6.8: Aluminum Oxides, Hydroxides, and Hydrated Oxides

The many forms of aluminum oxides and hydroxides are linked by complex structural relationships. Bauxite has the formula $Al_x(OH)_{3-2x}$ ($0 < x < 1$) and is thus a mixture of Al_2O_3 (α-alumina), $Al(OH)_3$ (gibbsite), and AlO(OH) (boehmite). The latter is an industrially important compound that is used in the form of a gel as a pre-ceramic in the production of fibers and coatings, and as a fire-retarding agent in plastics.

Knowledge of microstructural evolution in ceramic systems is important in determining their end-use application. In this regard alumina has been the subject of many studies in which the phase, morphology, porosity and crystallinity are controlled by physical and chemical processing. The transformation from boehmite [γ-Al(O)(OH)] o corundum (α-Al_2O_3) has been well characterized and is known to go through the following sequence:

$$\gamma\text{-Al(O)(OH)} \xrightarrow{\approx 500\ ^{\circ}\text{C}} \gamma\text{-Al}_2\text{O}_3 \xrightarrow{\approx 1000\ ^{\circ}\text{C}} \theta\text{-Al}_2\text{O}_3 \xrightarrow{>1100\ ^{\circ}\text{C}} \alpha\text{-Al}_2\text{O}_3 \tag{6.8.1}$$

The phase changes from boehmite through θ-Al_2O_3 are known to be topotactic (i.e., changes in crystal structure are accomplished without changes in crystalline morphology), however, each phase change is accompanied by a change in porosity. The θ- to α-Al_2O_3 phase transition occurs through nucleation and growth of the θ-Al_2O_3 crystallites. The α-Al_2O_3 phase transition temperature can be altered by the addition of certain additives. For example, because the α-Al_2O_3 phase occurs by nucleation, the addition of small seed crystals can lower the transition temperature between 100 and 200 °C. The addition of certain transition metals (chromium, manganese, iron, cobalt, nickel, and copper) has also been shown to decrease the transition temperature, while lanthanum or rare earth metals tend to increase the temperature. Finally, the addition of metal oxides has also shown to affect the growth rate in α-Al_2O_3.

A third form of Al_2O_3 forms on the surface of the clean aluminum metal, (6.8.2). This oxide skin is rapidly self-repairing because its heat of formation is so large (ΔH = 3351 kJ/mol). The thin, tough, transparent oxide layer is the reason for much of the usefulness of aluminum.

$$4\ \text{Al} + 3\ \text{O}_2 \rightarrow 2\ \text{Al}_2\text{O}_3 \tag{6.8.2}$$

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