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Application of holographic interference microscope in the investigation of crystal dissolution

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Real time holographic interference method was applied to investigate the crystal-solution interfacial layer during dissolution. The application of an etalon beam inclined with respect to the investigated beam enabled us to obtain interference fringe pattern in which the fringe contour intimately corresponds to the dependence of refractive index of the solution on the distance from the dissolving crystal. An analysis of the results showed a strong influence of convection, even in a 1 mm thick cuvettes, on the dissolution process. It has been also found that thermal effects involved during dissolution do not affect significantly the contour of interference fringes.

1. Introduction

Investigations of solution layer in the vicinity of the crystal surface is invaluable in the understanding of the mechanisms of growth or dissolution of crystals. This solution layer was examined by using different optical methods [1–5]. However, recently holographic interferometry has been more and more frequently used for this purpose, because it has some advantages over other methods. The holographic methods were, in particular, applied to the observation of convection-induced motions in solutions close to the surface of the growing crystals [6–8], as well as to the visualization of lines of equal concentration in the solution [6, 9]. In the majority of cases, the employed holographic setups allow to record the lines of equal concentration corresponding to interference fringes, which makes it possible to determine the value of concentration from one fringe to another (in a discontinuous way).

Application of two (reference and analysed) beams mutually inclined allowed us to obtain interference fringes, the shape of which corresponded to the character of the dependence of refractive index on the distance from the crystal. A holographic microinterferometer built in the Central Optical Laboratory [10–14], where a damping of the coherent noise is provided [15–18], was used for this purpose.

2. Theoretical fundamentals

Observations of the dissolving crystal have been made by using the method of real-time holographic interferometry [19–22] by comparing the etalon beam (formed in the microscope at the presence of the cuvette filled with a uniform solution) reconstructed from the hologram with the investigated beam being perturbed by the dissolving crystal introduced to the cuvette. Since in order to obtain the fringe pattern the angle of incidence of the reconstructing wave on the hologram was changed. Consequently, the direction of propagation of the etalon beam was changed to the same degree. As may be easily shown, the shape of the obtained interference fringe depends strictly upon the transversal distribution of the changes in optical path differences, averaged along the thickness of cuvette, for both the cuvette containing the crystal and without it.

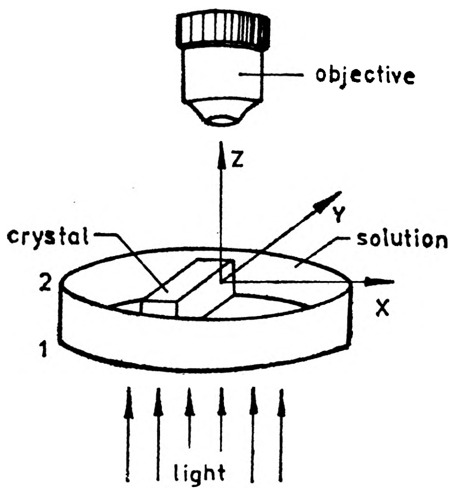

Fig. 1. The orientation of the co-ordinate axis in measuring system

In order to show this dependence we shall consider the case illustrated in Fig. 1. It is assumed that the crystal under investigation is immersed in a suitable solution contained in a cuvette the depth of which is equal to the thickness of the crystal. The origin of the x, y, z coordinate system (the z-axis of which follows the direction of the light wave propagation) is located at the middle point of the crystal wall at which the changes in the optical paths in the solution are investigated.

According to the principles of the real-time holographic interferometry, the light wave formed of the wave illuminating the object due to its passage through the cuvette filled with the etalon solution, or sometimes with distilled water, is recorded on the hologram. By assuming that the complex amplitude of the illuminating light wave on the surface 1 of cuvette at a given time is described by the expression

$$U_1(x, y) = a\exp[-i\varphi(x, y)], \tag{1}$$

the complex amplitude on the cuvette surface 2 may be represented as follows:

$$U_2(x,y) = a\exp\left\{-i\left[\varphi(x,y)+\frac{2\pi}{\lambda}n_e h\right]\right\}. \tag{2}$$

In the above expressions a is the real amplitude of the light wave, $\lambda = 632.8$ nm – wavalength of the used radiation, n_e – refractive index of the etalon medium, and h – thickness (depth) of the cuvette. If all the necessary conditions [21] are satisfied, then, according to the principles of holography, the light wave reconstructed from the hologram will be of the same form as that recorded on the hologram (and given by the expression (2)). If the angle of incidence of the reconstructing wave is changed during the reconstruction, the direction of propagation of the reconstructed wave will be changed by the same angle. Under the experimental conditions the incidence angle was changed so as to cause the rotation of the reconstructed wavefront around the x-axis, resulting in formation of an interference fringe field. The effect of the rotation by an angle α around the x-axis of the reconstructed wavefront on the phase distribution corresponds to the introduction of an additional linear factor due to which the complex amplitude of the etalon wave takes the form

$$U_e(x,y) = a\exp\left\{-i\left[\varphi(x,y)+\frac{2\pi}{\lambda}(n_e h - y\sin\alpha)\right]\right\}. \tag{3}$$

In real-time holographic interferometry independently of the above etalon wave, there appears an object wave $U_0(x, y)$ which is the incident wave $U_1(x, y)$ described by the expression (1) after its passage through the object. In the case of objects perturbing the incident light not too strongly (since only such objects may be examined by the interference methods) the object wave may be represented as follows:

$$U_0(x,y) = a\exp\left\{-i\left[\varphi(x,y)+\frac{2\pi}{\lambda}l_{1,2}(x,y)\right]\right\} \tag{4}$$

where $l_{1,2}$ is the optical path of the light ray striking the image plane at the point (x, y), resulting due to the coverage of the distance between the walls 1 and 2 of the cuvette (Fig. 1) covered by this ray along the trajectory $t_{1,2}$

$$l_{1,2}(x,y) = \int\limits_{t_{1,2}} n(x,y,z)\,dz. \tag{5}$$

Taking account of the fact that the light intensity distribution $I(x, y)$ across the interference field is given by the squared modulus of the sum of squared amplitudes, it can be easily shown that

$$I(x,y) = 2a^2\left\{1+\cos\left[\frac{2\pi}{\lambda}(l_{1,2}(x,y)-n_e h+y\sin\alpha)\right]\right\}. \tag{6}$$

Hence, it may be seen that when the solution in the cuvette has a uniform distribution of the refractive index (i.e., when $l_{1,2}(x, y) = n_e h$), the interference field has the form of fringes parallel both to x-axis and to each other, the mutual distance of the latter being

$$\delta = \frac{\lambda}{\sin\alpha}. \tag{7}$$

After inserting the crystal to the cuvette and filling it with the solution, the interference field undergoes changes such that the k-th interference fringe passes through the points satisfying the equation

$$y_k \sin\alpha + l_{1,2}(x, y) - n_e h = k\lambda. \tag{8}$$

If it is assumed that the length of the crystal wall on which the observation is made is much greater than the range of the changes of refractive index caused by the insertion of the crystal, then the changes in the refractive index in the y-direction of the accepted coordinate system may be neglected, and the optical path $l_{1,2}(x, y)$ will be a function of the x coordinate only. Under these circumstances the run of an interference fringe may be written in the form

$$y_k(x) = k\delta + \delta\frac{h}{\lambda}[n_e - n_s(x)] \tag{9}$$

where

$$n_s(x) = \frac{l_{1,2}(x)}{h} \tag{10}$$

is the value of the refractive index, averaged along the cuvette thickness, of the medium under investigation.

In the used optical system the inclination of the etalon wave corresponded to the negative values of the angle α, therefore δ in expressions (7)–(9) is also negative. Considering this fact, on the basis of the expression (9) it may be stated that the shape of the function $y_k(x)$ (shape of the interference fringe) is identical with the shape of the function $n_s(x)$.

The analysis of the results obtained may be conveniently accomplished by using the gradient of the refractive index

$$\frac{dn_s}{dx} = -\frac{\lambda}{\delta h}\frac{dy_k}{dx}. \tag{11}$$

3. Experimental

Observations of the KDP crystal dissolution were carried out by using the microscope objective of 10 × magnification and 0.24 numerical aperture. Such an objective enabled the tracing of interference fringes at a distance greater than 4–5 μm from the investigated crystal wall. The dissolution process was observed in cuvettes of 15 mm diameter and 1, 2 or 5 mm height. The bottom and the cover of the cuvette were, respectively, made of 1 and 0.15 mm thick glass plates. The KDP crystal of thickness equal to the height of cuvette was located on its bottom in such a way that the (100) face was perpendicular to the bottom. The cuvette together with the crystal was located in the field of view of the microscope and positioned in such a way that the interference fringes were perpendicular to the (100) face of the crystal. Then water or KDP aqueous solution of concentration ranging from 5.57 to 22.3 g/100 g H_2O was poured into the cuvette which was subsequently covered. The photography of the interference fringes was started after 30–60 s and continued at an interval of 5–60 s. All the experiments were conducted at the room temperature.

4. Results and discussion

A gradient of the refractive index appearing around the crystal as a result of crystal dissolution is caused by the gradient of both concentration and temperature. An example of the interference fringe pattern is shown in Fig. 2. In order to analyse the dependence of the refractive index gradient on the distance from the crystal surface, we measured the tangent dy/dx of the inclination

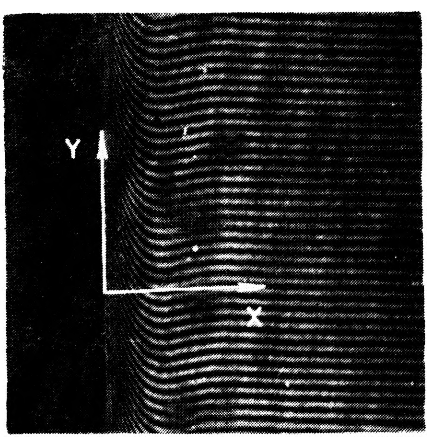

Fig. 2. Photograph of fringe field obtained after 6 min of the dissolution of KDP crystal in water. Thickness of the cuvette is 5 mm, $\delta = 24$ μm

angle of the fringe with respect to the normal to the crystal surface. According to expression (11), this tangent is proportional to the refractive index gradient. Fig. 3 represents the changes in the refractive index gradient with the distance from the crystal at different times, while Fig. 4 shows the changes occurring with time at different distance from the crystal.

An analysis of the curves, typically illustrated in Fig. 4, allows us to state that the dissolution process may be observed for 2 to 30 min depending on the initial concentration of the solution. Greater time intervals correspond to

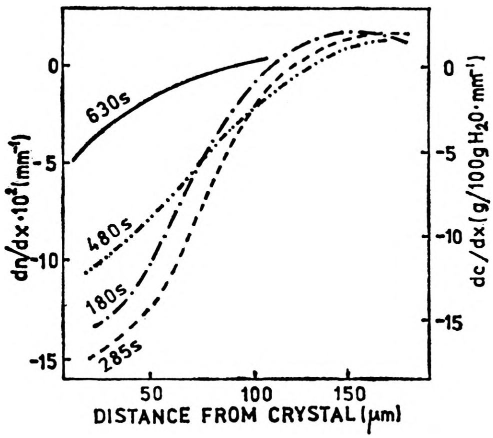

Fig. 3. Gradients of refractive index and concentration as the functions of distance from the crystal

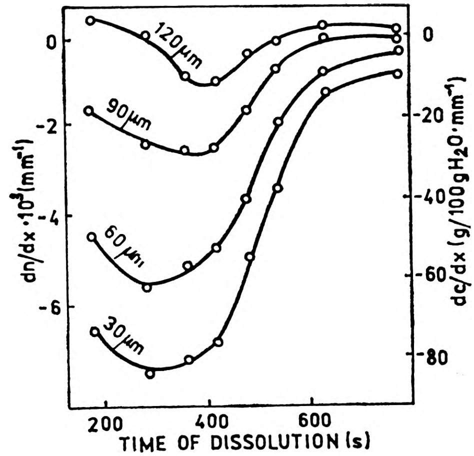

Fig. 4. Gradients of refractive index and concentration as the functions of time of dissolution

dissolution in solutions of lower initial concentrations. The employed setup does not allow us to measure the refractive index gradient thereafter, although a small fringe curvature may still be observed.

From the curves shown in Figs. 3 and 4 it may be seen that the highest gradient of the refractive index at the crystal surrounding appears after some time. This delay depends mainly on the cuvette thickness and amounts to about 6 min for the cuvette 5 mm high and ranges from 1.5 to 2.75 min for cuvettes 1 mm height.

In order to study the influence of the temperature gradient connected with crystal dissolution on the shape of the interference fringes separate experiments were carried out. In these experiments, instead of the crystal an electric heater, the dimensions of which were close to those of the crystals used for study, was introduced to the cuvette. From the available data, it was estimated that under the experiment conditions the crystal acts as a heat antisource 8 to 9 mW power. When the heater of this power was applied, no discernible changes in the shape and position of the interference fringes were observed. The changes in the fringe inclination (Fig. 5) could be observed first for the output power greater by two orders of magnitude. Under these conditions the thermal equilibrium in the cuvette was established after several seconds, and the refractive index gradient in the vicinity of the heater was equal to 0.66×10^{-3} mm^{-1}. This value corresponds to the temperature gradient of 4.8 K mm^{-1}, which has been calculated from the data reported by KRASIŃSKI et al. [5]. Assuming that the temperature gradient during the dissolution is less by two orders of magnitude, its influence on the shape of the interference fringes may be neglected.

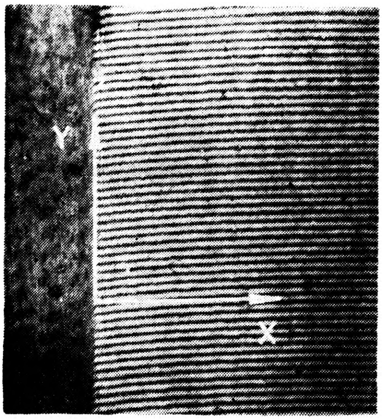

Fig. 5. Photograph of fringe field observed near the heater of power ca 1 W. Thickness of the cuvette is 5 mm, $\delta = 24$ µm

The shape of the observed interference fringes (Fig. 2) shows that the mean refractive index (averaged along the cuvette axis) initially decreases rapidly with an increase in the distance from the crystal, whereas thereafter first it increases slightly and then decreases again. This effect, especially well visible during the first 2–3 min of dissolution, is particulary sharp in the cuvettes of 5 mm thickness, when the crystal is dissolved in water. In the cuvette of 1 mm thickness and during dissolution in solutions of concentrations higher than 10 g of KDP/100 g of H_2O, this phenomenon is practically unobservable. It seems that this phenomenon is associated with a rapid diminution in the solution density in the vicinity of the dissolving crystal with increasing distance from the crystal surface. A high density gradient leads to the development of a convection current directed downward at the crystal surface and then to a rotational motion of the fluid which carries upward a significant portion of the solution of higher concentration. It may be expected that in this region the optical path of the light passing through the cuvette and the mean refractive index will increase. An analogous behaviour of dn/dx with the distance from the crystal was observed by WOJCIECHOWSKI and KRASIŃSKI [23] who used the Moiré fringes method.

The results obtained allow us to state that even in thin cuvettes (of 1 mm thickness) the convection currents, caused by the forces of gravity, perturb the dissolution medium so strongly that their influence on the kinetics of crystal dissolution can not be neglected.

The observation technique used here may be advantageous in the investigations of the influence of convection on the phenomena appearing in the vicinity of the crystal-solution boundary during dissolution or growth of the crystals from solution. However, only the application of this technique under the microgravitation would allow us to distinguish explicitly the convection and diffusion effects.

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Применение интерференционного голографического микроскопа для исследования растворения кристаллов

В работе представлен метод голографической микроинтергферометрии в реальное время при применении для исследования слоя раствора вблизи растворяющегося кристалла. Применение эталонного пучка, наклоненного относительно к предметному позволило получить интерференцион-