Influences of high magnetic field on glycine crystal growth

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Abstract

The effects of horizontal high magnetic field (8T) on both the orientation of the α-form glycine crystal and the growth rate were studied. The α-form glycine crystal is oriented in the high magnetic field in such a way that its crystallographic *c*-axis is at about 45° with the direction of magnetic field. This orientation is explained by the magnetic susceptibility anisotropy of the crystal structure. The crystal growth rate in the *c*-axis direction decreases by about 20% in a magnetic field (8 T). Mechanisms of the magnetic field effect on the growth rate are discussed.

Keywords

magnetic field effects, glycine, crystal growth, magnetic orientation,

1. Introduction

It is a dream for many scientists to control chemical, physical and biological phenomena by means of magnetic fields, as every material has its inherent magnetism, i.e., diamagnetism, paramagnetism or ferromagnetism. Recent superconducting magnet technology makes this dream come true, and many phenomena associated even with diamagnetic materials are affected by high magnetic fields. In our group, we have studied the influence of high magnetic fields (up to 15 T) on various chemical, physical and biological phenomena i.e., magnetic field effects (MFEs) on an organic photochemical reaction [1], MFEs on a metal dendrite deposition reaction [2], three-dimensional morphological chirality induction in inorganic membrane tubes using magnetic fields [3], magnetic separation of metal ions in solution [4], magnetic control of thermal convection in liquid solutions [5], magnetic separation of plastic chips [6], and MFEs on the movement of *E. coli* [7].

Control of crystallization is also one of the current interests for chemists and biologists. It is important to improve crystal quality, especially for proteins, for X-ray structural analysis in biochemistry or medicinal chemistry. Orientation of inorganic and organic aggregates is very important technique for improving the quality of materials in material chemistry. Our group has studied magnetic orientation of organic crystals [8] and carbon nanotubes [9]. By using quasi-microgravity generated by magnetic force, X-ray crystallographic quality of lysozyme crystals is improved [10]. Although, from the above-mentioned studies, it is shown that a high magnetic field is a useful tool for controlling crystallization, there still remain many problems to be solved as to the role of magnetic fields in crystallization.

There are a few reports on the effects of *vertical* magnetic fields on crystal growth [10-13], since the vertical magnetic force is expected to vary effective earth's gravity, which is a cause of natural convection of solution. In the case of a horizontal magnetic field, the magnetic force is perpendicular to the gravity. Therefore, it is interesting to examine whether a horizontal magnetic field affects crystal growth analogously.

In this paper, we investigated effects of a *horizontal* magnetic field of 8 T on both orientation of glycine α-form crystals, which is one of the typical amino acid crystals, and its growth rate, in order to examine the effects of *horizontal* magnetic field. It is shown that a horizontal field affects not only crystal orientation but also crystal growth rate. Mechanisms of these effects are discussed.

2. Experimental

A horizontal magnetic field was applied using a superconducting magnet (Oxford, Spectromag-1000, 8 T).

Magnetic orientation: Glycine (Nacalai Tesque, analytical grade) was dissolved in hot distilled water (~343K) to prepare a 27 wt% solution of glycine. The hot solution (ca. 10cm^3) was poured into a glass vessel (50 mm × 31 mm ×30 mm). The vessel was placed in the magnet bore, and a second vessel was placed outside of the bore as a control. Glycine α-form crystals were obtained by cooling the hot solution to 293K and keeping its temperature at 293 K for 12 hr, as the degree of supersaturation of the solution was 66% at 293 K. The temperature of the vessels was controlled by circulating water from a thermostat. Water in the vessel was removed and the orientation of crystals was recorded by a camera after taking the vessel out of the bore.

Crystal growth rate: Seed crystals were prepared from super saturated glycine solution. Single crystals (ca. 1.0 mm) of lozenge shape were used as seeding crystals, because their crystal axes are known.[14] A seed crystal was fixed at the center of a plastic dish (φ30 mm×11mm) with a quick-adhesive glue in such away that the *c*-axis of the crystal was in parallel with the field direction. Glycine was dissolved in hot water (~323K) to prepare 21wt% solution for the crystal growth. The plastic dish containing the hot glycine solution (ca. 3.0cm^3) was placed at the center of the magnet field, and the temperature of the solution was kept at 298K. The crystal growth rate was measured after the crystal grew constantly. The growth of a glycine crystal in magnetic field was observed by a fiberscope (Olympus R100-095-090-50) - an illuminator - a CCD camera and a video recorder system.

Behavior of the solution during crystal growth was observed by the Schlieren method [15]. Collimated white light from a tungsten lamp was introduced to a sample cell attached to a glycine single crystal on the bottom and filled with the supersaturated solution (ca. 4-8 %). The transmitted light was condensed by a lens, partially blocked off by a thin plate at the condensed point, and then projected on a screen. The Schlieren image on the screen was monitored by a CCD camera and a video recorder.

3. Results and Discussion

Magnetic orientation: Figure 1 shows photographs of α-form glycine crystals in the absence and presence of a magnetic field of 8T. The crystal system of α-form glycine crystals is monoclinic, and the typical shape of glycine crystal was lozenge (typically, ca. 4 mm × ca. 2 mm × ca. 2 mm). The crystals are randomly oriented at zero field (a). In a magnetic field of 8 T, lozenge α-form glycine crystals are oriented so that their *c*-axis is at an angle of about 45° with the direction of magnet field (b).

The magnetic orientation of glycine crystals shown in Fig. 1 can be explained by the anisotropic magnetic susceptibility of α-form glycine crystal. The crystal symmetry is monoclinic and the cell dimensions are as follows [14]; a =5.10Å, b = 11.97Å, c = 5.45 Å, β = 111.7° and Z = 4. The space group is C_{2h}^5 ($P2_1/n$). Figure 2(a) shows the crystal structure of α-form glycine. The upper part of (a) indicates the relationship between the experimentally obtained crystal shape and the crystallographic axes. The lower part of (a) shows schematically the molecular arrangement in the crystal. The crystallographic *ac*-plane contains the C-O···H-N intermolecular bonds, and the bimolecular layers consisted of the C-O···H-N intermolecular bonds are accumulated along the direction to *b*-axis. Figure 2(b) shows the arrangement of magnetic axes in the crystal viewed along the χ_3 axis. The χ_3 axis corresponds to the crystallographic *b*-axis. The χ_1 axis is at an angle of about 46° with the *c*-axis on the *ac*-plane and the one magnetic axis is perpendicular to each of the others [16]. The magnetic axis which is perpendicular to both the χ_1 and χ_3 is labeled χ_2. The magnetic susceptibilities are estimated from the magnetic anisotropy data and the average susceptibility to be $\chi_1 = -50.412$, $\chi_2 = -52.002$, and $\chi_3 = -56.582$ (10^{-6} cm^{3}mol^{-1}) [17].

The magnetic anisotropy energy $E(N, \theta, H)$ of an α-form glycine crystal is given by eq. (1) [8],

$$E(N, \theta, H) = -(1/2)\, \mu_0 n[\chi_2 + (\chi_1 - \chi_2)\cos^2\theta]\, H^2 \qquad (1)$$

where μ_0 is the magnetic permeability of vacuum, n is the mole number of the crystal, χ_i is the molar magnetic susceptibility along the i axis, θ is the angle between the χ_1 and the magnetic field direction, and H is the magnetic field strength. In eq. (1), the χ_3 does not appear, because the χ_3 is fixed along the gravity direction in the present experimental condition. Because $|\chi_1| < |\chi_2|$, the magnetic anisotropy energy becomes the smallest in a magnetic field when θ equals 0°. When $\theta = 0°$, the χ_1 is parallel to the direction of the magnetic field. This means that the crystallographic *c*-axis makes at an angle of about 46° with the direction of the magnetic field. Magnetic orientation of glycine crystal growth is, therefore, explained by the minimization of its energy in a magnetic field.

Crystal growth rate: Figure 3 shows the growth length of the crystallographic *c*-axis of the α-form glycine crystal. Crystal growth rates in the absence and presence of a magnetic field of 8 T were obtained using the same crystal, since the absolute growth rate varies slightly from crystal to crystal. The magnetic field was changed from 0 T to 8 T or 8 T to 0 T during the crystal growth, since it takes 18 min to change the field intensity. Fig. 3 (a) shows the glycine crystal growth when it is initially grown at zero field for 15 min and then grown at 8 T. Figure 3 (b) shows the crystal growth when it is grown initially at 8 T, followed by the growth at zero field. From the slopes of the straight lines in the figure, the growth rates at zero field and 8 T are estimated to be 0.0261 and 0.0222 mm min^{-1}, respectively, in case (a) and 0.0184 and 0.0138 mm min^{-1}, respectively, in case (b). In both cases the growth rate is decreased by about 20% by applying a magnetic field of 8 T.

The behavior of the glycine solution in the vicinity of the crystal during crystal growth was examined by the Schlieren method, as it is suitable for observing the density or refractive index change in solution. Figure 4 shows a Schlieren image at zero field. The dark silhouette at the center was a glycine crystal (about 2 mm). A bright layer on the crystal surface, indicated by a in Fig. 4, is attributable to the low density solution caused by deposition of glycine on the surface. A less bright vertical band over the crystal, indicated by b in the figure, is also attributable to the low density solution. The bulk solution near the bright layer (a) and the vertical band (b) undergoes the steady-state convection indicated by two curved arrows in the figure, as reported [15]. This fact means that the bright layer solution of low density (a) flows upwards as the vertical band (b). This convection of the solution is caused by the density gradient due to deposition of glycine on the seed crystal surface. Effect of a magnetic field of 8 T on the Schlieren image of the above solution was examined. However, no remarkable effect was observed, showing the image is less sensitive for observation of a relatively small magnetic field effect.

In addition, *in situ* observation of the glycine solution during crystallization reveals that micro-crystals with a few μm in length grown in the bulk solution move around and occasionally attach on the seed crystal surface. Glycine crystal grows via two processes, *i.e.*, deposition of solute and attachment of micro-crystals.

Magnetic field effects on the glycine crystal growth rate may be explained by the mechanical forces which influence glycine transportation from the bulk solution to the seed crystal surface.

The isotropic magnetic energy E of a substance is given by eq. (2),

$$E = (1/2)\mu_0\chi H^2 \qquad (2)$$

where χ is the isotropic magnetic susceptibility of the substance.

The mechanical force, $F(z)$, due to the magnetic energy can be obtained by differentiating (2),

$$F(z) = -\,\partial E/\partial z = \mu_0\chi H\partial H/\partial z + (1/2)\mu_0(\partial\chi/\partial z)H^2 \qquad (3)$$

where $\partial \mathrm{H}/\partial z$ is the gradient of H in the z direction, and $\partial\chi/\partial z$ is the gradient of χ in the z direction. The first term of the right-hand side of eq. (3) is called magnetic force. This term is dependent on the direction of magnetic field gradient and its intensity is proportional to $H\partial H/\partial z$. The second term of the right-hand side of eq. (3), which is usually neglected, is tentatively called the magnetic susceptibility force. This term is not dependent on the field direction but the susceptibility gradient direction and is in parallel with the gradient.

The magnetic force on the supersaturated solution seems negligibly small, since $H\partial H/\partial z$ along the bore tube axis is very small in the present experimental condition. The magnetic susceptibility force is calculated by assuming that the glycine concentration of the bulk solution is that of supersaturated solution, the concentration on the surface of the crystal is the saturated concentration and the thickness of the concentration gradient layer is that observed by the Schlieren image (0.04 mm). Since the concentration gradient between the bulk and the boundary layer solutions is estimated at 5. 0 g cm^{-3} cm^{-1} and the magnetic susceptibility of glycine is -0.71×10^{-6} cgs emu, the magnetic susceptibility gradient is estimated to be -3.55×10^{-6} cgs emu cm^{-1}. Then, the force is estimated to be 11,400 dyn cm^{-3} at 8 T, whose direction is normal to the crystal surface. The value is comparable to the gravitational forces normal to the solution layer on a crystal, since they are about 4900 dyn cm^{-3} for a horizontal upper surface and 0 dyn cm^{-3} for a vertical surface, depending on the direction of the surface. This simple calculation might somewhat overestimate the intensity of the magnetic susceptibility force. Nevertheless, the calculation means that the magnetic susceptibility force may be strong enough to influence the convection of the solution. Because of the magnetic susceptibility force, the thin layer solution covering the crystal surface may be uniformly pressed on the crystal surface. The rate of convection might decrease, as the fluidity of the solution at the layer would decrease. Therefore, it is not unlikely that the magnetic susceptibility force retards partly the glycine transportation to the crystal surface due to convection. The Lorentz force does not affect the glycine crystal growth, since glycine is mostly dissolved in neutral form in water. Furthermore, the microcrystal attachment on the crystal surface may be depressed by the magnetic susceptibility force as well, since microcrystal may be transported by convection of the solution. Therefore, magnetic suppression of glycine crystal growth is partly explainable by the magnetic susceptibility force.

Effects of vertical magnetic fields on the crystal growth are mainly interpreted in terms of magnetic force [11-13]. However, the present result using a homogeneous and horizontal magnetic field, in which the effect of magnetic force is less significant, suggests the importance of the magnetic susceptibility force for controlling the crystal growth.

4. Conclusion

Influence of a horizontal magnetic field on glycine crystal growth was examined. α-Form glycine crystals were oriented in a high magnetic field (8T), with their crystallographic *c*-axis at about 45° with the field direction. This magnetic orientation of α-form glycine crystals may be explained by their anisotropy of magnetic susceptibility. The growth of α-form glycine crystals along the *c*-axis was suppressed by the high magnetic field (8T). The magnetic suppression of crystal growth is discussed in terms of the magnetic susceptibility force which is caused by the magnetic susceptibility gradient in the vicinity of the crystal surface.

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Figure captions

Figure 1 Top view photographs of glycine α-form crystals grown in (a) 0 T and (b) 8 T. An arrow indicates the direction of magnetic field.

Figure 2 The crystal structure of a glycine α-form crystal. (a) The relationship between the crystal shape and the crystallographic axes and molecular arrangement in the crystal. (b) The relationship between crystal shape and magnetic axes of the crystal.

Figure 3 The growth length of glycine crystal in the c-axis. (a) Magnetic field is changed from 0 T to 8 T. (b) It is changed from 8 T to 0 T. (see text)

Figure 4 A Schlieren image of the glycine solution during crystal growth at zero field. The dark Silhouette at the center is a seed crystal. Two curved arrows indicate the direction of convection.

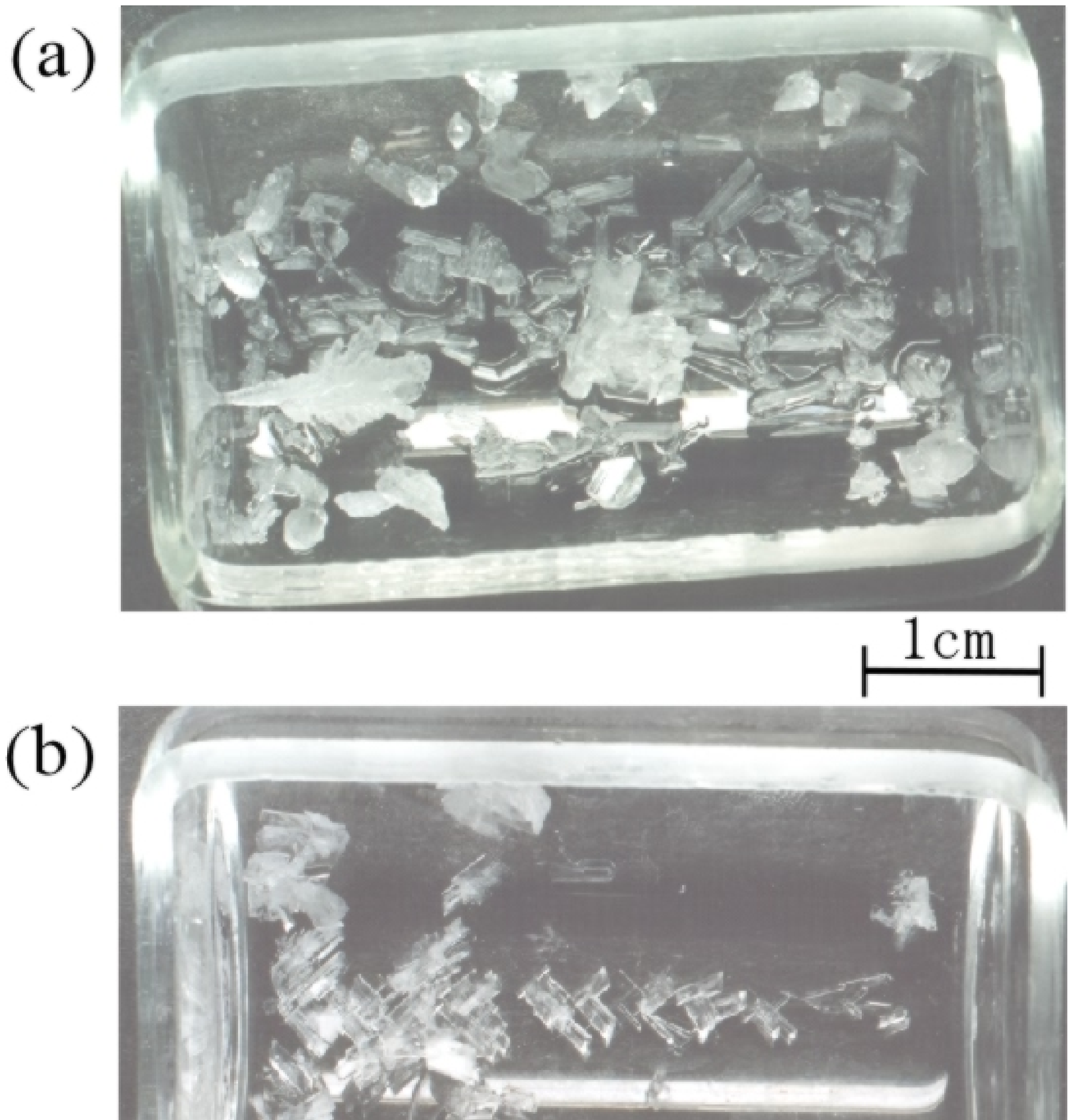
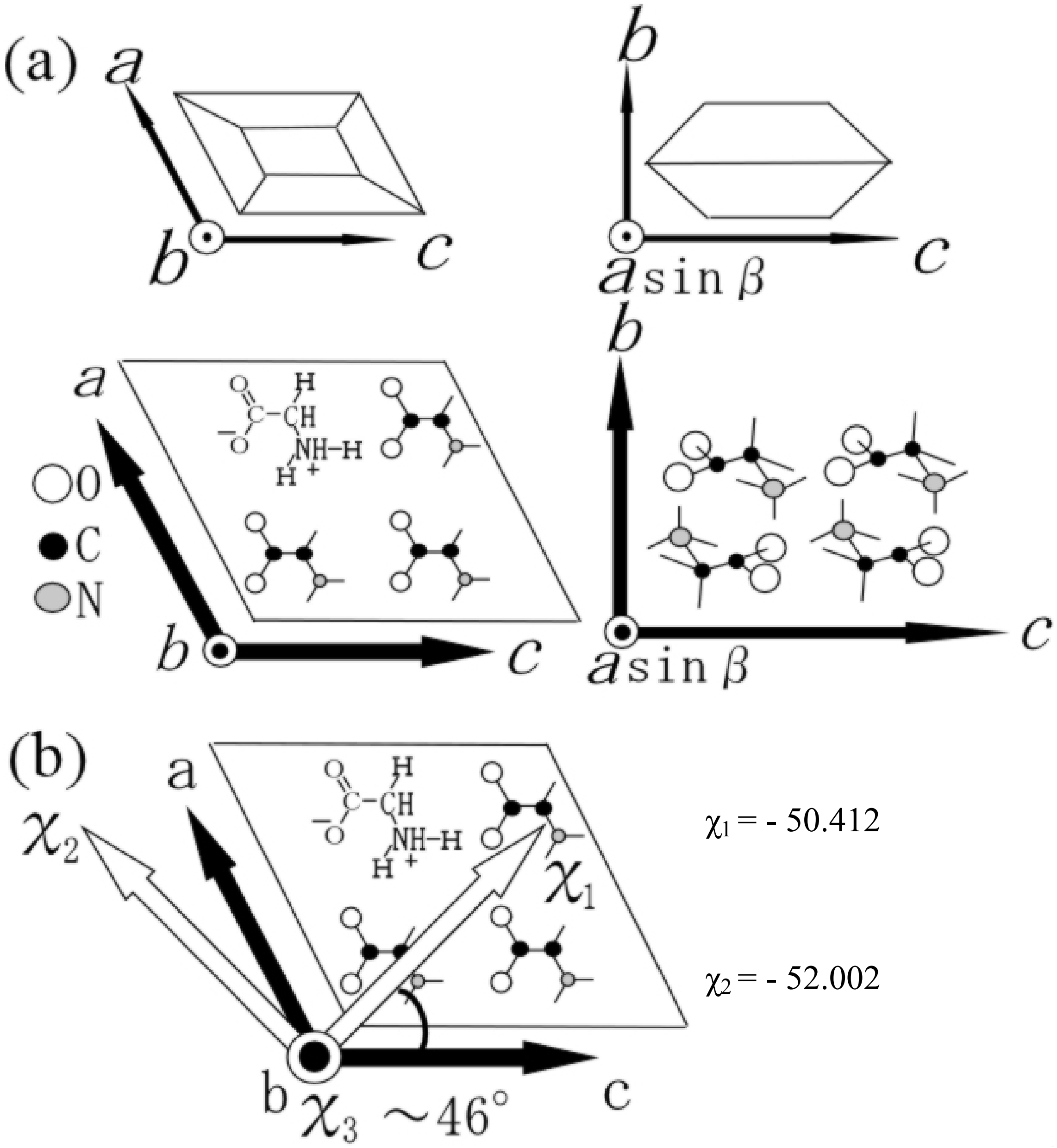


Figure 1 M. Sueda et al.

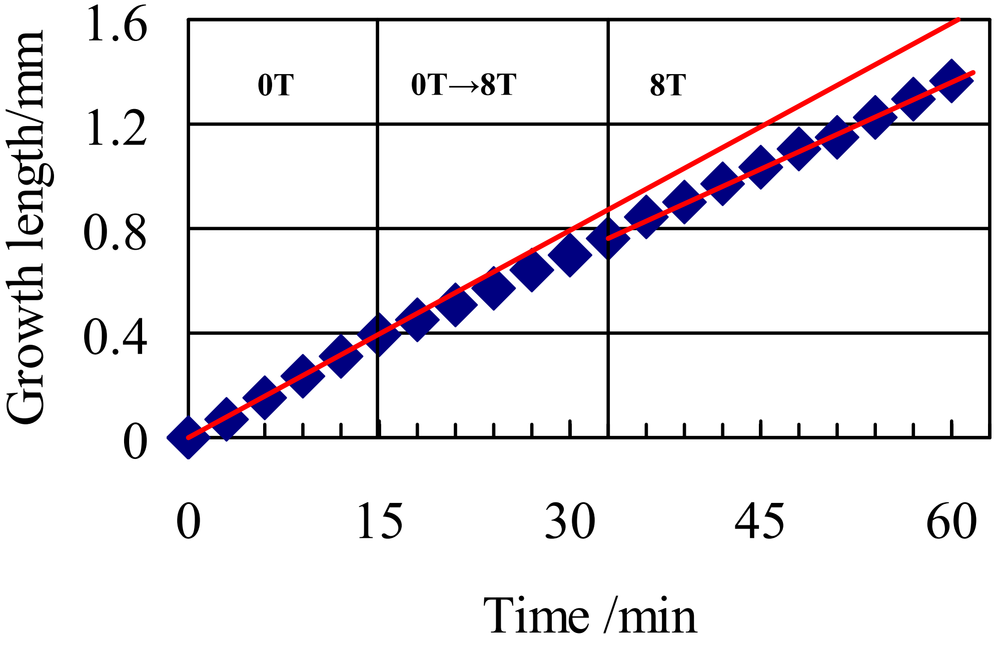


$\chi_1 = -50.412$

$\chi_2 = -52.002$

Figure 2 M.Sueda et al.

(a) 0T→8T



(b) 8T→0T

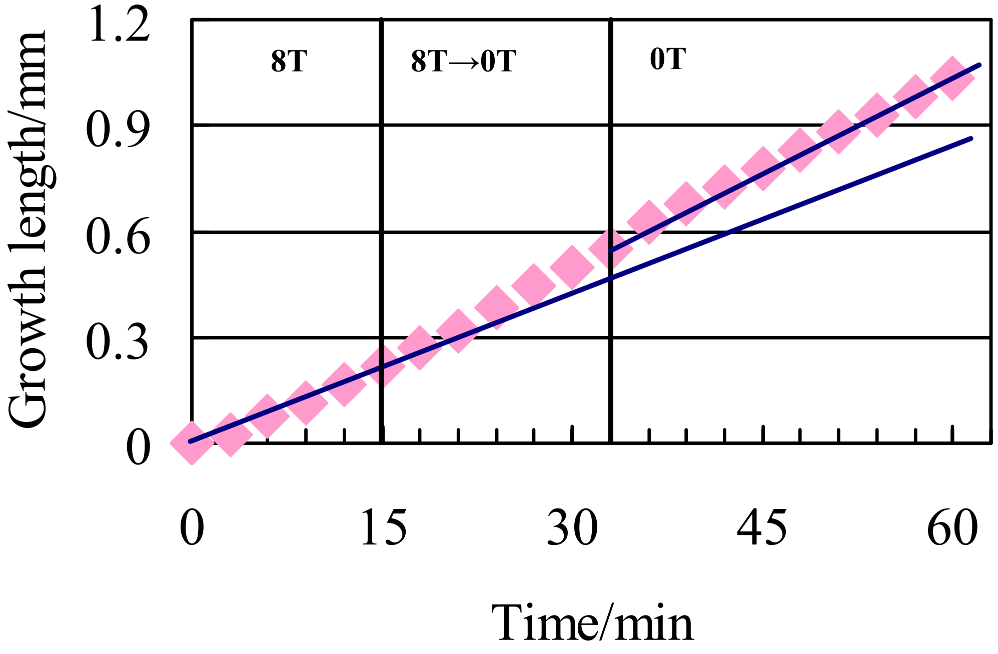


Figure 3 M. Sueda et al.

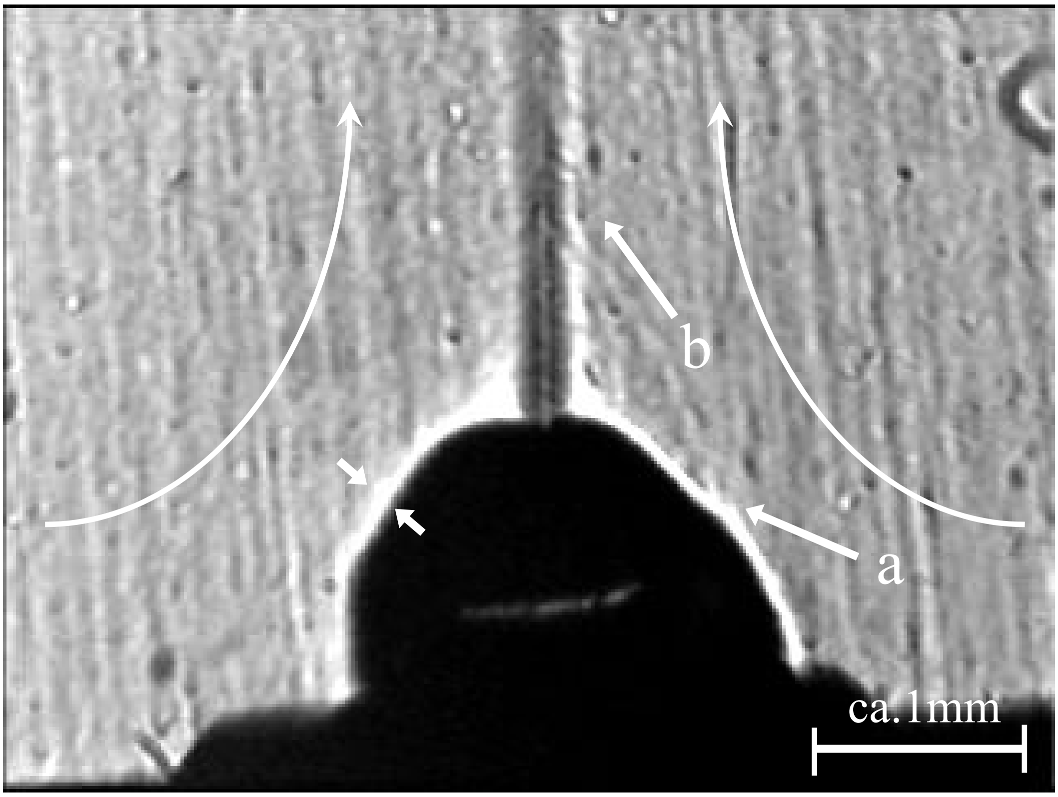


Figure 4 M. Sueda et al.