Kinetic model for transformation from nano-sized amorphous TiO₂ to anatase*Giridhar Madras**

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Abstract

We propose a kinetic model for the transformation of nano-sized amorphous TiO₂ to anatase with associated coarsening by coalescence. Based on population balance (distribution kinetics) equations for the size distributions, the model applies a first-order rate expression for transformation combined with Smoluchowski coalescence for the coarsening particles. Size distribution moments (number and mass of particles) lead to dynamic expressions for extent of reaction and average anatase particle diameter, which are compared with experimental data [*Chem. Mater.* 2002, **14**, 4145]. Data at different temperatures yield activation energies for coalescence and transformation rate coefficients, as well as an overall endothermic transformation energy for combined transformation and dehydration.

Keywords: solid-solid transformations, amorphous titania, anatase, coarsening by coalescence

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Introduction

Titanium dioxide has been extensively investigated to understand its photocatalytic, electronic, and optical properties. Applications include the photocatalytic oxidation of organic pollutants for water purification; electrical devices such as sensors, batteries, and capacitors; and pigment additives. Nanocrystalline TiO₂ exists in several polymorphic forms¹, including amorphous and anatase². The transformation between polymorphs involves fundamental issues of kinetics and thermodynamics, and has been intensely investigated both experimentally and theoretically^{3,4,5,6}. TiO₂ polymorph transformations occur at high temperatures and involve a solid phase reaction with attendant dehydration. Associated with the heating, coarsening by coalescence reduces the surface energy. As different polymorphs are more or less stable because of surface energy effects, the coarsening profoundly influences the transformation process. For a particular size particle, the most stable polymorph will be favored as the transformation product¹.

We have recently investigated⁷ TiO₂ transformation from anatase to rutile, which occurs at temperatures higher than the amorphous to anatase reaction. A distribution kinetics model was proposed to represent the transformation and concomitant coarsening of TiO₂. Based on population balance equations for the size distributions of the dimorphs, the model applied a first-order rate expression for transformation combined with Smoluchowski coalescence for coarsening of anatase and rutile particles. Two moments of the size distributions (number and mass of particles) led to dynamic expressions for extent of reaction and average particle diameter. The model quantitatively described the time-dependent data of Banfield and coworkers^{4,5} reasonably accurately, and provided activation energies for anatase coalescence and transformation. The temperature dependence of the equilibrium constant for the microscopically

reversible transformation revealed an endothermic enthalpy change, which was attributed to the accompanying dehydration.

We propose to model the transformation of nanometer-sized amorphous TiO₂ to anatase in the same manner, representing coalescence by classical Smoluchowski theory and transformation by an overall first-order reaction. The model is based on two assumptions; first, we consider that coalescence is the dominating mechanism of coarsening. Second, the microscopically reversible transformation from A (amorphous) to B (anatase) for nanoparticles is assumed independent of size. The rationale is that diffusion-limited reaction processes will be extremely rapid in ultra-small particles. The processes defining the assumed mechanism satisfy TiO₂ mass (x) conservation,

where k_p and k_r are the first-order rate coefficients for the microscopically-reversible polymorph transformation from A to B and B to A, respectively.

Equation (1) is written as an equilibrium or chemical reaction, with forward and reverse rate constants whose ratio defines the equilibrium constant. This formalism is appropriate for a solid-solid transformation because each TiO₂ particle (and its associated water) is in fact behaving like a large molecule or cluster during the transformation. Our physical picture of the transformation is that it occurs independently in each particle, each acting like a large molecule undergoing a chemical reaction. Because transformation is faster than agglomeration,

coarsening, or sintering, it determines the local equilibrium. The rates of transformation reflect the number of particles transforming in unit time. The model is formulated in terms of numbers of particles, not moles of TiO₂ and thus the model treats the particles as each representing a large molecule. Nevertheless, the overall transformation is first-order and has a latent heat.

Along an equilibrium phase boundary, two or more phases, for example, two polymorphs in a single component system, may be in equilibrium. In case of interfaces and very small particles, the system can be in a series of constrained equilibrium states, for example, at constant number of atoms per particle. Thus this process is intermediate between that of large molecular clusters in solution (to which Eq 1 clearly applies) and bulk crystalline solids in which surface effects can be neglected and the Gibbs phase rule can be applied in a classical sense. Once hydration is considered, the two types of particles, A and B, are no longer even of the same composition. It is a chemical reaction with bonds in the crystal breaking apart and reforming in different conformations. Our approach is consistent with a thermodynamic treatment of a reversible chemical reaction, rather than a first-order phase transition. Thus, in our interpretation, the reversible transformation from A to B is effectively a chemical reaction with nonzero heat of transformation. The release of H₂O (dehydration) during the transformation further supports this view. The ratio $K = k_p/k_r$ is a local, microscopic equilibrium constant that refers to the transformation as it is occurring, not to the final state of lowest free energy. Equation 1 thus applies, not for macroscopic thermodynamic equilibrium, but only microscopically under the constraint of the initial particle sizes. In Eq 1, H₂O loss by dehydration also occurs, but is not explicitly written in the TiO₂ mass action representation. The proposed model differs from other approaches by combining microscopic Eq 1 with the observed macroscopic coalescence processes of Eqs 2 and 3.

The temperature-dependent parameters, k_A and k_B , in Eqs 2 and 3 are the coalescence rate coefficients for particles A and B. For continuous distributions the population balance equations^{8,9} are written,

$$\begin{aligned} \partial c_A(x,t)/\partial t = & -2 k_A c_A(x,t) \int_0^\infty c_A(x',t) dx' + k_A \int_0^x c_A(x',t) c_A(x-x',t) dx' \\ & - k_p c_A(x,t) + k_r c_B(x,t) \end{aligned} \quad (4a)$$

and

$$\begin{aligned} \partial c_B(x,t)/\partial t = & -2 k_B c_B(x,t) \int_0^\infty c_B(x',t) dx' + k_B \int_0^x c_B(x',t) c_B(x-x',t) dx' \\ & + k_p c_A(x,t) - k_r c_B(x,t) \end{aligned} \quad (4b)$$

The mass moments are defined as

$$c_i^{(n)}(t) = \int_0^\infty c_i(x,t) x^n dx \quad (5)$$

where $n = 0$ and 1 are respectively the number and mass of amorphous ($i = A$) and anatase ($i = B$) particles. We define a temperature-dependent equilibrium constant, $K = k_p/k_r$, and apply the integration over x to Eq 4a and 4b to derive the moment equations,

$$dc_A^{(0)}/dt = -k_A \{c_A^{(0)}\}^2 - k_p [c_A^{(0)} - K^{-1} c_B^{(0)}] \quad (6)$$

$$dc_B^{(0)}/dt = -k_B \{c_B^{(0)}\}^2 + k_p [c_A^{(0)} - K^{-1} c_B^{(0)}] \quad (7)$$

$$dc_A^{(1)}/dt = -k_p [c_A^{(1)} - K^{-1} c_B^{(1)}] \quad (8)$$

and

$$dc_B^{(1)}/dt = + k_p [c_A^{(1)} - K^{-1} c_B^{(1)}] \quad (9)$$

As in an earlier study, we formulate kinetics in terms of particle numbers. Here, assuming coalescence is second-order and transformation first-order in particle numbers immediately yields Eqs 6 and 7 by mass action kinetics. Equations 8 and 9 are simply mass conservation relations.

Simultaneous differential Eqs 6 and 7 can be readily solved numerically. For the special case $1/K = 0$ ($k_r = 0$), an analytical solution can be obtained in terms of the initial condition,

$$c_A^{(0)}(t=0) = c_{A0}^{(0)},$$

$$c_A^{(0)}(t) = c_{A0}^{(0)} \exp(-k_p t) / [1 + (k_A/k_p) c_{A0}^{(0)} (1 - \exp(-k_p t))] \quad (10)$$

and provides a convenient check of the numerical computation. Simultaneous Eqs 8 and 9 can be integrated analytically; in terms of the initial conditions, $c_A^{(1)}(t=0) = c_{A0}^{(1)}$ and $c_B^{(1)}(t=0) = c_{B0}^{(1)}$, the solutions are

$$c_A^{(1)}(t) = c_{A0}^{(1)} (1 + K)^{-1} \{1 + K \exp[-k_p (1 + 1/K) t]\} \quad (11)$$

$$c_B^{(1)}(t) = c_{B0}^{(1)} + c_{A0}^{(1)} - c_A^{(1)}(t) \quad (12)$$

where Eq 12 is a mass balance between initial masses of A and B and their values at any time t .

The fractional transformation is defined as

$$\alpha(t) = 1 - c_A^{(1)}(t)/c_{A0}^{(1)} = 1 - (1 + K)^{-1} \{1 + K \exp[-k_p (1 + 1/K) t]\} \quad (13)$$

where Eq 11 has been substituted. Rearranging Eq 13 yields

$$-K (1 + K)^{-1} \ln [1 - \alpha (1 + 1/K)] = \chi = k_p t \quad (13a)$$

where χ , defined as the left-hand side of Eq 13a, involves the amorphous weight fraction. The average particle mass is the ratio of first to zeroth moments,

$$c_A^{avg}(t) = c_A^{(1)}/c_A^{(0)} \quad \text{and} \quad c_B^{avg}(t) = c_B^{(1)}/c_B^{(0)} \quad (14)$$

and is related to the average diameter D_B^{avg} of the spherical B particles by

$$D_B^{avg}/D_{B0}^{avg} = [c_B^{avg}(t)/c_{B0}^{avg}]^{1/3} \quad (15)$$

in terms of the initial value, $D_B^{avg}(t=0) = D_{B0}^{avg}$.

Results and discussion

The equilibrium constant K and rate coefficient k_p are obtained by regressing experimental data of the transformation such that a linear plot of the parameter for amorphous weight fraction, χ , is linear with time with a slope of k_p , as indicated by Eq 13a. The experimental data and the linear regression are shown in Figure 1.

The time variation of the average particle size of anatase is obtained by solving Eqs 6 and 7 numerically by Mathematica® for the zeroth moment. Then one substitutes the expression for the first moment (Eq 11) into Eq 14 with values of K and k_p obtained from Figure 1. The values of k_A and k_B are obtained by nonlinearly regressing the experimental data² for the variation of average particle diameter with time at various temperatures (Fig 2) and were found to be equal to 12 and 1.2 times k_p , respectively, at all temperatures. The satisfactory fit of the model to a variety of experimental data supports the validity of the model.

Figure 3 shows the Arrhenius plot depicting the variation of the rate coefficient, k_p , and the equilibrium constant, K , with temperature. The activation energy for k_p , obtained from linear regression of the Arrhenius plot, is $E_p = 89$ kJ/mol. Because k_A and k_B are multiples of k_p , the activation energies of all the rate coefficients are the same. From the slope of the Arrhenius plot of equilibrium constant, the heat of transformation can be determined as $\Delta H = 51$ kJ/mol. The value is endothermic principally due to the heat needed for dehydration.

In summary, we have developed a kinetic model based on distribution kinetics that successfully simulates the experimental data for the transformation of nano-sized amorphous TiO₂ to anatase.

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Figure Captions

Figure 1. Time dependence of variable χ for amorphous to anatase transformation. The points represent experimental data² and the lines are based on the current model (Eq 13a).

Figure 2. Time dependence of the average particle size at various temperatures. The points represent experimental data² and the lines are based on the current model (Eq 15).

Figure 3. Arrhenius plots of the equilibrium constant (K) and rate coefficients for coalescence (k_A) and transformation (k_p).

Figure 1.

Figure 2.

Figure 3.

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