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ORIGINAL ARTICLE

AFM Investigation of Borax (100) Face: Two-Dimensional Nucleation Growth

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ABSTRACT

It has been studied the surface topography of (100) face of borax crystals under *in situ* optical microscopy and *ex situ* atomic force microscopy (AFM). The results show that the growth mechanism of the (100) face of borax crystal is *via* hillocks generated by two-dimensional nucleation indicating birth and spread mechanism. The hillocks can occur with more than one hillock on the surface of (100) face. The two-dimensional nuclei are circular in shape with the step height between 60 and 130 unit cells.

Key words: Two-dimensional nucleation, borax, AFM.

Introduction

Several researchers has proven that AFM is to be a very powerful technique for investigating surfaces at low to high resolution and for studying, *in situ*, the dynamic processes of crystal growth and dissolution. Ulcinas *et al*. (2007) studied direct observation of spherulitic growth stages of $CaCO_3$ by AFM. Suharso (2006) investigated the relationship between growth hillocks of (010), (001) and (111) face of borax crystal and supersaturation interpreted by spiral growth theory. Kwak and Sindo (2005) observed the facet formation on various faces of aragonite in aqueous acetit acid. Kutnetsov *et al.* (2000) studied the surface morphology of the (010) face of potassium hydrogen phthalate (KAP) crystals using AFM. They found that the macroscopic hillocks and smaller polygonal hillocks are formed by groups of cooperating spirals or by single spirals. At low supersaturation, growth of the (010) face occurs by a combined spiral and two-dimensional nucleation mechanism. Krasinki and Rolandi (1996) reported *ex situ* AFM investigation of surface topographies of the (100) and (101) faces of as-grown potassium dihydrogen phosphate (KDP) crystals. Growth hillocks, step bunching, growth spirals, two-dimensional nucleation and hollow cores were detected. Maiwa *et al*. (1998) investigated the growth mechanism of the (111) and (100) faces of barium nitrate crystals growing from aqueous solutions *via ex situ* AFM. Growth hillocks induced by dislocations and growth islands formed via two-dimensional nucleation were observed on both faces. Jiang *et al*. (2001) used *ex situ* AFM to study the growth mechanisms of the cadmium mercury thiocyanate (CMTC) crystals. Simultaneous spiral dislocation controlled growth and two-dimensional nucleation growth have been observed on (110) faces of CMTC crystals. Pina *et al*. (1998) studied growth on the (001) face of barite *in situ* at room temperature using contact mode AFM. They observed that growth under moderate supersaturation conditions growth follows the birth and spread model; two-dimensional nuclei form simultaneously with the advancement of molecular height cleavage steps.

The aim of this research is to give evidence that the two-dimensional nucleation growth hillocks occur on the surface of (100) face of borax crystals by in situ optical microscopy technique and supported by *ex situ* technique of AFM. This report will be very useful to give well understanding of the growth mechanism of borax crystal.

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Material and Methods

The seed crystals were produced from 30 gram of Univar AR grade borax dissolved in 100 mL of Milli-Q water by heating up until 60 °C and filtered through filter paper. The solution was quickly cooled down into petri dish that covered by a transparent plastic, producing 40-200 mm well crystals.

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.) circulating water bath with temperature controller, Pulnix TM-9701 Camera (Progresive Scanning Full Frame Shutter Camera), a Computer. During the growth experiments, a digital thermometer (HANNA Instruments, HI 8424) monitored temperature of the sample solution compartment. The images of the growing seed crystals were recorded using the video camera. The single crystals were grown at 20°C with a relative supersaturation of 0.089 and 0.21. As soon as the crystals grew into an acceptable size for the AFM experiment, individual crystal were taken out carefully and dried with a tissue. Then, the seed crystals were gently placed on the AFM sample holder using a 'blue tack'. Ex situ AFM investigations were then conducted immediately.

Digital Instruments Nanoscope E AFM was used in the contact mode. AFM observed was conducted in atmospheric using a 12 mm or 150 mm scanner and wide triangular shaped 200 mm cantilevers made of gold-coated Si_3N_4, with force constant of 0.12 N/m.

Result and Discussions

According to Sangwal and Rodriguez-Clemente (1991), dislocation growth hillocks (spiral growth hillocks), characterized by small step separation, appear on a surface while the crystal grows at high temperatures and/or high supersaturation. Hillocks of non-dislocation origin are produced by the occurrence of two- dimensional nucleation at some point on the surface where supersaturation is higher than the rest of the surface. Due to this local increase in supersaturation, these points act as centers of repeated two-dimensional nucleation for growth fronts, which spread and pile upon one another to produce the hillocks. From the experiments using *in situ* optical microscopy and atomic force microscopy (AFM), it was found that two-dimensional nucleation growth hillocks occur on the (100) face of borax crystal.

Fig. 2, 3, 4 and 5 show the two-dimensional nucleation growth hillocks on the (100) face of borax crystals. The surface of this face under *in situ* optical microscopy can be seen in Fig. 1. From Fig. 2, 3, 4 and 5, it is observed that all these hillocks are generated by two-dimensional nucleation. The height of the steps existing on the growth hillocks in Fig. 3 and 4, are from 60 to 130 unit cell (unit cell of the (100) face = 1.18 nm).

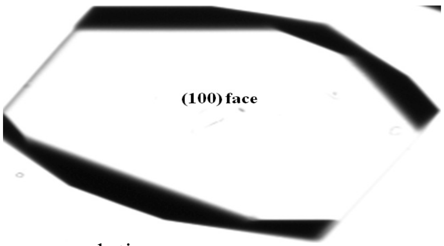

Fig. 1: Borax crystal grown in aqueous solution

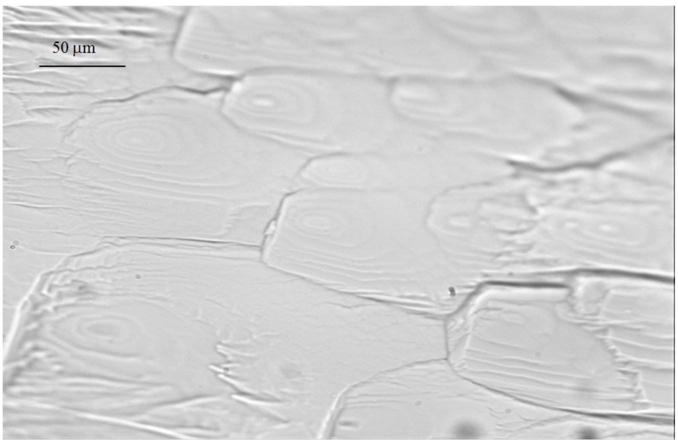

Fig. 1: *In situ* optical microscopy image showing birth and spread growth on the (100) face of borax crystal (s-1=0.089)

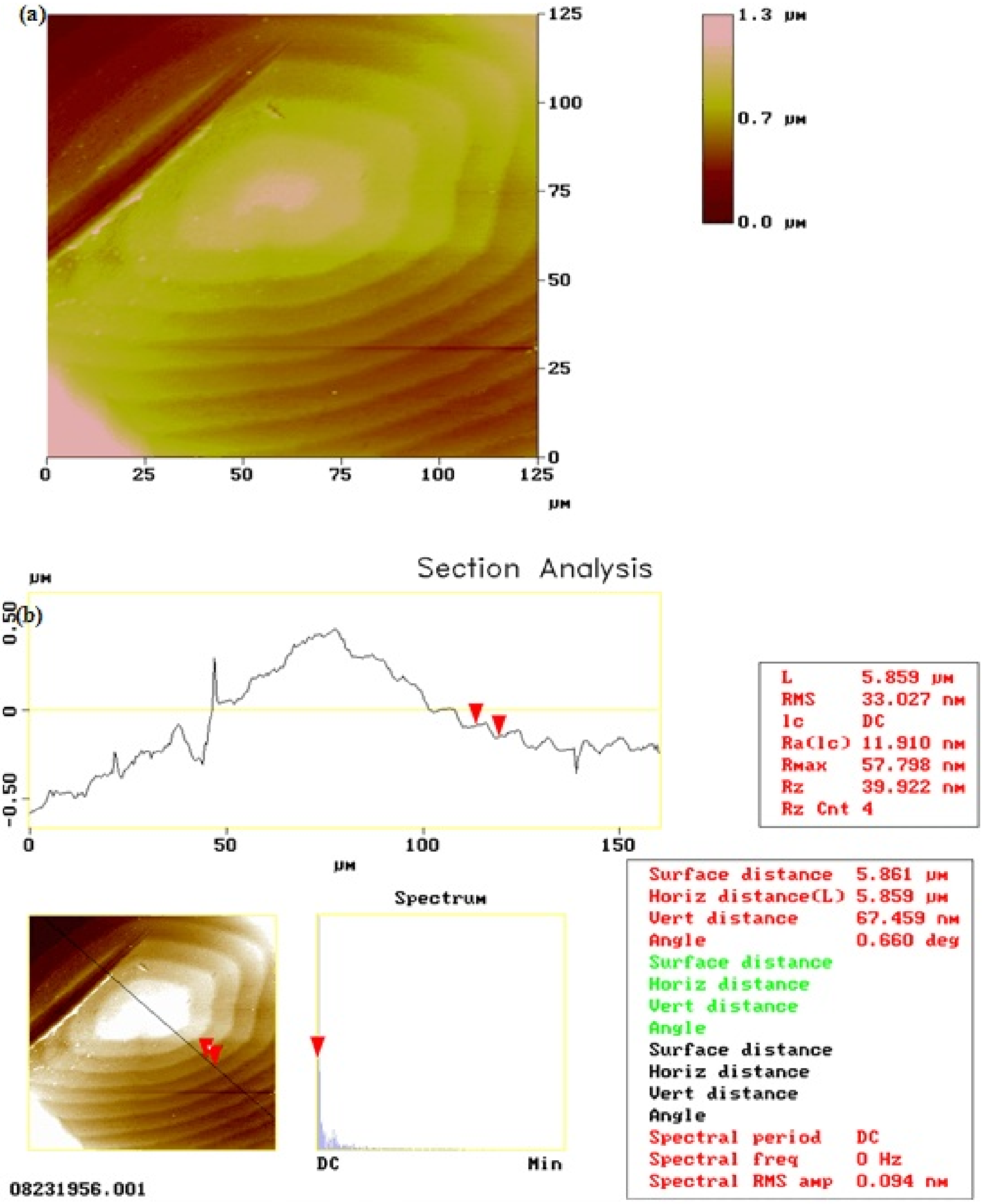

Fig. 3: (a) Images of two-dimensional nucleation hillock on the (100) face of borax crystal (s-1 = 0.21); (b) Section analysis of step height of the (100) face of borax crystal at relative supersaturation of 0.21

Fig. 3 and 4 show an interesting example of a growth hillock. It seems to be a typical hillock originating from dislocations with a shape which is typical of the loops produced by a pair of spirals with opposite sign. Looking more precisely on the center of the hillocks, two-dimensional nucleation can be seen as source of the growth hillocks on the (100) face of borax crystals. This reason is strongly supported by *in situ* optical microscopy image in Fig. 2.

Based on thermodynamic consideration of the effects of strain on crystal stability, Frank (1951) and Cabrera and Levine (1956) stated that for sufficiently large Burgers vectors, a growth spiral should contain a hollow core. In the case of inorganic KDP (potassium dihydrogen phosphate) crystal, hollow cores are observed on the (101) face for all dislocations with $b > 1$ (De Yoreo, *et al*., 1997 and Krasinki and Rolandi, 1996). For macromolecular crystals (canavalin, thaumatin and lipase), hollow cores are observed in some cases (Kutnetsov, *et al*., 1999 and Land, *et al*., 1995) and not observed in other cases due to the small value of the elastic energy associated with the dislocation (*e.g.* canavalin crystals). In the case of borax crystals, hollow cores are not observed on the (100) face for all of the

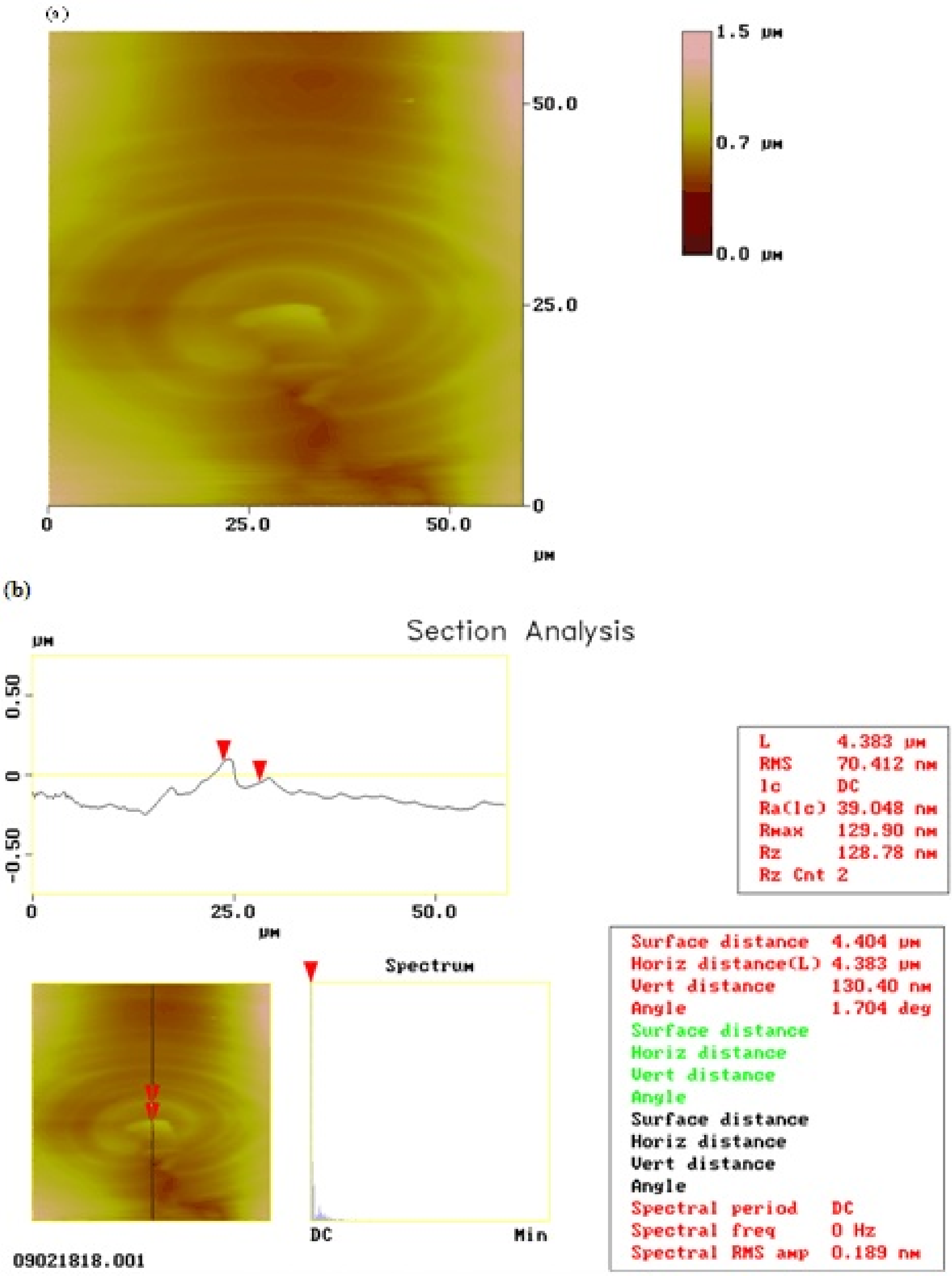

Fig. 4: (a) Images of two-dimensional nucleation hillock on the (100) face of borax crystal (s-1 = 0.21); (b) Section analysis of step height of the (100) face

images. Therefore, this is consistent with the growth of the (100) face by two-dimensional nucleation growth hillocks. Two-dimensional nucleation mechanism was also found on the (101) face of KH_2PO_4 crystal with huge islands without any signs of dislocation outcrop (Shangfeng, Y., *et al*., 1999).

During the last few years, numerous examples of two-dimensional nucleation in crystal growth from low supersaturated solutions were reported and discussed. Kutnetsov, V.A., *et al*. (2000) reported that at low supersaturation (0.03 to 0.05), the shallow hillocks are formed by repeated two-dimensional nucleation growth mechanism on the (010) face of potassium hydrogen phthalate (KAP) crystals. It was also found that at the low relative supersaturation (0.025 to 0.21) two-dimensional nucleation occurs on the (100) face of borax crystal.

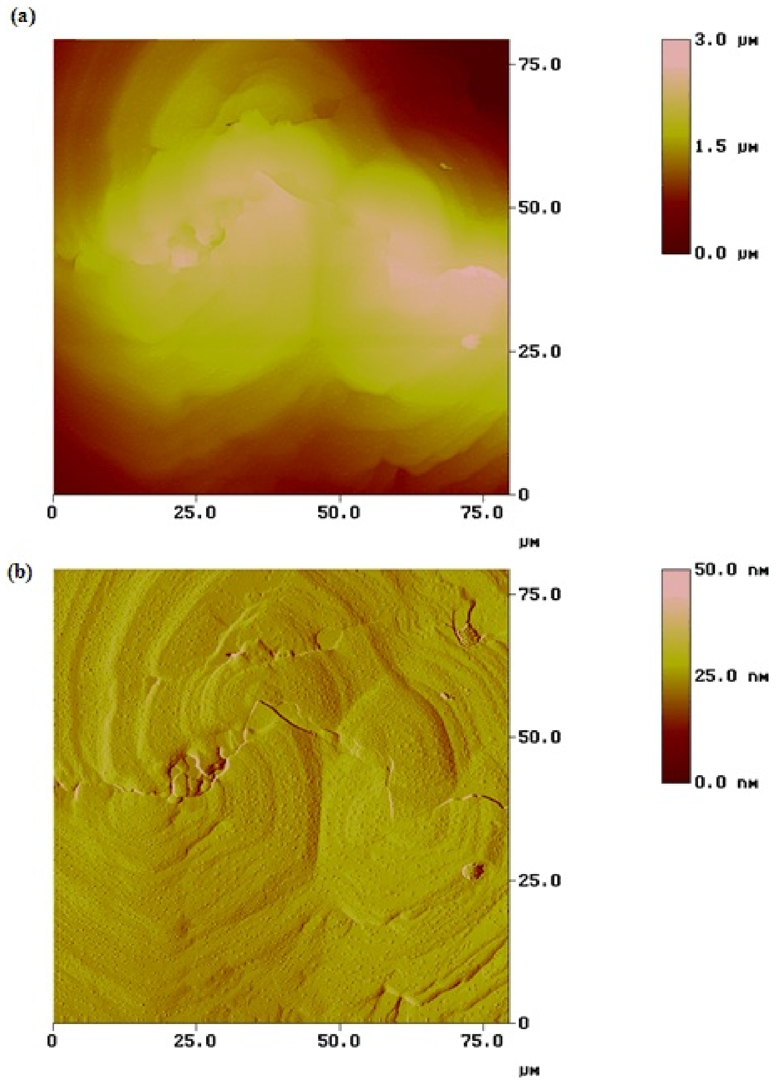

Fig. 5: (a) AFM height image of growth hillocks on the (100) face of borax crystal; (b) AFM deflection Image (s-1=0.21)

On the (100) face of borax crystal, another type of growth hillock was observed, as shown in Fig. 5. Three hillocks have been produced by two-dimensional nucleation and overlap each other. Furthermore, the two-dimensional nucleation nature of this type of growth hillocks could be discerned clearly from the deflection image (Fig. 5(b)).

Conclusions

AFM investigation has produced very useful information about the surface characteristics of the (100) faces of borax crystals. This information can support the image obtained from *in situ* optical microscopy. The growth mechanism of the (100) face of borax crystal is *via* hillocks generated by two-dimensional nucleation indicating birth and spread mechanism with a macrostep height at the range of relative supersaturation from 0.089 to 0.21. The hillocks can occur with more than one hillock on the surface of (100) face. The two-dimensional nuclei are circular in shape with the height between 60 and 130 unit cells.

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