Morphology development and crystal growth in nanocrystalline aggregates under hydrothermal conditions: Insights from titania

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Abstract—High-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) peak broadening (Scherer) analysis were used to study coarsening and morphology development of nanocrystals. Experimental work used synthetic, equidimensional anatase (TiO₂) particles about 5 nm in diameter. Under hydrothermal conditions (100–250°C, 15–40 bars), rapid growth occurs along [001], driven in part by the relatively high surface energy of [001] and in part by a kinetic effect involving a cyclic generation of highly reactive adsorption sites. Rapid growth along [001] depresses the <101> growth rate until [001] surfaces shrink to a critical cluster size. A second major coarsening mechanism significantly reduces the surface energy, especially under acidic conditions. This mechanism involves topotactic attachment of primary particles at high energy surfaces (most commonly [112], less commonly [001]) and can result in elongate single crystals. Oriented attachment may be an important coarsening mechanism under a wide range of conditions encountered in the laboratory and in natural environments.

1. INTRODUCTION

The vast majority of materials produced by chemical weathering and microbial alteration of natural minerals are nanocrystalline. These high surface area materials are extremely reactive constituents of soils and sediments (Gribb and Banfield, 1997; Banfield and Hamers, 1997). The stability, behavior, and fate of these materials over geologic time are critically dependent upon initial size and morphology. Furthermore, relationships among particle size, phase stability (Gribb and Banfield, 1997; McHale et al., 1997), and materials properties such as piezoelectricity, surface reactivity, magnetism, and ductility are extremely important (Siegal, 1996; Matijevic, 1986). Thus, understanding coarsening behavior and morphology evolution is critical for efficient materials synthesis and quality control.

In general, studies of crystal growth and morphology evolution involve analysis of interactions between ions or molecules and crystal surfaces. Classically, coarsening has been described in terms of growth of large particles at the expense of smaller particles, driven by surface energy reduction (Ostwald ripening). In this paper we present results that show that a second mechanism of crystal growth may be especially important in the nanocrystalline regime. The effects of additives and impurities on surface energy, ion availability, and steric hindrance are also considered. Our results provide important insights into the ways in which nanocrystals change under hydrothermal conditions that may be generally relevant to crystal growth under diverse natural and laboratory conditions.

2. EXPERIMENTAL PROCEDURES

Nanocrystalline anatase (~5 nm in diameter) was synthesized via the sol gel method (Bischoff, 1992; Gribb and Banfield, 1997). Following synthesis, anatase sols were dialyzed using a Spectra/Por (MWCO = 2000) membrane in DI water (changed 11 times) to remove the byproducts of synthesis. Prior to dialysis, sols of anatase had not gelled and had low viscosity (similar to that of water). Following dialysis, the sols had gelled and were highly viscous, indicating that the pH had risen to near the isoelectric point of anatase (measured pH ~ 5.5). This coincides with the isoelectric point range reported by Bischoff (1992).

Suspensions (~3 mg anatase/g sol) were placed in the Teflon cups of Parr Instrument Company’s 4744 general purpose acid digestion bombs and heated in a furnace at temperatures ranging from 100°C to 250°C (internal bomb pressures were 15–40 bar) for times ranging from 1 h to 255 h. Bombs were removed and allowed to cool to room temperature. The H⁺ activities at hydrothermal conditions were estimated based on room temperature pH measurements using Soluble, a FORTRAN program that calculates speciation (Roselle and Baumgartner, 1995). Equilibrium constants for hydrochloric acid were taken from Sverjensky et al. (1991).

Hydrothermally treated sols were diluted, and one drop of diluted sol was placed onto a Formvar® coated copper grid for examination using the Philips CM200 200 kV HRTEM with a Cs aberration corrector.

Several drops of undiluted sol were placed on a zero-background quartz plate and allowed to dry for XRD analysis. Scans were performed using the Scintag PAD V four-axis X-ray diffractometer, a step size of 0.01°, and a count time of at least 5 s per step ranging from 21° to 41° 2Θ. Particle size was determined from peak broadening using Scintag’s DMSNT software and the Pearson VII profile peak shape. Instrumental broadening was determined by profile fitting the <101> and [001] peaks of three different scans of macrocrystalline anatase (verified by TEM to be crystalline and to have d > 1 µm) on a zero-background quartz plate. After subtracting the instrumental broadening from the DMSNT generated full width at half maximum, particle size was calculated using the Scherer equation with a prefactor of 0.94. Particle sizes were measured only for the <101> and [001] peaks due to intensity constraints.

It is well known from diffraction theory that the Scherer equation is biased toward larger particles because it measures the volume rather than surface area weighted average. This is consistent with the TEM versus XRD results of Gribb and Banfield (1997). However, these authors showed that the Scherer size can be effectively used to study particle size evolution, especially when the size distribution is fairly tight and the particle size is small.
3. RESULTS

3.1. Titania Hydrothermally Coarsened in DI Water

The starting material (Fig. 1) consists mainly of small (∼5 nm) equidimensional particles. XRD data analysis shows that anatase crystals treated hydrothermally do not coarsen equidimensionally. Rather, growth occurs in three stages involving different average growth rates along [001] and <101> (Fig. 2). The first stage involves rapid growth along [001] and slower growth along <101>. During the second stage, growth continues to be rapid along [001] but slows dramatically along <101>. The third stage of particle growth involves an acceleration of <101> growth and a deceleration of [001] growth. Finally, growth rates along both [001] and <101> are approximately equal. These distinct growth stages are most clearly seen in the dependence of the ratio of the magnitude of average crystallite size along [001] to that along <101> with time. This ratio exhibits a maximum from 10 to 50 h in response to slow growth along <101>, and the ratio decreases coincident with the acceleration of growth along <101> (Fig. 3).

TEM data show the development of a bimodal population of particle types as particles coarsen: smaller equidimensional particles similar to the starting material and larger particles with well developed faceting (Fig. 4). Morphology development is first observed in particles in the 7–10 nm range, and particles larger than 10 nm consistently show well developed morphology.

A second coarsening mechanism is also observed. TEM data show that anatase particles can attach at crystallographically specific surfaces, forming elongate single crystals composed of two or more primary crystallites. In anatase coarsened in DI water, this behavior occurs infrequently. However, it is a common mechanism when the pH of the suspension is decreased to 3.0 using hydrochloric acid.

3.2. Titania Hydrothermally Coarsened in HCl Solutions

The addition of hydrochloric acid to titania suspensions dramatically changes coarsening rates and the morphological
development of anatase particles. Specifically, the data suggest a diminished difference between the [001] and $<101>$ growth compared to that observed in DI water trials (Fig. 5). Of greater significance, however, is the increased frequency of coarsening by oriented attachment. Our results show that the importance of this mechanism is strongly dependent on acid concentration. It is common in suspensions prepared with HCl ($-\log[a_{H^+}] = 3.0$ under hydrothermal conditions) and frequently produces single crystals composed of more than 10 primary crystallites (Fig. 6). Figure 7 shows the evolution of the chains of particles, starting with the attachment of two primary crystallites. Attachment appears to occur most commonly on [112], less commonly on (001), and rarely on [101]. Increasing concentration of HCl to 0.01 M ($-\log[a_{H^+}] = 2.1$ under hydrothermal conditions) and 0.13 M ($-\log[a_{H^+}] = 1.2$ under hydrothermal conditions) does not result in enhanced frequency of particle attachment. Rather, the frequency of attached particles is similar to that observed in additive-free suspensions. The same is
true for suspensions adjusted using NaOH \((-\log[a_{H^{+}}] = 8 - 11)\).

Particle size along [001], determined by XRD, typically does not reflect coarsening due to oriented attachment. This is because junction on {112} forms chains the long axes of which are inclined to [001], parallel to 112°.

3.3. Titania Hydrothermally Coarsened in Solutions of Organic Compounds

Addition of organic compounds to suspensions prior to hydrothermal treatment dramatically effects coarsening. TEM data indicate suppression of the oriented attachment coarsening mechanism when glycine is added to 0.001 M HCl suspensions. In addition, XRD reveal that the presence of glycine in solution results in a dramatic suppression of the period of fast growth, or fastest growth along [001] (Fig. 8). Other organic acids, such as acetic acid and adipic acid, also suppress the oriented attachment mechanism. The details of the interactions between organic molecules and surfaces will be reported separately (Penn and Banfield, in prep.).

4. DISCUSSION

Two primary coarsening mechanisms were observed. The first involves single particle growth via addition of Ti ions to surfaces from solution at rates that depend on temperature, additives, and the crystal structure and energies of crystallographically distinct surfaces. The second mechanism involves growth by addition of solid particles to surfaces. This occurs in a precise, crystallographically controlled manner, resulting in coherent interfaces and leading to the development of single homogeneous crystals. Twinning and other intergrowths can occur because attachment requires structural accord only in the two dimensions defined by the junction plane (see Penn and Banfield, 1998a, and Uyeda et al., 1973). Furthermore, misorientations produced by twists and tilts at the plane of attachment can produce defects, ranging from pure tilt to pure screw dislocations (see Penn and Banfield, 1998b and Chun et al., 1995).

4.1. Morphology Evolution

Reduction in surface energy is the primary driving force for simple particle growth and morphology evolution is driven by the further reduction in energy due to minimization of the area of high surface energy faces. Preliminary growth from equidimensional primary particles is characterized by rapid development of morphology, resulting in formation of distinctly faceted crystallites dominated by [101] surfaces. This is followed by a period in which growth along [001] far exceeds growth along <101> and, thus, (001) faces are shrinking. The fact that growth along <101> nearly stops during the period of rapid [001] growth suggests a solubility limited system. Work by Willis (1992) on titanium ion speciation in hydrothermal aqueous solutions supports this possibility (titanium ion concentrations were typically calculated to be in the ppb range, even at high temperature and low pH).

Detailed examination of the advancing crystal faces and an understanding of the relative surface energies of crystal faces leads to an expectation that particle morphologies will be dominated by [101] and that growth along [001] will be rapid in comparison to [101]. Donnay-Harker (1937) rules predict that the surface energy of the (001) faces is approximately 1.4 times that of the {101} faces. Considering growth to be perpendicular to a particular set of faces, crystal morphology will be defined by the slowest growing faces because the fastest...
growing faces shrink (Mullin, 1972). However, we propose that there is an additional structure-related reason for rapid growth on (001). Figure 9a is a schematic of an anatase nanocrystal viewed down [010]. Shaded octahedra contain Ti (darkest shading indicates Ti at $y = 0, 1.0$; intermediate shading indicates Ti at $y = 0.5$) and unshaded octahedra show possible sites for Ti addition during growth. We assume that Ti will attach preferentially to sites where there exists the largest number of O$^-$ (or OH) in appropriate positions to create an octahedral coordination environment. Sites “ready” for Ti attachment, those with three existing O, are outlined in bold. Note that these are all on (001). Figure 9b shows the results of attachment of new Ti octahedra (lightest shading). For sites on (001) labeled “A”, attachment generates additional sites bounded by three O$^-$ or OH groups. Thus, filling these preferential attachment sites on (001) leads to continuous generation of new sites for further preferential attachment, involving three appropriately positioned oxygen atoms. This is not true for attachment of either a single Ti or a pair of Ti on {101}, labeled “B” and “C”. For attachment of two Ti ions on {101} (“B”), only one highly reactive site is generated. After this site is filled (bold site in area “B”), subsequent sites have only two appropriately positioned O ions. Side-by-side attachment of two Ti ions on {101} (“C”) leads to one very highly reactive site that, in turn,
generates only sites bound by two O ions. Consequently, it is apparent that a continual source of highly undersaturated sites is only generated on (001). This probably contributes significantly to the very rapid rate of extension along [001].

Figure 10 shows that initial growth rates along [001] are approximately twice as fast as along \(<101\rangle\). This corresponds to three Ti layers added to (001) for each two Ti layers added to [101]. As shown in Fig. 11, this implies a slow decrease in the relative contribution of (001) to the surface area of an individual growing particle. In the second phase of coarsening, growth slows dramatically along \(<101\rangle\) (Fig. 10) and the ratio of the growth rates is approximately 3 to 3.5. During this stage, the surface area of individual (001) faces decreases. The (001) surfaces are bounded by \{101\} faces (Fig. 12). Since the \{101\} faces are advancing at a far slower rate, the (001) advancement becomes limited by the advancement of \{101\}. Thus, as predicted by classical theory, rapid growth on the fastest growing surface is terminated. However, the (001) faces do not completely grow out of existence. They shrink to a constant cluster size ranging from 1.9 to 5.7 nm (5 to 15 unit cells). Constant (001) surface area, despite expansion of \{101\} surface area, implies that growth along [001] is 2.7 times as fast as along \(<101\rangle\) (one \(d_{101}\) for each \(d_{001}\)). Preservation of a cluster serves to reduce the overall energy because, without it, the intersection of \{101\} planes at the (001) terminus of the crystallite would result in an acute angle. The final cluster size is presumably determined by the balance between the energy savings of avoiding a highly unsaturated surface cluster (e.g., a single unit cell) and the energetic cost of having a comparatively high energy (001) surface.
4.2. Oriented Attachment and Coarsening

Hydrothermal coarsening of anatase in deionized water occasionally produces crystals that have attached in a crystallographically specific and oriented manner. The frequency of observed attachments in the most acidic solutions studied (pH 1 and 2) is little different from that observed in samples hydrothermally treated in deionized water. Attachments across the anatase {112} surfaces are common in solutions of hydrochloric acid at a pH around 3. Furthermore, higher pH (by addition of NaOH) does not enhance the frequency of attachments. The room temperature isoelectric point of nanocrystalline anatase is reported to range from pH 5 to 7 (Bischoff, 1992). We hypothesize that oriented attachment may be favored by flocculation of particles. Thus, oriented attachment could be expected at pHs close to the isoelectric point. Unfortunately, we do not know how the isoelectric point of different crystallographic surfaces changes with respect to temperature. Bérubé and De Bruyn (1968) studied the change in the isoelectric point of titania with changing temperature and found that it decreases by more than half of a pH unit with increasing temperature from 25°C to 95°C. Our results may indicate that the isoelectric point is close to pH 3.0 for anatase {112} surfaces at P_{sat} and 250°C. However, these results are not conclusive, as many materials are seen to coagulate under conditions in which surfaces are strongly charged.

Acetic and adipic acids (in similar concentrations) appear not to increase the frequency of attachment and may suppress it. This may be the result of adsorption of acetic or adipic acid molecules or ions to the surface of anatase crystallites, effectively blocking the attachment mechanism. At room temperature, FTIR results show that adipic acid does adsorb strongly to anatase surfaces (Penn and Banfield, in prep.). In addition, the fact that oriented attachment occurs only rarely in acetic acid and adipic acid solutions may be due to the relationship between hydrogen ion activity and isoelectric point changes at hydrothermal conditions. If, as we hypothesize, the oriented attachment mechanism is strongly active only under conditions near the isoelectric point, the relationships between the hydrogen ion activity and the change in isoelectric point with respect to temperature and pressure becomes extremely important. Detailed results of speciation calculations, discussion of the interactions between organic molecules and surfaces, and the expected impact on crystal growth will be reported elsewhere (Penn and Banfield, in prep.).

Oriented attachment occurs most commonly on {112}, occasionally on (001), and rarely on {101}. This mechanism effectively serves to reduce overall surface energy by eliminating the surfaces at which the crystallites join. In the most common case of {112} attachment, it is the highest surface energy face (observed) that is eliminated. This mechanism is quite distinct from Ostwald ripening, which involves the dissolution of fine particles and growth of larger particles. Clearly, both mechanisms operate in our samples. The latter mechanism operates simultaneously with oriented attachment because of the high driving force for addition of ions from solution to newly formed particle–particle junctions. Clearly, coarsening data reflect the sum of two different processes with different kinetics.
The importance of the oriented attachment and subsequent growth mechanism in other materials and in natural nanocrystalline aggregates remains to be seen. We predict that it should be common where particles are in contact with a solution under pH conditions near the isoelectric point. Organic molecules may hinder or modify oriented attachment. Organics adsorbed in a crystallographically specific manner can suppress (as in the cases of adipic acid, acetic acid, and glycine; see above) or modify the oriented attachment mechanism by preventing contact between the faces on which adsorption has selectively occurred.

Oriented attachment could be important in nominally dry aggregates (where surfaces are hydrated, but where there is no free flowing water) and in periodically wet environments. Particle movement needed to achieve orientation within random aggregates may be provided by Brownian motion and other physical and energetic effects. Alternatively, rotation of crystal structures is predicted during sintering under shear stress in the molecular dynamic simulations of randomly attached Cu particles by described Zhu and Averback (1996), suggesting the existence of a strong driving force toward achieving orientational accord. Coarsening by oriented attachment may be especially important where there is preexisting preferred orientation (e.g., in sheared materials). In addition, it may operate in a modified Ostwald ripening mechanism in which orientation, in addition to size, impacts on the survival and consumption of particular grains of a polycrystalline material. Specifically, randomly oriented particles surrounded by coincidentally closely oriented nearest neighbors coarsen and survive, and particles surrounded only by unoriented nearest neighbors are consumed. In cases in which attachment does not occur, traditional Ostwald type coarsening is predicted to be the predominant mechanism of crystal growth.

Considerable recent interest has centered on the question of biogenicity of ancient nanocrystalline materials because of the possible interpretation of these as evidence for terrestrial and extraterrestrial life (e.g., MacKay 1996). Our work demonstrates that the microstructures and morphologies of nanocrystalline materials may change dramatically at quite low temperatures over long periods of time. The issue of morphology evolution is of direct importance to materials science because growth and morphology evolution dramatically modify physical properties and surface reactivity. Finally, understanding the fundamental processes of crystal growth and morphology evolution is important in attaining control of material properties and in understanding the impact of environment on natural and synthetic materials.

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REFERENCES


