

AN INVESTIGATION OF TWINNING PHENOMENA IN GIBBSITE

Lee, F^{1*}, van Bronswijk, W², Parkinson, G¹, Reyhani, M¹, Vernon, C³

A J Parker Cooperative Research Centre for Hydrometallurgy

¹ *Nanochemistry Research Institute, Curtin University of Technology, Australia*

² *Department of Applied Chemistry, Curtin University of Technology, Australia*

³ *Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia*

Abstract

The quality of gibbsite with respect to calcination is determined by the strength, size and purity of gibbsite agglomerates. Agglomerates are typically made up of hexagonal or diamond shaped crystallites, which are commonly twinned. Twinning plays a significant role in the formation of hexagonal gibbsite crystals, hence an investigation into this phenomenon was conducted with the use of spectroscopic and microscopic techniques.

Polarised light microscopy identified six-fold rotational twinning in large ($>5\mu\text{m}$) hexagonal gibbsite crystals. The occurrence of six-fold twins was observed to increase with time. The technique also identified gibbsite, which did not exhibit twinning. These crystals were smaller in size ($<5\mu\text{m}$) with diamond or hexagonal morphology. Polarised Raman spectroscopy of the OH stretching region and the associated Al-O region indicated differences in bond orientation due to twinning. Crystallographic axes of each twin domain were determined. The directions of orientation of the twin boundaries were used to determine the mode of twinning.

Twinning was not observed during early stages of growth, and a number of possible causes for subsequent twinning have been investigated, including localised changes in liquor concentration at nucleation, transformation due to pressure or temperature changes during growth, or the nucleation of a metastable structure which is only sustainable as a single crystal at small dimensions, beyond which stabilisation is provided via twinning.

The occurrence and nature of twinning within the individual components of agglomerates may be a relevant consideration in determining their strength during calcination.

1 Introduction

Alumina production via the Bayer Process is governed by the crystallisation of gibbsite $\text{Al}(\text{OH})_3$. Precipitates are typically agglomerates consisting of crystals of various morphologies. Successful calcination to smelting quality alumina depends upon the morphology, size and purity of agglomerates. Individual crystals of gibbsite generally exhibit a hexagonal plate-like morphology. Diamond and prismatic crystals have also been observed (Rossiter et al., 1998). Twinning within hexagonal crystals of gibbsite on the $\{110\}$ face, with a rotation axis about $[130]$, is observed in both synthetic and naturally occurring gibbsite samples (Sweegers et al., 1999). Twinning is cyclic, forming six distinct domains, each separated by two twin boundaries. Reflection twins on the $\{110\}$ and $\{100\}$ face have also been reported (Fleming et al. 1997; Miers, 1902). In this study, spectroscopic and microscopic techniques have been used to characterise gibbsite twinning phenomena and to elucidate the mechanism for twinned hexagonal gibbsite formation.

2 Results and Discussion

The different crystal habits of gibbsite were characterized using Polarised Light Microscopy (PLM), Raman spectroscopy, and Atomic Force Microscopy (AFM). PLM micrographs indicated that various twinned morphologies exist in gibbsite grown from sodium aluminate solutions (Figure 1c, 1d & 1e). Cyclic twinning via a rotation axis $[130]$ was observed in synthetic and industrial gibbsite samples. Under crossed polarisers, six domains were identified and their crystallographic orientations determined by observing extinction directions with rotation. Distinct twin boundaries along the $\{110\}$ faces were also observed, having finite width. These boundaries appeared to be in extinction under all degrees of rotation. In addition to cyclic twins, reflection twins on the $\{110\}$ face were also observed. Single crystal-line gibbsite crystals in the diamond and hexagonal morphology were identified during early stages of growth, particularly under conditions of low driving force (Figure 1a & 1b). The presence of these crystals

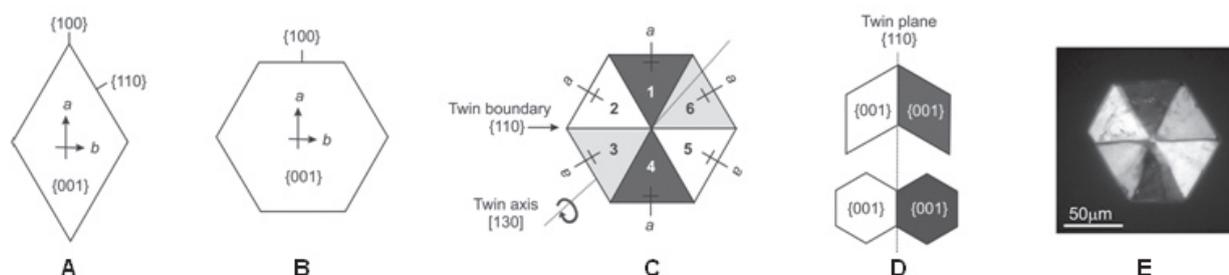


Figure 1

Gibbsite crystal morphologies

A: Diamond. B: Hexagonal. C: Hexagonal cyclic 6-fold twin. D: Reflection twins. E: PLM micrograph of a six-fold gibbsite twin.

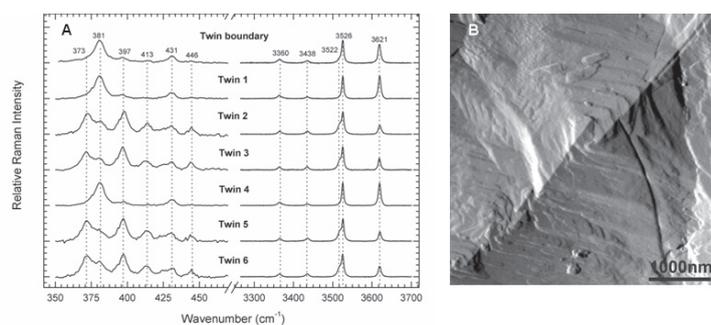


Figure 2

A: Raman spectra of a twinned hexagonal gibbsite crystal, depicting differences in bond orientation between boundaries and domains. B: AFM deflection image of a spiral dislocation formed on a twin boundary.

indicates that twinning does not occur at nucleation. PLM has revealed that undefined regions of twinning in hexagonal crystals smaller than $5\mu\text{m}$ exist. Defined regions of twinning become apparent as the size of the crystal increases. This suggests that twinning may occur in order to stabilize the hexagonal morphology as size increases.

Raman spectroscopy was utilised to determine the structure of twin domains and boundaries in hexagonal six-fold gibbsite twins. Spectra were acquired in the OH stretching ($3300\text{--}3700\text{cm}^{-1}$), O-Al-O and Al-O-H ($350\text{--}450\text{cm}^{-1}$) bending regions (Wang & Johnston, 2000). This enables the orientation of the twin domains and boundaries to be determined. Figure 2a depicts the peaks associated with each twin domain and the twin boundaries. Peaks at 373 and 3522cm^{-1} represent bonds that are vibrating in the bc plane and along the crystallographic b -axis of the crystal respectively. This suggests that twin domains 1 & 4 are orientated with their crystallographic a -axis parallel to the Raman incident beam as bonds vibrating along the b -axis or in the bc plane are not excited. Twins 2,3,5 and 6 show the emergence of peaks at 373 and 3522cm^{-1} indicating the orientation of these domains are not solely in the a direction. The twin boundaries were determined to be regions of order with an a -axis direction similar to that of twins 1 and 4. Using vector analysis of the b -axis direction of adjacent twin domains, twin boundaries were determined to be a plane of inversion rather than reflection. Inversion twin boundaries are non-planar and often result in concave or convex arrangements of adjacent twin domains. A study of the topography of twinned crystals via AFM indicated that twin bounda-

ries were not planar. Spiral dislocations were often observed along twin boundaries (Figure 2b). The different direction of growth steps on either side of a twin boundary suggests that growth is directed by the orientation of each twin domain.

3 Conclusions

Gibbsite twins have been identified by PLM. The crystallographic orientations of domains within twinned crystals were determined via Raman spectroscopy. AFM topographical studies indicated that twin boundaries are non-planar inversion planes with dislocations prominent along each boundary. Twinning has implications to the Bayer process, as twinned crystals are often observed in industrial gibbsite agglomerates. Twin boundaries, having a greater number of dislocations, may act as sites for preferential agglomeration. Additionally, boundaries may act as planes for cleavage, decreasing the strength of twinned crystals relative to single crystals. This may have implications during the calcination of gibbsite.

Acknowledgements

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