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In situ AFM investigation of gibbsite growth in high ionic strength, highly alkaline, aqueous media

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ABSTRACT

In situ atomic force microscopy (AFM) was used to study the growth mechanism of the gibbsite basal (001) face and prismatic (100) face in high ionic strength (4 M NaCl + 1 M NaOH) and highly alkaline solution (pH = 13.4). The height of the steps on the gibbsite (001) faces can vary from less than one nanometre (elementary steps) to several nanometres (microsteps) and finally to dozens of nanometres (macrosteps). The lateral advancement rates of micro/macrosteps are related to the height of steps. Step coalescence occurs during lateral advancement, driven by Ostwald ripening. There are three possible pathways for the formation of micro/macrosteps on basal (001) face, all of which are controlled by layer-by-layer growth mechanism. Gibbsite structure suggests that the frequent and random formation of the elementary steps on basal (001) face can be attributed to weak inter-layer hydrogen bonds along the c-axis of gibbsite unit cell. The prismatic (100) faces are characterised by microstep trains along gibbsite [001] direction. These microsteps grow higher along gibbsite [100] direction, advance laterally and step coalescence also occurs. Two dimensional islands often form on the terrace adjacent to the edges of micro/macrosteps, suggesting that the step edge should be a preferred site for island nucleation due to the Ehrlich–Schwoebel effect.

1. Introduction

In alumina industry, gibbsite ($Al(OH)_3$) precipitation from supersaturated sodium aluminate solution is one of the most important steps in the production of alumina (Al_2O_3) from bauxite by the Bayer process (Fu et al., 2014; Watling, 2000; Watling et al., 2000; Zeng et al., 2007). In the chemical reaction of precipitation, sodium aluminate is decomposed to gibbsite and hydroxide ion

$$Al(OH)^-_{4(aq)} = Al(OH)_{3(solid)}\downarrow + IG + OH^-_{(aq)} \quad (1)$$

The precipitation of gibbsite has been widely studied in the last few decades. Most of the previous research has focused on developing kinetics models for gibbsite growth and agglomeration under various batch precipitation conditions. However, the investigation of the growth mechanism of gibbsite is of high interest, because the precipitation process takes place at the surface. Only a few studies have focused on building the relationships between gibbsite surface morphology and its growth mechanism using tools such as scanning electron microscopy (SEM) and ex situ atomic force microscopy (AFM).

Brown (1972a, b) used SEM to examine the changes of surface topography of gibbsite crystals as a function of alumina supersaturation. Under high alumina relative supersaturations ($\sigma = (C_{initial} - C_{equlibrium}) / C_{equlibrium} = 1.5$), the basal planes of gibbsite developed a wave-like appearance. The wave-fronts are the boundaries of layers growing over gibbsite surfaces. Few straight steps were observed. As crystal growth continued, the supersaturation decreased and surface irregularities were smoothed out. Under medium alumina relative supersaturation ($\sigma = 1.0$), bunching of the growth layers was less marked as incorporation of ions into the crystal lattice became more orderly. Under low alumina relative supersaturation ($\sigma = 0.5$), crystal surfaces became flat and smooth. Below $\sigma = 0.25$, the gibbsite crystal growth rate became negligibly small. Thus, they concluded that the crystal growth of gibbsite under the Bayer conditions occurs by a two-dimensional (2D) nucleation mechanism with little or no contribution from screw dislocations.

Using ex situ AFM, Lloyd et al. (1998) found that the surfaces of (001) basal plane were covered with over-lapping (001) plates that are 0.5 nm thick, titled at an angle with respect to the underlying basal plane. From this, it was suggested that gibbsite growth is dominated by the spreading of these plates within the relative supersaturation levels of $\sigma = 0.5$–1.0.

Ex situ AFM studies by Freij et al. (1999, 2004) identified the presence of defects on the basal face of gibbsite, which might influence the crystal growth processes. Under low relative supersaturations ($\sigma \leq 0.4$), the basal face of gibbsite grew by step growth. Under medium relative supersaturations ($\sigma \geq 0.8$), the continuous birth and spread

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mechanism dominated the growth of gibbsite basal face. In between these two levels of supersaturation, growth occurs by both step growth and birth and spread mechanisms, suggesting that the continuous birth and spread mechanism has been demonstrated by a remarkable cyclical, "smooth → rough → smooth → rough" growth process. Freij and Parkinson (2005)) also revealed that gibbsite growth in industrial Bayer liquor is almost inhibited on the prismatic faces, indicating that organic impurities industrial Bayer liquor adsorb strongly to the growth sites on the prismatic faces and prevent the incorporation of gibbsite growth units.

However, the limitations of using the ex situ AFM technique have restricted further study of gibbsite growth mechanism. In order to observe the growth sequence of the gibbsite surface, a series of AFM images at the same location on the same gibbsite crystal need to be collected after each growth period. Such frequent collection of the same gibbsite particle from the Bayer solution can lead to artefacts on the gibbsite surface morphology during the separation from the solution. The nature and extent of the changes to the surface morphology will obscure information about the actual growth processes, this is known as the "shut-off effect" (Sweegers et al., 2002).

In this study, in situ atomic force microscopy (AFM) was employed to study the gibbsite growth on basal (001) face and prismatic (100) face of industrial gibbsite crystals to promote the current understanding of gibbsite growth mechanism. Considering that that the glass window of AFM cantilever holder cannot resist highly caustic Bayer solution (~5 M NaOH), the synthetic liquor used for in situ AFM investigation contains 4 M NaCl and 1 M NaOH, supersaturated in aluminate at 25 °C (Fu et al., 2015a, b). Although the composition of this synthetic liquor is different from industrial Bayer liquor, both liquors provide a high ionic strength and alkaline solution for gibbsite crystallization, in which the predominant anion species for aluminium are $Al(OH)_4^-$ (Fu et al., 2015a, b; Sposito, 1996).

2. Experimental

2.1. Materials

Sodium hydroxide, sodium chloride, and aluminium trihydrate were obtained from Sigma–Aldrich (USA). Industrial gibbsite crystals produced by Queensland Alumina Limited (QAL) are used as substrate for AFM observation. The crystals were typically 50–100 μm in diameter, which were washed by Millipore water for 30 min at 30 °C. Water used was purified via a Millipore system with a resistivity of 18 MΩ/cm. All glassware were cleaned and rinsed with Millipore water.

The stock solutions (4 M NaCl + 1 M NaOH) were prepared by dissolving sodium chloride and sodium hydroxide in Millipore water. Based on the literature review in 1.0 Introduction, the medium relative supersaturation (around $\sigma = 1.0$) could be best fit for investigating gibbsite growth. Moreover, preliminary results show that under high relative supersaturations ($\sigma \geq 1.5$), AFM cantilever cannot be calibrated, since the cantilever deflection keeps increasing due to uncontrollable gibbsite nucleation on the surface of cantilever.

The synthetic liquor with supersaturated aluminate was prepared in a speed wave®4 microwave digester produced by Berghof GmbH Co. The microwave digestion was carried out in three stages. In the first stage, the reactor contents including 5 ml stock solution and a certain amount of aluminium trihydrate in each vessel were heated to 150 °C for 5 min with a ramp up time of 3 min followed by heating at 180 °C for 5 min with ramp up time of 3 min. In the third stage, the solutions were heated at 200 °C for 5 min with a ramp up time of 5 min. The total time required for digestion is about 40 min (including cooling time in the microwave digester).After the digestion, the synthetic liquor was filtered through a 0.2-μm pore size Nylon membrane filter. Then the liquor was divided into two parts. One part was immediately diluted for ICP-OES test to measure the supersaturated aluminium concentration (0.30 mol/L). The other part of the synthetic liquor was sealed and allowed to stand under static condition in an air-bath oven at 25 ± 1 °C for three months. After that, the liquor was analysed by ICP-OES test to obtain the apparent equilibrium concentration of aluminium (0.14 mol/L). Therefore, the relative supersaturation used in this study was 1.14, calculated by the formula $\sigma = (c_{Al(OH)_4^-} - c_{Al(OH)_4^-(eq)})/c_{Al(OH)_4^-(eq)} \cdot ^{\infty}$

2.2. In situ AFM experiments

In situ observations of gibbsite growth were made by Contact Mode using a MFP-3D-BIO (Asylum Research) equipped with a piezoelectric scanner capable of scan areas to a maximum of 90 × 90 μm. Surfaces were imaged using commercially available Si_3N_4 cantilevers that have triangular tips with a length of 200 μm, and a force constant of approximately 0.06 N/m. Tip Radius was less than 15 nm. The synthetic solution supersaturated in alumina was input as a continuous flow through an AFM fluid cell with an internal volume of 5 ml using a syringe pump. All images were collected using flow-through rates greater than 5 ml/h. In situ measurements of temperature in this flow-through environment were 25 ± 1 °C.

To determine the flow condition on the surface of gibbsite particles during the AFM observation, the Reynolds numbers (Re) were calculated by using the AFM cell diameter ($D = 3.5$ cm) and height ($H = 1$ cm) to determine the cross-sectional flow area. The corresponding hydraulic diameter L ($L = 2HD/(D + H) = 1.56$ cm $= 0.0156$ m) was used as the characteristic length, and the volumetric flow rate was used as the characteristic velocity V ($V = 5$ ml/h $= 1.389 \times 10^{-9}$ m/s).The dynamic viscosity of synthetic liquor μ is 0.00533 Pa·s, measured by an Ares rheometer (TA Instruments Ltd). The density of synthetic liquor ρ is 1181.15 kg/m^3. The Reynolds number is calculated based on the following Eq. (2):

$$Re = \frac{\rho \cdot L \cdot V/(D \cdot H)}{\mu} \tag{2}$$

The calculated Re is equal to 0.48×10^{-5}, which indicates that laminar flow ($Re < 2000$) occurred on the surface of gibbsite particles during the AFM observation. At this velocity (5 ml/h), the fluid of synthetic liquor tends to flow without lateral mixing indicating that local supersaturation fluctuations on gibbsite surface might occur which could potentially affect the growth of the elementary steps.

3. Results and discussion

The gibbsite basal (001) planes in Fig. 1 consist of overlapping steps and at an angle to the overall basal plane. Instead of typical straight steps, the edges of these stepson basal (001) plane exhibit irregularly wave-front shape (Brown, 1972a). The irregularity of wave-fronts can be attributed in part to the fact that dislocations are sometimes present in the terraces (Cubillas et al., 2009). For industrial Bayer liquor, a range of impurity solutes are present which may bond more strongly to the steps of gibbsite crystals in a way that disturbs the crystal integration of subsequent solute molecules, create pinning sites (De Yoreo and Vekilov, 2003). The steps bulge out between the pinning sites resulting in irregular wave-fronts.

The wave-fronts (solid arrows ①–⑥ in Fig. 1) are the boundaries of step growing over crystal surfaces, which can be divided into two types of growth patterns. The first type of growth pattern includes wave-fronts ①, ② and ③, in which wave-fronts kept spreading rightward in the form of step advancement with different growth rates. With the increase of crystallization time, the area surrounded by wave-fronts ②and ③ reduced and the distance between wave-fronts ① and ②increased, indicating that the growth rate of wave-front ② is much higher than those of wave-fronts ① and ③. Height analysis reveals that the step height of wave-front ② is about 9.5 nm, much lower than the height of wave-front ① (~33.9 nm) and wave-front