GROWTH OF THE (001) FACE OF BORAX CRYSTALS

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ABSTRACT

The growth rates of borax crystals from aqueous solutions in the (001) direction at various relative supersaturations were measured using in situ cell optical microscopy method. The result shows that the growth mechanism of the (001) face of borax crystal at temperature of 20 °C is spiral growth mechanism.

Keywords: *Growth mechanism, borax.*

INTRODUCTION

The quality of sodium borate tetrahydrate, $Na_2B_4O_7 \bullet 10H_2O$, (borax) is solely determined by grade and specifically shaped crystals of high purity [1]. According to Teodossiev and Kirkova [2] the quality of the high-purity product depends both on the concentrations of the impurities and the product appearance, which are mainly determined by the size and morphology of the crystals. Thus, knowledge about crystallization of borax is of direct relevance to the industrial production of borax. In addition, fundamental studies of borax crystallization will provide results of relevance to the crystallization of other economically important materials.

The growth mechanism of borax crystal has been reported *via* spiral mechanism. Takoo [3] stated that existence of growth spirals on different habit faces suggests that screw dislocations play their role in the development and growth of respective faces in particular and of borax crystals in general. However, investigations of growth rate of borax crystal still give limited information. None of the research reported has produced sufficient data of growth rates for each face of the crystals, over a wide range of relative supersaturation. Most of the researchers studied from a big crystal.

This paper studies the growth rate mechanism of the (001) face of borax crystal by using *in situ cell* optical microscopy under various relative supersaturations. The *in situ cell* optical microscopy was allowed to measure the growth rates of the (001) face of borax crystals. The morphology of borax crystal can be seen in Fig 1.

The objective of this research is to improve fundamental knowledge about crystallization of borax, including the mechanism of growth and crystal growth rate equation required in the modeling and design of industrial crystallizers. This information will be very useful for borax industry.

EXPERIMENTAL SECTION

Solubility of Borax in Water

The driving force for crystallization is usually expressed as a supersaturation ratio, defined as [4]:

$$S = \frac{A}{A^*}$$

Where A and A^* are the initial and the equilibrium solute concentrations. The solubility of borax in water used has been reported by Nies and Hulbert [5], and Sprague [6].

Experimental Set-up

In situ cell optical microscopy method described by Lee and Parkinson [7], Lowe *et al.* [8], Suharso [9] and Suharso et al. [10] was used. Optical microscopy *in situ* growth experiments were conducted using a set up that consists of a Nixon Optiphot-2 Microscope with automated video image capture, a Grant W14 (Grand Instruments Ltd.)
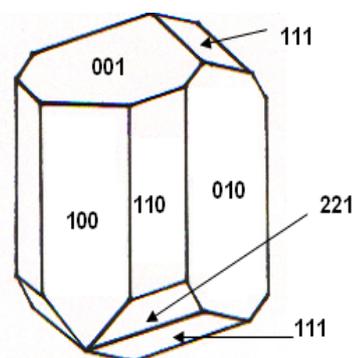

Figure 1 The morphology of borax crystal [11-13]

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circulating water bath, Pulnix TM-9701 Camera (Progresive Scanning Full Frame Shutter Camera), and a Pentium II Computer. The aim of this set up is to keep temperature and supersaturation constant. During the growth experiments, a digital thermometer (HANNA Instruments, HI 8424) monitored temperature in the sample solution compartment. The images of the growing seed crystals were recorded using the video camera and the Optimas Software, Version 6.2 (Optimas Corporation, Bothell, Wa, USA.).

Seed Preparation

The seed solution was prepared from 30 gram of Univar AR grade sodium tetraborate dissolved in 100 mL of Milli-Q water by heating up until 60 °C and filtering through filter paper. The solution was quickly cooled down into petri dish that covered by a transparent plastic, producing 40-200 μm well crystals. Only single seed crystals between 40 - 120 μm in size were used to investigate the growth rate.

Preparation of Growth Solutions

The growth solution was dissolved in 200 mL of Milli-Q water by heating up until 60 °C and filtering through a 0.45 μm filter membrane. The filtered solutions were placed into waterbath at temperature of 20 °C with covered plastic bottle for 3 hours before used. To place solutions into sample compartment, the growth solution was pumped by peristaltic pump *via* rubber tubing. The experiments were performed at temperature of 20 °C and relative supersaturations from 0.18 to 1.

RESULT AND DISCUSSION

Fig 2 shows the effect of relative supersaturation on the growth rate (GR) of the (001) face at temperature of 20 °C. The mean growth rate of this face increases with increasing relative supersaturation.

The general term of growth rate,

$$GR = k(s-1)^n$$

where the growth rate constant, k, is related to temperature, T, by the Arrhenius' equation:

$$k = k_o \exp\left(\frac{-E_a}{RT}\right).$$

Therefore, the growth kinetic model may be written as:

$$GR = k_o \exp\left(\frac{-E_a}{RT}\right)(s-1)^n \qquad (1)$$

where k_o is the kinetic coefficient, $(s-1)$ is the relative supersaturation, n is growth order and E_a is the activation energy. This equation is used to determine the dependence of growth on supersaturation and to determine the activation energies of individual crystal faces.

The experimental results obtained for the growth rates of (001) face can be fitted by Equation 1 using non-linear regression tool of SPSS (unweighed analysis). When calculating all data and using the power law model, the power, n, is 1.76, the activation energy is 50.6 kJ/mol and the kinetic coefficient is 9.36 x 10^9 μm/min with a correlation coefficient of 1. Given that the range of the activation energy for surface integration control is between 40-60 kJ/mol and growth order, n, is higher than 1, it is concluded therefore, that the (001) face of borax crystal growth is not diffusion controlled. If diffusion controlled, the growth rate is directly proportional to the supersaturation [4].

From Fig 2, the growth rate equation for power law model calculated from all data obtained may be written as

$$GR = 4.03(s\text{-}1)^{1.76}$$

and for the growth kinetic model as

$$GR = 9{,}36 \times 10^9 \, exp(\text{-}50600 \, J \, /RT)(s\text{-}1)^{1.76}$$

where correlation coefficient (R^2) is 1. This implies that the (001) face grows *via* a spiral growth mechanism.

The data from Figure 2 can be also analyzed by birth and spread model. Therefore, to investigate if growth occurs *via* a birth and spread mechanism,

$$\ln\left(\frac{GR}{(s-1)^{5/6}}\right) versus \, 1/(s-1) \text{ is plotted (Fig 3).}$$

Liu *et al.* [14] and followed by Lee and Parkinson [7] used this equation and stated that by plotting this equation, the birth and spread model rate equations, both for mononuclear and polynuclear model, can be linearised, but not the growth rate equation for the spiral growth mechanism. The plot of this equation is given in Fig 3 and shows a linear relationship (correlation coefficient = 0.92) which indicates that the growth of (001) face may also occur by a birth and spread mechanism.
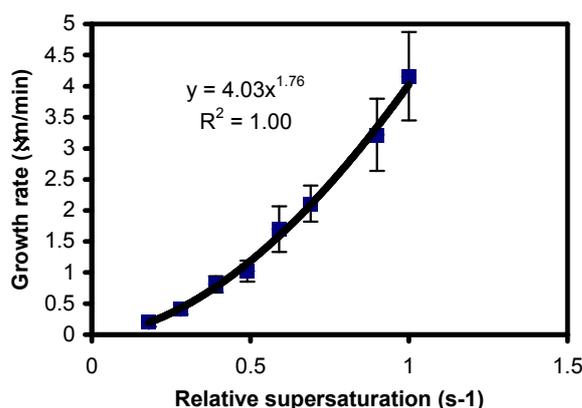
Figure 2 Growth rates of (001) face of borax crystal as a function of relative supersaturation (y is growth rare and x represents relative supersaturation)
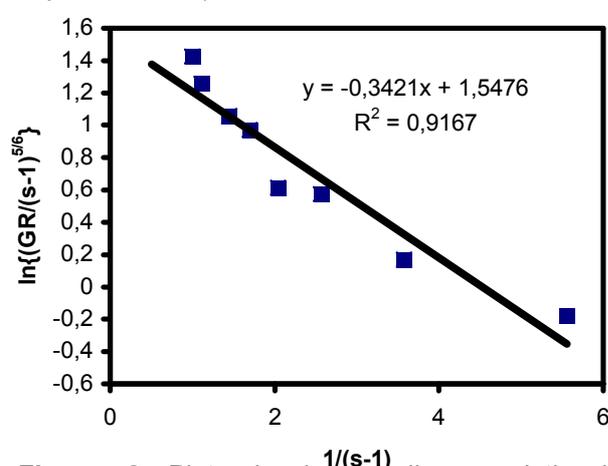

Figure 3 Plot showing a linear relationship indicative of birth and spread growth mechanism on the (001) face (y is $\ln\{(GR/(s-1)^{5/6}\}$ and x represents $1/(s-1)$)

On the basis of the quality of fit of the data, the power law model (correlation coefficient is 1) is better than birth and spread model (correlation coefficient is 0.92), it is concluded that the growth rate of the (001) face occurs *via* a spiral mechanism.

CONCLUSION

1. The growth rate equation of the (001) face of borax crystal at temperature of 20 °C can be written as $GR = 9{,}36 \times 10^9\ exp(-50600\ J\ /RT)(s-1)^{1.76}$ with correlation coefficient of 1.
2. The growth mechanism of the (001) face of borax crystal at temperature of 20 °C is spiral growth mechanism.
3. Based on the activation energy obtained, 50.6 kJ/mol, the growth rate of the (001) face is surface integration control under these conditions.

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