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Kinetic theory of crystallization of nanoparticles

Katsuhiro Tsukimura^{1*}, Masaya Suzuki¹, Yohey Suzuki¹, Takashi Murakami²

¹AIST, ²The University of Tokyo

We here describe a kinetic theory of the crystallization of nanoparticles, where nanoparticles are dissolving and crystals are forming in solution. The theory assumes that a crystal nucleates only on a nanoparticle, the crystal stops growing at a certain size, and the concentration of metal ion in solution is close to the solubility of the nanoparticles. On the basis of these assumptions, we have derived integral equations for R(t) (crystal ratio as a function of time). We have solved the integral equations with a successive approximation method. When time t is less than tinflec (= $r_{max/G}$, r_{max} : maximum radius of crystal, G: growth rate of crystal), R(t) is close to fourth power of time; when t is larger than tinflec, R(t) is close to an exponential-type function. The kinetic theory has been applied successfully to the transformation of ferrihydrite nanoparticles to goethite or hematite crystals, and the crystallization of TiO₂ (Fig. 1). The theory shows that the nucleation rate of crystal essentially determines the crystal-lization rate, and that induction period is observed when the growth of crystal is slow. Some non-thermodynamic parameters such as the turbulence of solution and the size of system can also affect the crystallization rate. For example, the stirring of solution prevents crystals to deposit and makes the crystals grow larger, which in turn makes the crystallization rate high.



Keywords: kinetic theory, nanoparticle, nucleation, growth, ferrihydrite, titania