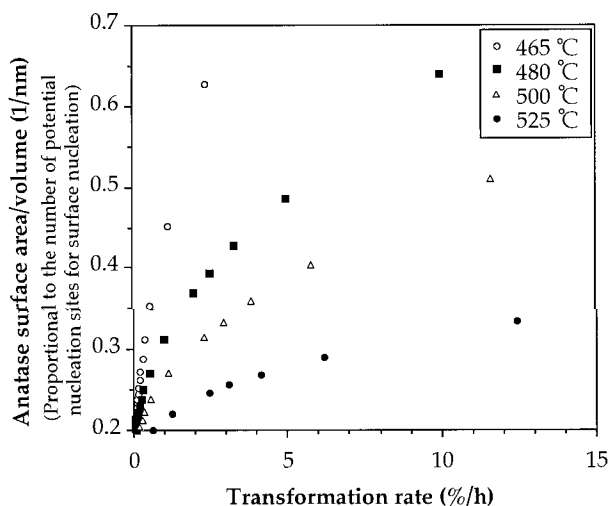
Consideration of the observed effect of particle size on reaction rate allows us to refine further the list of likely rate-limiting factors. The rate-limiting factor or factors must be altered by small particle size in such a way that transformation rate increases as size decreases. The expected effect on reaction rate of each of the size-dependent factors identified above will be considered in further detail.

For reactions involving surface nucleation, the number



**FIGURE 7.** Average size of anatase in kinetic samples containing the first-detected rutile. Data includes additional experimental data from other sol-gel derived samples of anatase that the trend is consistent for a wide range of temperatures and times.

of potential nucleation sites is proportional to total surface area of a sample for constant crystallite shape. In this case, the potential nucleation sites increase as the average crystallite size decreases for a sample of constant volume. Evidence for surface nucleation in the anatase to rutile transformation was previously reported. Shannon and Pask (1964) observed surface nucleation in coarsely crystalline anatase TiO<sub>2</sub>. Kumar (1993) concluded that surface nucleation of rutile occurs also in nanocrystalline anatase using non-isothermal Avrami analysis of differential scanning calorimetry (DSC) data. If surface nucleation does indeed occur in the anatase to rutile transformation in nanocrystalline TiO<sub>2</sub>, the increase in the potential nucleation sites is consistent with the observed trend of increasing reaction rate with decreasing size of reacting anatase crystallites. Another possible source of the size effect on anatase to rutile reaction rate is the change in driving force for the reaction at small crystallite size. The driving force for the reaction is the difference in free energy between the reactant and product phases. The free energy of an individual phase depends on particle size through surface energy contributions to total free energy according to  $G_{\text{total}} = G_v + \gamma_s \cdot (\text{surface area})$ , in which  $G_{\text{total}}$  is the total free energy of the phase;  $G_v$  is the molar free energy of the bulk;  $\gamma_s$  is the surface energy per unit area for the material; and surface area is a function of average crystallite size and is calculated in units of area per mole. If the surface energies of the reactant and product phases are unequal, then the difference in free energy between the phases, which is equivalent to the driving force for the transformation, will differ for finely and coarsely crystalline samples. Specifically, the difference in free energy varies with the inverse of crys-



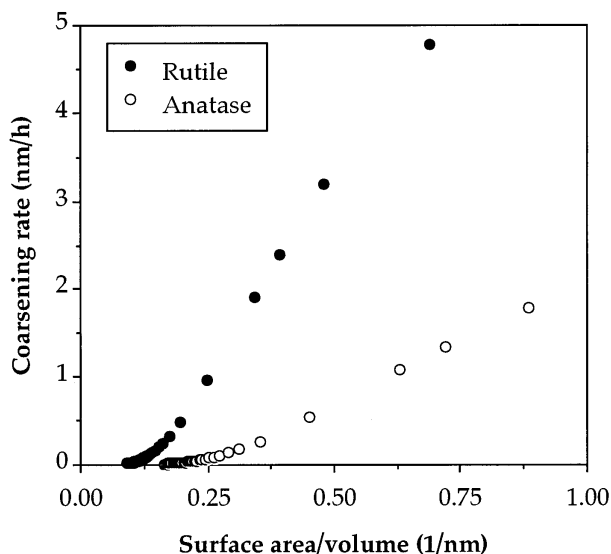
**FIGURE 8.** Total surface area per unit volume calculated using average anatase crystallite size vs. transformation rate. The approximately linear correlation at small crystallite sizes is consistent with the number of potential nucleation sites dominating reaction rate. (Surface areas of 0.6/nm and 0.2/nm are equivalent to average crystallite diameters of approximately 10 nm and 30 nm, respectively).

tallite size because of differing surface energy contributions to the free energy of the individual phases.

We have established that under the condition of differing surface energies of the phases involved, the driving force for a reaction is size dependent. For the change in driving force with crystallite size to be consistent with the experimentally observed increase in reaction rate with decrease in crystallite size, the free energy change for the anatase to rutile transformation must be increased (more negative) at small crystallite sizes, i.e., anatase must have a higher surface energy than rutile.

Current surface energy data for anatase and rutile is incomplete. For rutile, two theoretical estimates of the surface energy, 1.5 J/m<sup>2</sup> (Moinov and Reznichenko 1967) and 1.42 J/m<sup>2</sup> (Brace and Walsh 1962), and one experimental measurement of excess grain boundary enthalpy (closely related to grain boundary energy), 1.3–1.7 J/m<sup>2</sup> (Terwilliger and Chiang 1995), were found in the literature. No values of surface energy were found for anatase. Simple estimation methods scale surface energy with density and would therefore predict that anatase has lower surface energy than rutile. Experimental coarsening data reported here also supports a lower surface energy for anatase (Fig. 2). The driving force for coarsening is the lowering of total surface energy and is directly proportional to the surface energy of a material ( $\gamma_s$ ). Figure 9 shows that for the same total surface area, the coarsening rate of rutile is significantly faster than anatase. This difference in rate implies that there exists a greater driving force for the coarsening of rutile, which in turn implies that rutile has a higher surface energy than anatase.

If the theoretical and experimental evidence for anatase



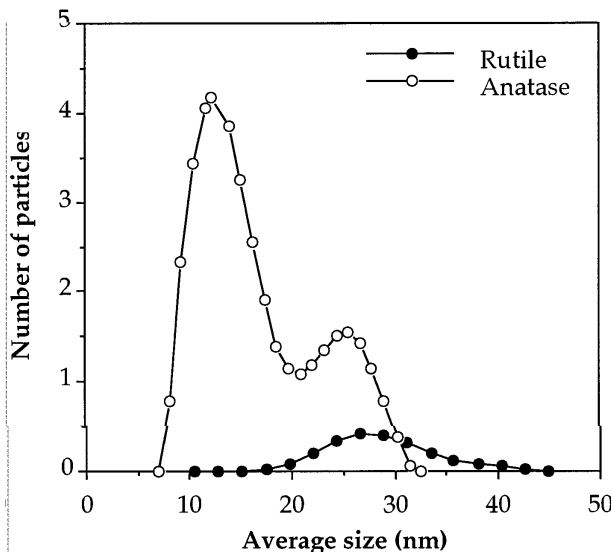
**FIGURE 9.** Coarsening rate of anatase and rutile vs. surface area showing that for the same total surface area, rutile coarsens significantly faster. (Surface area has been normalized to unit volume to allow comparisons with the total surface area present in a sample.)

having a lower surface energy than rutile is correct, the driving force for the anatase to rutile transformation decreases with decrease in crystallite size. This is inconsistent with the observed increase in reaction rate with decreasing crystallite size, and therefore, the free energy change for the reaction is unlikely to be the cause of the particle-size effect on reaction rate.

The final possibility to be considered as the cause of the increase in transformation rate at small particle size is the strain energy associated with nucleus formation. The strain energy associated with the formation of a rutile nucleus is likely to be significant because the molar volume of rutile is approximately 10% less than that of anatase. This strain energy may be affected by crystallite size through the pressure on small crystallites because of surface tension and surface curvature. The pressure because of surface tension is given by:

$$\Delta p = \frac{2\gamma}{r}$$

in which  $\Delta p$  is the increase in pressure on a crystallite with radius,  $r$ , over that of a flat surface, and  $\gamma$  is the surface tension of the material. The increase in pressure is mechanically equivalent to an applied hydrostatic pressure of  $\Delta p$  on the particle. Because of the negative volume change for the anatase to rutile transformation, such a hydrostatic pressure would reduce the strain energy associated with rutile nucleus formation. A reduction in the strain energy associated with nucleus formation can be considered a reduction in one of the energy barriers to the transformation, and such a reduction tends to increase reaction rate. Thus, the strain energy associated with nu-



**FIGURE 10.** Size distributions calculated by Warren-Averbach analysis for sample held at 525 °C for 1.2 h. Approximately 9.6% of the sample is rutile. Areas under distribution curves were adjusted to reflect relative amounts of anatase and rutile present in sample.

nucleus formation emerges as a possible cause of the observed size effect on transformation rate.

Of the size-dependent factors identified initially, two have been found to be qualitatively consistent with the increase in transformation rate at small crystallite size: the number of potential nucleation sites and the strain energy associated with rutile nucleus formation. There are several ways in which the relative importance of the two factors may be distinguished. The first is identification of the location of nucleation (surface vs. interior of crystallites). Evidence for nucleation in the interior of crystallites would eliminate the size dependence of the number of nucleation sites and would be consistent with a maximum reduction in strain energy for nucleus formation. Evidence for surface nucleation would support the hypothesis that the increase in nucleation sites at small crystallite size is of primary importance. (In this case, reduction of strain energy would also contribute to increased reaction rate because strain energy for nucleus formation would still be reduced, but not to the degree that it would be for nucleation in the interior of the crystal). As previously discussed, the observation of surface nucleation in coarsely crystalline TiO<sub>2</sub> (Shannon and Pask 1964) and Avrami analysis of DSC data from nanocrystalline TiO<sub>2</sub> (Kumar 1993) provide indirect evidence for surface nucleation in nanocrystalline TiO<sub>2</sub>. Further examination of kinetic samples to locate partially reacted crystals and find direct evidence for the location of nucleation, as well as to investigate the crystallographic orientation between the anatase and rutile, is the subject of ongoing research.

Distinguishing between the number of potential nucleation sites and strain energy may also be accomplished

by quantitative analysis of kinetic data. Experimental data show that a linear relationship exists between coarsening and transformation rates (Fig. 5). Coarsening rate is a function of size through total surface area, which is inversely proportional to diameter and so the observation that coarsening and transformation rate have the same functional form, as indicated by the linear relationship, suggests that transformation rate also depends on a variable that varies as 1/diameter.

Both the number of potential nucleation sites and strain energy vary as 1/diameter. However, the relationship of the two factors to overall transformation rate differs. Both factors are nucleation-related phenomena, and nucleation rate rather than growth rate is assumed to be rate limiting. This assumption is supported by TEM data, which indicate a low abundance of partially reacted crystals and support rapid growth rate relative to nucleation rate. The number of favorable nucleation sites is directly proportional to the nucleation rate, whereas the strain energy associated with nucleus formation is one of several terms composing the energy to form a thermodynamically stable nucleus, and the energy to form a stable nucleus is exponentially related to nucleation rate. Because nucleation rate is directly proportional to the overall transformation rate, transformation rate is directly proportional to the number of potential nucleation sites and exponentially dependent on the strain energy for nucleus formation.

If the number of potential nucleation sites is rate-limiting, a linear relationship between transformation rate and nucleation sites should exist because of the direct proportionality between the two quantities.

Figure 8 is a plot of transformation rate vs. total surface area of anatase (assumed to be directly proportional to the number of favorable nucleation sites for surface nucleation). In the range of total surface area of anatase of 0.6 to 0.2 nm<sup>2</sup>/nm<sup>3</sup> (corresponding to average diameters from 10 to 30 nm, respectively), there is an approximately linear trend, as is predicted if the number of potential nucleation sites is rate limiting.

At larger particle sizes (lower total surface area) transformation rate is faster than is consistent with the linear trend. However, transformation rates in the nonlinear region are slow (approximately 1% per hour and less) and correspond to small absolute amounts of transformation. The small amounts of excess transformation in this region is likely to be due to rutile coarsening at the expense of anatase. Figures 2 and 9 show that rutile continues to coarsen at larger sizes at which the coarsening of anatase has slowed to a negligible rate. In this region, rutile is likely to be coarsening at least in part at the expense of anatase crystallites. During coarsening, the flow of material occurs from the smaller crystals to the larger crystals because the larger crystals have a lower volume potential. In the samples considered here, the small crystals are predominantly anatase crystallites and the large crystallites are rutile. Therefore, rutile is likely to increase in volume by acquiring material at least partially from anatase crystallites, and this coarsening transformation may



explain the small amount of excess transformation at large crystallite sizes.

If the number of potential nucleation sites is the factor responsible for the observed size-effect on transformation rate, we expect that, for a given temperature, there will be a limiting size of anatase crystallite at which the number of nucleation sites have decreased to the point that the transformation rate will be negligible. This prediction is consistent with the experimental observation that coarsely crystalline samples of anatase undergo no noticeable transformation at the temperatures at which the transformation takes place rapidly in nanocrystalline materials. We also expect that as the temperature increases, the number of potential nucleation sites, as well as other rate-limiting factors involved, would become less important because of the greater available energy. This result may be occurring in the macrocrystalline anatase (diameter of  $\sim 0.15 \mu\text{m}$ ), which showed no detectable transformation of crystals held at 885 °C for 3.5 h but 97% transformation in material held at 1000 °C for 4.5 h. Thus, the number of nucleation sites emerges as the most probable cause of the increase in anatase to rutile transformation rate in nanocrystalline TiO<sub>2</sub>.

#### Phase stability as a function of crystallite size

The phenomenon of a size difference between coexisting anatase and rutile illustrated by Figure 2 has been previously reported. Sheinkman et al. (1984) studied the anatase-to-rutile transformation using high-temperature electron microscopy and attributed the larger size of rutile to recrystallization accompanying the transformation. Kumar (1995) presented evidence suggesting that the difference in average sizes is due to the critical size of the rutile nucleus being larger than the primary size of the anatase crystallites.

Conclusions reached in Sheinkman et al.'s study are not considered applicable to the discussion of data presented here because much higher temperatures (1000 °C) and larger initial anatase crystallite sizes (50–70 nm) were used in that work. In the range of temperatures used in this study, data that showed no evidence for significant discontinuous grain growth indicated that coarsening rather than recrystallization occurred.

Materials and conditions used in the study by Kumar (1995) are similar to those used in this study. Kumar argues that the larger average size of rutile results from the critical nucleus of rutile being larger than the average particle size of the primary crystallites of anatase. Kumar notes that for transformation of phase a to phase b by means of a nucleation and growth process, the radius of a stable nucleus b in a matrix of a is given by:

$$r_c = -2 \frac{g_i}{g_v + g_e}$$

in which  $g_i$  is the energy to create the interface between the a matrix and the b nucleus,  $g_v$  is the volume free energy difference between a and b (i.e., the driving force for the reaction) and  $g_e$  is the strain energy associated

with nucleus formation. Although it is not explicitly stated by Kumar, the  $g_i$  and  $g_e$  terms must be significant for the rutile critical nucleus size to be larger than the primary anatase crystallite size. In the case of the solid-to-solid anatase to rutile transformation, strain energy ( $g_e$ ) may very well be large from the large volume change accompanying the transformation (–10%), and it is conceivable that the critical size nucleus of rutile in a matrix of anatase is greater than that of the primary anatase crystallites (4–10 nm) from this strain energy.

It is important, however, to consider how the  $g_i$  and  $g_e$  terms associated with the formation of nuclei are altered in the situation occurring in nanocrystalline TiO<sub>2</sub>, in which the critical nucleus size approaches the primary size of the crystallites undergoing the transformation. Nuclei of rutile reach the critical nucleus size by random thermal fluctuations. If any rutile is formed in a sample of nanocrystalline anatase, then there exists enough thermal energy for rutile to reach the critical nucleus size. If there is enough thermal energy for random fluctuations to produce rutile nuclei of stable size, then there exists enough thermal energy for rutile to grow to sizes below the critical nucleus size, i.e., sizes in the range of the primary anatase crystallites. It is therefore possible that a random fluctuation could cause a rutile embryo (unstable nucleus) in a primary anatase crystallite to fluctuate to the size of the anatase crystallite. The result would be a small crystallite consisting entirely of rutile. At this point, we are no longer considering a nucleus of rutile in an anatase matrix, but an individual crystallite of rutile, for which both the  $g_i$  and  $g_e$  terms become zero. If rutile is the stable phase, as is assumed in Kumar's paper, then there exists no driving force for the small rutile crystallite to fluctuate back to an anatase crystallite. Hence, arguments using critical nucleus size are not applicable in cases in which critical nucleus size approaches primary crystallite size.

Critical nucleus size is also presented by Kumar (1995) as an explanation for crystallization of metastable anatase from solution. In this case, Kumar considered the critical radius to depend only on the volume free energy and the energy required to form a new surface (the new surface in this case being the interface between the solid-phase TiO<sub>2</sub> nucleus and the solution in which it is forming). Under the assumption that rutile is the stable phase,  $g_v$  will be more negative for the crystallization of rutile than for anatase, which, if considered independent of other factors, would result in the critical nucleus size of rutile to be smaller than that of anatase. Kumar's conclusion that rutile has a larger critical nucleus radius implies that the energy to form a new surface, the  $g_i$  term, for anatase is lower enough in magnitude than the value for rutile so as to overcome the effect of rutile having a more negative  $g_v$ .

We can estimate the necessary difference in magnitude of the  $g_i$  term for anatase to have a smaller critical nucleus size than rutile. Neglecting the strain energy to form a nucleus, which is reasonable in the case of crystallization

from solution in which the liquid matrix is able to expand to accommodate the forming crystallites, the critical nucleus radius will be given by

$$r_c = -2 \frac{g_i}{g_v}$$

in which  $r_c$  is the critical nucleus radius,  $g_i$  is the energy to create the surface of the nucleus, and  $g_v$  is the difference in free energy between the matrix and the nucleus. Using values of  $g_v$  for anatase and rutile based on the molar free energies of formation of  $-883.266$  and  $-889.406$  kJ/mol, respectively, at  $T = 298.15$  K (JANAF Thermochemical Tables 1985), one can calculate that the interfacial energy of anatase in solution needs to be 10% less than that of rutile for the critical nucleus radius of anatase to be smaller than that of rutile. [To be rigorously correct, the  $g_v$  values used for this calculation should be for TiO<sub>2</sub> (solution)  $\rightarrow$  TiO<sub>2</sub> (solid), rather than the free energy of formation values that were used above, so although the relative magnitude of the surface energies (anatase less than rutile) is correct, the absolute magnitude of the difference in surface energies may contain error.] Coarsening data presented in this report suggest that the surface energy of anatase is significantly smaller than the surface energy of rutile; thus, anatase having a smaller critical radius than rutile is a plausible explanation for crystallization of the metastable anatase phase from solution.

As an alternate explanation for both the observed difference in average size of coexisting anatase and rutile and the crystallization of anatase from solution, we propose that anatase is the stable phase of TiO<sub>2</sub> at very small crystallite sizes. This hypothesis may be explained theoretically in terms of the surface energy contributions to total free energy at very small crystallite sizes. The stability of one phase relative to another is based on the free energy difference between the phases. The experimentally measured difference in free energies of bulk anatase and rutile is small, 6.14 kJ/mol at 298.15 K (JANAF Thermochemical Tables 1985). If anatase has a surface energy per unit area that is less than 90% of the surface energy of rutile (the value of 90% is necessary to counteract the increase in surface area per volume for the less dense anatase phase), then there exists a critical size of anatase crystallite for which a rutile crystallite containing the same number of TiO<sub>2</sub> molecules has equal total free energy and for which smaller sizes of anatase crystallites have lower free energy than the corresponding rutile crystallites. (Note that to determine relative stability, equal amounts of TiO<sub>2</sub> must be considered and that crystallites of anatase and rutile having the same number of TiO<sub>2</sub> formula units will not be the same size because of unequal densities.)

We may evaluate the magnitude of the critical size for anatase stability (not to be confused with critical nucleus size) using a value of 1.5 J/m<sup>2</sup> for the surface energy of rutile (average of reported values) and assuming that the surface energy of anatase is 85% of this value (1.275

J/m<sup>2</sup>). (The estimate that the surface energy of anatase is 85% of that of rutile is used to demonstrate the order of magnitude of the surface energy effect and was chosen based on the conditions that 85% is a physically reasonable difference in surface energies and is below the limit for observable effect of 90%.) According to  $G_{\text{total}} = G_{\text{volume}} + \gamma_s \cdot (\text{surface area/volume})$  and inserting the specified values, the total free energy of anatase crystallites is lower at diameters of 2.8 nm and below than rutile particles containing the same number of TiO<sub>2</sub> molecules (diameters of 2.7 nm and below). Thus, under the condition that the surface energy of anatase is at least as small as 85% that of rutile, anatase is the stable phase of TiO<sub>2</sub> for crystallites having diameters of 2.8 nm and below. If the surface energy of anatase is less than 85% of the surface energy of rutile, anatase will have an even larger critical size, i.e., be stable up to even larger crystallite sizes. If the surface energy of anatase is between 85 and 90% of the surface energy of rutile, the critical size will be less than 2.8 nm and rapidly approach zero as the surface energy of anatase approaches 90% of that of rutile. Coarsening data reported here (Fig. 9) strongly suggest that the surface energy of anatase is significantly smaller than that of rutile and likely to be in the range necessary to reverse the stabilities of anatase and rutile at a physically reasonable crystallite size.

The proposed reversal of stabilities of anatase and rutile at small crystallite size resolves the question of why the "metastable" anatase phase is the majority product of industrial (Lowenheim and Moran 1975), sol-gel (Bischoff 1992), and aerosol (Juillet et al. 1973) synthesis methods for TiO<sub>2</sub>. Presumably in all syntheses, solid phase TiO<sub>2</sub> begins as a cluster of a few molecules. Because the largest structural unit shared by anatase and rutile is only two TiO<sub>6</sub> octahedra (compared with the over 300 octahedra present in a 2.8 nm diameter particle), the phase of the TiO<sub>2</sub> nuclei that crystallizes from solution or aerosol is determined at very small crystallite sizes at which anatase may in fact be the stable phase and thus possess the greater driving force for crystallization.

The hypothesis of size-dependent stability can also explain the discrepancy in average size of the first-formed rutile and coexisting anatase (Fig. 2). Figure 10 shows that the larger average size of the rutile crystallites is not the result of the majority of rutile crystallites actually being larger than the coexisting anatase, but rather is due to the relatively tight rutile size distribution being located at the large-size end of the anatase size distribution. We propose that this relationship between the size distributions is primarily the result of preferential transformation of the largest crystallites in the anatase size distribution. TEM evidence suggests that individual crystallites of anatase transform rapidly and completely to rutile, and if this does occur, then immediately following transformation, rutile crystallites will be approximately the size of the parent anatase crystallite (a slight difference in size would occur from the differing densities of the materials). Under the conditions of rapid transformation of individual

crystallites of anatase, the rutile size distribution in Figure 10 from an early stage in the transformation (sample is 9.6% transformed to rutile) is approximately representative of the size distribution of the parent anatase crystallites and shows that the parent anatase crystallites are found at the large-size end of the anatase size distribution.

Because rapid coarsening occurs in both anatase and rutile in the early stages of the experiment and rutile coarsens faster than anatase, the locations of and relationship between the size distributions at 9.6% transformation (Fig. 10) cannot be considered an exact determination of the size of the first-formed rutile crystallites or of the relationship of the size of the first-formed rutile crystallites to the anatase size distribution. The faster coarsening rate of rutile undoubtedly contributes in part to the relative location of the rutile size distribution. However, it is unlikely that the faster coarsening rate of rutile is solely responsible for the much larger average size of rutile at early times in the reaction when the faster rate has had little time during which to produce a significant effect.

Preferential transformation of the large crystallites in the initial anatase size distributions is consistent with size-dependent stability, as proposed in the critical size hypothesis, in the following manner: to initiate transformations that are kinetically inhibited, such as the solid-solid anatase to rutile transformation, it is often necessary to overstep the equilibrium transition point to provide enough driving force to overcome kinetic barriers. The critical size hypothesis proposes phase stability as a function of size and an equilibrium transition size for anatase. Again using values of  $\gamma_{s, \text{rutile}} = 1.5 \text{ J/m}^2$  and  $\gamma_{s, \text{anatase}} = 0.85 \cdot \gamma_{s, \text{rutile}}$ , one can calculate that the driving force for the anatase to rutile transformation changes from 0 kJ/mol at the hypothetical equilibrium transition size of 2.8 nm to 4.84 kJ/mol (80% of the limiting value of bulk TiO<sub>2</sub>) for a 13 nm anatase crystallite (approximate size of first-detected rutile, Fig. 7). The apparent size constraint on the initiation of the transformation is supported by experimental data that show the size of the anatase containing the first-detected rutile over a wide range of temperature and time (Fig. 7) is approximately the same. This may represent the necessary amount of coarsening anatase must undergo over and above the equilibrium transition size, at which point the driving force for the transformation is zero, so that enough driving force exists to initiate the transformation. Thus, we propose that the difference in average size of coexisting anatase and rutile in the initial stages of the reaction is due mainly to the preferential transformation of the large crystallites of the anatase size distribution, which, according to the critical size hypothesis, are the least stable crystallites in the distribution and thus experience the greatest driving force for transformation.

As a final point, we would like to address an apparent contradiction between the proposed increase in stability of anatase at small crystallite sizes and the observed increase in transformation rate at small crystallite sizes.

This contradiction is resolved by the distinction between thermodynamics and kinetics. As discussed in the section on kinetics, reaction rate depends on many factors, only one of which is the driving force for the reaction. A decrease in driving force with decrease in crystallite size, as is consistent with the critical size hypothesis, is not in conflict with the observed increase in reaction rate; however, it would indicate that the free energy change for the reaction is not a rate-limiting factor for crystallites at small crystallite sizes.

In summary, particle-size effects are clearly important to transformation kinetics and phase stability for very finely crystalline materials. Experimental data reveal extensive correlations between coarsening and transformation in nanocrystalline TiO<sub>2</sub> (Figs. 3–6). Analysis of these relationships suggests the number of potential nucleation sites is the rate-limiting factor in the anatase to rutile transformation at low temperatures. Pressure on small anatase crystallites from surface curvature may also promote reaction rate by reducing the strain energy accompanying the formation of a rutile nucleus, although the relative importance of this factor has not yet been determined. Additionally, our experimental data and theoretical analysis suggest that the stabilities of anatase and rutile may reverse when surface energy contributions to total free energy exist that make anatase the stable phase at very small crystallite sizes.

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