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The convection during $NaClO_3$ crystal growth observed by the phase shift interferometer

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Abstract

An optical diagnostic system consisting of the Mach–Zehnder interferometer with the phase shift device and an image processor has been developed for the study of the kinetics of the crystal growing process. The dissolution and crystallization process of $NaClO_3$ crystal has been investigated. The concentration distributions around a growing and dissolving crystal have been obtained by using phase-shift of four-steps theory for the interpretation of the interferograms. The convection (a plume flow) has been visualized and analyzed in the process of the crystal growth. The experiment demonstrates that the buoyancy convection dominates the growth rate of the crystal growing face on the ground-based experiment. © 2001 Published by Elsevier Science B.V.

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1. Introduction

The crystal growth is a process related to heat and mass transfer which dominates the morphological instability near the growing interface, and it is an important factor for the quality of crystal. The characteristics of the flow in the crystal growing solution determine the micro-structure of the growing crystal. For understanding and visualizing the flow pattern in the transparent solution, the optical interferometry is one of the ideal measurement methods, which has many advantages such as non-destructive, full flow field visualization and quantitative measurement. The interferometry has been widely used to study crystal growth solution, but most works on the optical technique give only a little information that deals with the fluid mechanics together with the process of crystal growth [1,2]. Onuma et al. [3] use schlieren technique to observe the buoyancy convection, and use Mach–Zehnder interferometry to study and measure the thickness of the diffusion boundary layer, the boundary layer is observed and measured by judging the bending of the interferometer carrier fringes.

In the present work, the optical diagnostic system consisting of the Mach–Zehnder interferometer and phase-shift device increases the measuring sensitivity in comparison with the conventional two-beam interferometer, and an image processor has been developed for studying

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the mechanism of crystal growth based on the fluid mechanics. The process of dissolution and crystallization of the $NaClO_3$ crystal has been monitored. The buoyancy convection in the growth cell introduced by the exchanges of the solution's concentration gradient under gravity [4] has been visualized as a plume flow in the crystal growing process, which influences the mass transfer of the crystallization interface and dominates the growth rate of the crystal growing face. In this research work, the interval of carrier fringes of the interferometer is adjusted in the infinite case. The fringes given in this paper are introduced only by the change of concentration when the crystal is dissolving and growing. The buoyancy convection and the thickness of the diffusion boundary layer are visualized very clearly.

The optical interferometry is a good measurement for the study of the crystal growth. This technique may be used to observe the crystal growth process together with the fluid convection process, and the effect of the gravity. The experimental results are given in the present paper.

2. Experiment theory

2.1. Interferometry theory

Two coherent light beams meet together and then the interferometric fringes are created as the result of interference. These fringes carry out the physics quantities of the flow field in which the light passes through. Suppose that $A_1(x, y)$ and $A_2(x, y)$ are the complex amplitudes of the two light beams, which have the same vibration direction, of equal frequency, and transmit in the $x{-}y$ plane. The two complex amplitudes are expressed as follows:

$$A_i(x, y) = a_i(x, y) \exp[j\phi_i(x, y)] \quad (i = 1, 2), \tag{2.1}$$

where $\phi_i(x, y)$ is the optical phase determined by the wavelength of light λ and the optical distance $L_i(x, y)$ as

$$\phi_i(x, y) = \frac{2\pi}{\lambda} L_i(x, y) \quad (i = 1, 2). \tag{2.2}$$

The superposition light intensities of the two light beams are

$$\begin{aligned} I(x, y) &= |A_1(x, y) + A_2(x, y)|^2 \\ &= I_0(x, y) + I_c(x, y) \cos \Delta(x, y). \end{aligned} \tag{2.3}$$

Here,

$$I_0(x, y) = a_1^2(x, y) + a_2^2(x, y), \tag{2.4}$$

$$I_c(x, y) = 2a_1(x, y)a_2(x, y), \tag{2.5}$$

$$\Delta(x, y) = \phi_2(x, y) - \phi_1(x, y). \tag{2.6}$$

It shows that the interference fringes will occur when these two light beams have been superposed, the fringes include the information of amplitude and phase. The phase of light and the difference of the optical distance are calculated by the analysis of these fringes.

2.2. Phase shift theory

For the analysis of the interferometric fringes to get the physical parameter from these fringes, the four-steps phase-shift theory has been used. The basic theory of phase shift is introducing a phase change [5,6] in the object beam or in the reference beam, getting a changed intensity distribution of the interferometric pattern, and then calculating and obtaining the distribution of phase. In this paper, the method of equal four-steps phase-shift is used, and the shifting step is within the range between 0 and $\pi/2$. As the phase has been shifted in the step $\delta = 2\varepsilon$, the four patterns of fringes are expressed by the following formulas, respectively:

$$A(x, y) = I_0\{1 + \gamma \cos[\phi(x, y) - 3\varepsilon]\}, \tag{2.7}$$

$$B(x, y) = I_0\{1 + \gamma \cos[\phi(x, y) - \varepsilon]\}, \tag{2.8}$$

$$C(x, y) = I_0\{1 + \gamma \cos[\phi(x, y) + \varepsilon]\}, \tag{2.9}$$

$$D(x, y) = I_0\{1 + \gamma \cos[\phi(x, y) + 3\varepsilon]\}. \tag{2.10}$$

Then it gives

$$\phi_0 = tg^{-1}\left\{\frac{\sqrt{|[(A-D)+(B-C)][3(B-C)-(A-D)]|}}{|(B+C)-(A+D)|}\right\}, \tag{2.11}$$

where $\phi_0 \in [0, \pi/2]$. In order to unwrap the phase, it is extended to the range $[-\pi, \pi]$. The value of the optical phase $\phi(x, y)$ can be calculated by the flowing equation:

$$\phi(x, y) = \begin{cases} \phi_0(x, y) & (B-C) > 0,\ (B+C)-(A+D) > 0, \\ \pi - \phi_0(x, y) & (B-C) > 0,\ (B+C)-(A+D) < 0, \\ -\pi + \phi_0(x, y) & (B-C) < 0,\ (B+C)-(A+D) < 0, \\ -\phi_0(x, y) & (B-C) < 0,\ (B+C)-(A+D) > 0. \end{cases} \tag{2.12}$$

2.3. The method of phase shift

There are several kinds of methods that can fulfill the phase shift. In the present research work, a pipe piezoelectric transducer (PZT) is used for the phase shift. The length of the PZT will be changed linearly with the voltage ΔV applied at the PZT element expressed as

$$\Delta L = \frac{2dL}{D_0 - D_1} \cdot \Delta V. \tag{2.13}$$

Here, D_0 and D_1 are the inner and outer diameters of the PZT pipe, respectively, L is the length of the PZT pipe, and d is the strain voltage ratio constant of the material of PZT. The PZT is installed on the mirror M_2 in the reference beam of interferometer (Fig. 1), and it will use the mirror to change the light distance and fulfill the procedure of phase shift.

2.4. The method of phase unwrapping

Phase unwrapping procedure is the most important in phase shift interferometry since an incorrect phase unwrapping results in serious mistakes of the concentration distribution. The phase unwrapping procedure used in the present research is based on extending the phase gradient technique [7]. From formula (2.12), $\Phi(x, y)$ is the step function, a threshold value must be confirmed to judge the phase fringe patterns in 2π steps, and then to set up compensation function $\Phi_0(x, y)$, a continuous phase function $\Phi_c(x, y)$ will be obtained:

$$\Phi_c(x, y) = \Phi(x, y) + \Phi_0(x, y). \tag{2.14}$$

Because of the image noises, sometimes the step boundary of phase fringes is not clear, the threshold value can be confirmed as a range. When the discrepancy of two nearest gray values is smaller than the minimum value of the range, they are not the boundaries. When the discrepancy of two nearest gray values is larger than the maximal value of the range, they are the boundaries. And when the discrepancy of two nearest gray values is in the threshold range, they are the doubt points, the gray value of points near the two doubt points must be used to judge the phase fringe patterns in 2π steps. The software for the phase unwrapping based on the extending phase gradient technique has been developed in the laboratory.

3. Experiment and result

3.1. Optical system

The diagram of the optical diagnostic system is shown in Fig. 1. A He–Ne laser beam passes through the lens L1 and L2 to form a expanded parallel light beam, and then the beam is split by the splitter Bs1 into two parallel light beams. One

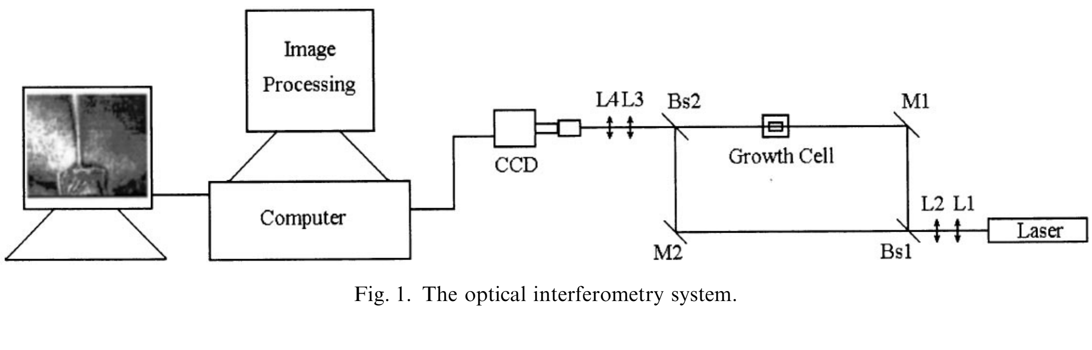

Fig. 1. The optical interferometry system.

is used as the object beam, and another is used as the reference beam. The object light beam is reflected by the mirror M1 first, and passes through the crystal growth cell, then passes through the beam splitter Bs2. The reference light beam is reflected by the mirror M2 which is installed on the element of piezoelectric ceramics to fulfill the action of four steps phase shifts, and then reflected by the beam splitter Bs2. At this point, the object beam and the reference beam meet and form an interferometric fringe pattern. The fringes carry out the concentration gradient of the solution flow field in the crystal growth cell. The image system is composed of the lenses L3, L4 and the CCD camera. The area measured by the interferometer is $5\,mm \times 4\,mm$, and the resolution is about $2\,\mu m$.

3.2. The experiment condition and the image recording system

The 46.43% concentration of $NaClO_3$ solution prepared at 21.00°C is injected into the crystal growth cell of $20.0 \times 12.0 \times 14.0\,mm^3$ dimension. A seed crystal of $NaClO_3$ ($1.80 \times 0.82 \times 5.02\,mm^3$) is placed in the growth cell. The upper surface of the crystal is face (0 0 1). The left and the right faces are faces (0 1 0). At the beginning, the solution is under saturated, so the crystal dissolves slowly. When the temperature of the solution is decreased gradually from 20.00°C down to 17.00°C in 6 h, the solution is turning into super saturation, then the crystal starts to grow gradually.

The image recording system records the interferometric fringe images one by one in every 120 s. The total recording time was 130 min, and 65 images were taken. The crystal growing time was 6 h and 10 min. The four step phase shift interferograms are taken in less than 3 s at one acquisition. The acquisition time is much lesser than that of the concentration change of the solution in the growth cell. All the interferograms of the four-step phase shift are stored in the computer for the post interpretation.

3.3. Results and analysis

As described above, when the crystal is put into the growth cell, the solution is under saturated, and the crystal dissolves at the beginning. The concentration of the solution around the crystal is larger than that in the solution away from the crystal, so the solution around the crystal moves downward in the growth cell as shown in Fig. 2a, and forms a flow. The flow is buoyancy convection, which is introduced by the exchange of concentration under earth's gravity. In the present experiment, the interferometric fringe relates to the concentration gradient of the crystal solution, and it can be seen clearly in the flow field. When the temperature declines to 20°C, the solution becomes saturated and the crystal does not dissolve further, and it does not grow further too.

Because the concentration gradient is formed already at the beginning, the concentration of the solution in the growth cell has a gradient, as shown by the fringes which are parallel to each other (Fig. 2b). When the temperature is decreased gradually from 20.00°C to 17.00°C in 6 h, the solution is supersaturated, and the crystal starts growing gradually. The concentration of the solution around the crystal is lesser than that in the solution away from the crystal, so the solution in the boundary layer of the crystal moves upward in the growth cell, and forms a plume flow, as shown in Fig. 2c–h. The flow is also the buoyancy-convection driven by the exchange of the concentration under the earth gravity. This experiment demonstrates that the buoyancy convection is shown clearly and the mass transfer carried out is due to the convection during the crystal growth. This convection influences the growth rate of the crystal. The size of the crystal is $1.94 \times 0.90 \times 5.12\,mm^3$ after 130 min, and $2.44 \times 1.02 \times 5.44\,mm^3$ after 6 h and 10 min. Because the convection is parallel to face (0 1 0) and vertical to the center of face (0 0 1), the mass transfer of face (0 1 0) is more intense than that of face (0 0 1), so the growth rate of face (0 1 0) must be faster than that of face (0 0 1). The average growth rate of these two faces in this experiment are given as

$$1.6\times10^{-8}\,m/s \quad \text{for face (0 1 0)},$$

$$1.0\times10^{-8}\,m/s \quad \text{for face (0 0 1)}. \tag{3.1}$$

Besides these results, the experiment also demonstrates that there is a diffusion boundary layer near

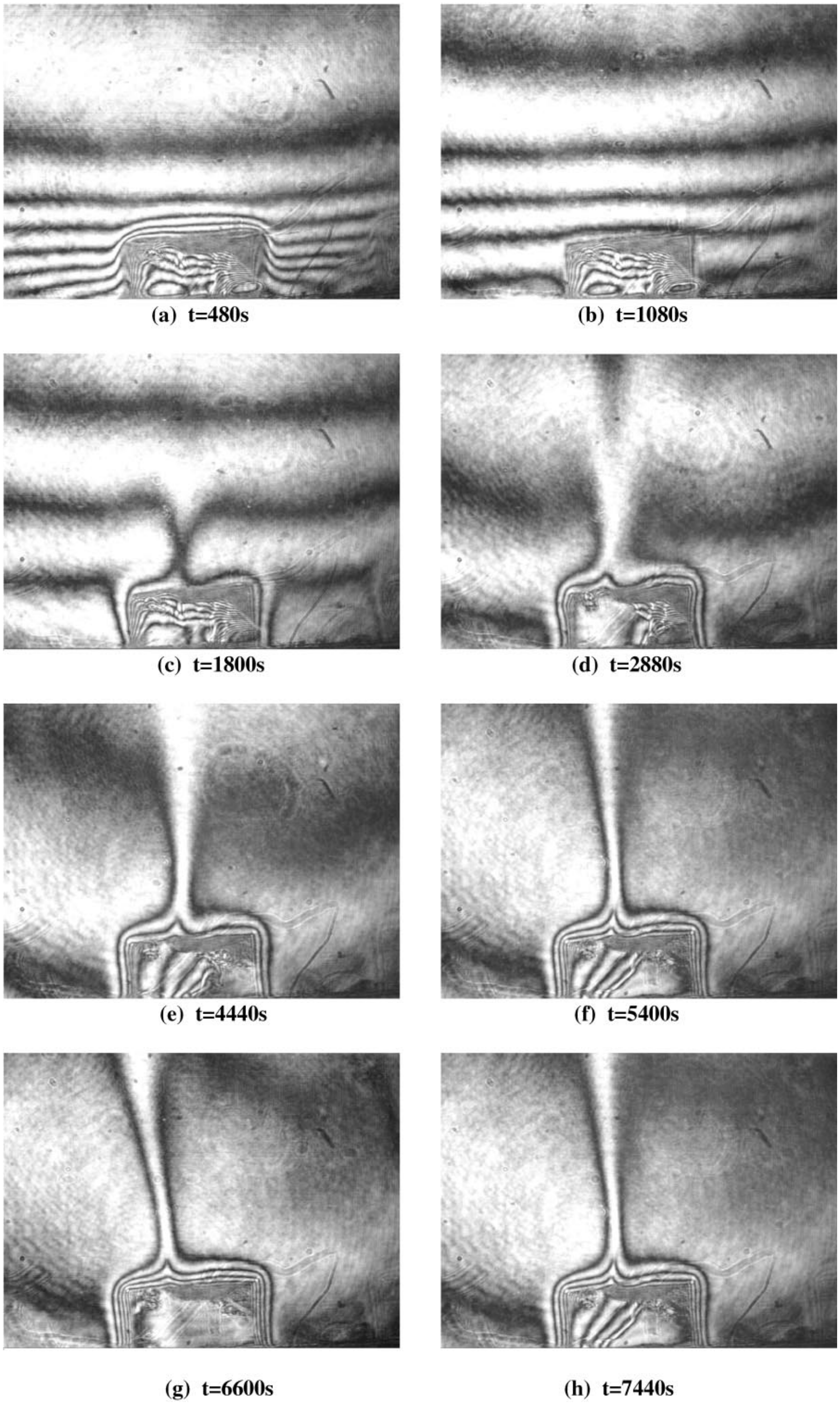

Fig. 2. The dissolution (a) and crystallization (b)–(h) interferograms of $NaClO_3$ crystal.

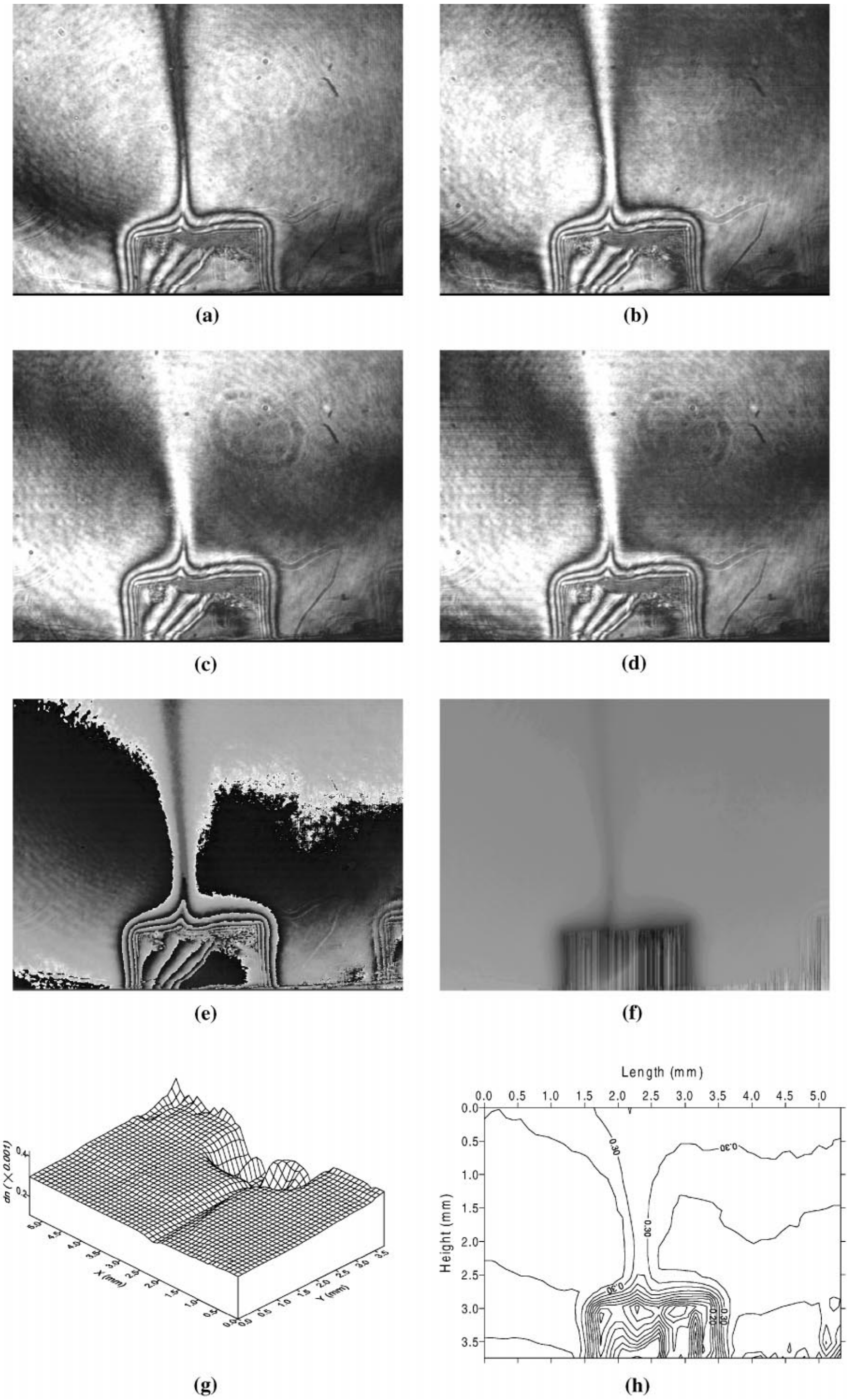

Fig. 3. The interferograms of four steps phase shift (a)–(d), phase calculation (e), phase unwrapping (f), the distribution of refractive index gradient (g) and the contour map (h).

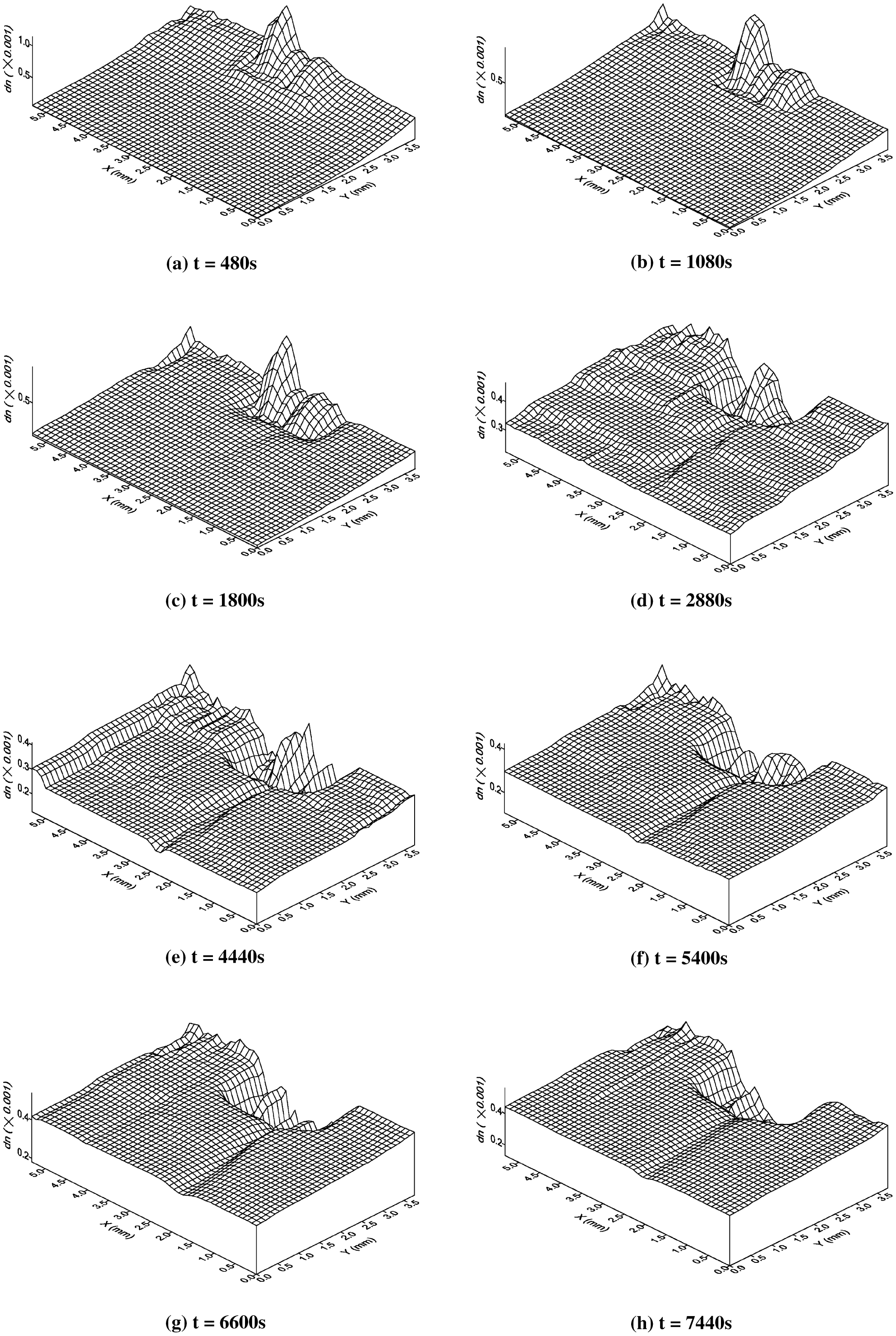

Fig. 4. The developing process of the distribution of refractive index gradient in the solution of the growing crystal $NaClO_3$.

the interface in both cases of the dissolving and the growing. The dissolving diffusion boundary layer of the solution under saturation is larger than that of the growing diffusion boundary layer of the solution in super saturation. Because of the gravity, the growing diffusion boundary layer near interface is as thin as 300 μm in the present experiment. The concentration gradient exists only in the diffusion boundary layer, and the growth rate is faster as the concentration gradient is large.

3.4. The interpretation of the interferometric fringes pattern

According to Bedarida and Piano [8], the relationship between the concentration C and index n is

$$n = 1.32415 + 0.00136C, \quad (3.2)$$

and the differential coefficient is

$$\mathrm{d}n = 0.00136\,\mathrm{d}C. \quad (3.3)$$

So the change of concentration dC is linear with the change of index dn.

The four-steps phase-shift interferograms were recorded in the present experiment as an example shown in Fig. 3a–d. The phase calculation and unwrapping have been operated, the results are shown in Fig. 3e and f. Refractive index distribution of the solution and the contour map have been obtained. The refractive index is related directly to the concentration of the solution, as shown in Fig. 3g and h. In Fig. 3g, the only distribution of the refractive index gradient outside the crystal is the right data measured and calculated from the interferograms of the four steps phase shift. The developing process of the refractive index gradient distribution in the solution is given in Fig. 4, according to the interferograms shown in Fig. 2. It is clear that the concentration gradient changes during the whole process of crystal growth.

4. Conclusion

In the present research, the convection driven by the exchange of concentration of solution is very slow compared with the time of signal (four step phase shift interferograms) acquisition. The phase shift interferometry may be used as the quasi-real-time'' mode to measure and visualize the change of the solution concentration during the crystal growth, and to study the heat and mass transfer. This technique supports the observation of the crystal, growing together with fluid process, It is beneficial in understanding of fluid flow phenomena of crystal growth process. Using the Mach–Zehnder interferometer, the measurement of $NaClO_3$ crystal growing in situ has been obtained successfully. The dissolution and crystallization of $NaClO_3$ crystal have been studied experimentally, the distribution of refractive index gradient has been calculated, and the buoyancy convection (plume flow) during the crystal growth has been visualized and analyzed. The experiment demonstrates that the buoyancy convection is created by the exchange of concentration of the solution in a very thin boundary layer of about 200 μm, which influences the growth rate of the crystal growing faces.

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