Pattern formation in noise-reduced electrochemical deposition

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Noise-reduced electrodeposition is performed in an agarose gel medium containing $CuSO_4$ solution. Instead of random fractal-like patterns usually seen in $CuSO_4$ aqueous solution electrodeposition, the deposit shows a more ordered morphology. The dendritic pattern with an evident main stem can be seen. Alternating tip splitting has been observed during the dendritic growth. It is suggested that the suppression of convective noise near the growing interface is responsible for the appearance of dendrites in this experiment. The alternating dendrite tip splitting is interpreted as the result of alternating accumulation and depletion of impurities in front of the growing interface.

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I. INTRODUCTION

Pattern formation in the electrodeposition system has been investigated intensively over the past decade [1]. The obtained pattern, though varying from one report to another, has a morphology resembling that associated with the diffusion-limited aggregation (DLA) model [2]. It is generally believed that growth patterns depend on the boundary conditions of the growing interface [3]. Anisotropy on the one hand, and fluctuation and noise near the growing interface on the other hand, are the two competing factors which determine the stability of the interface and hence the growth morphology. If the effect of anisotropy is greater than the effect of noise or fluctuation, the growing interface will be stable, and a faceted or dendritic pattern will be generated. A fractal-like morphology, however, may develop in the case of insufficient anisotropy. The idea to increase the stability of the growing interface by minimizing noise in the system was demonstrated using computer simulations. In the noise-reduced DLA model [4], one keeps a record of how many times each of the perimeter sites (empty sites adjacent to the cluster) becomes a termination point for a randomly walking particle instead of adding a particle to the aggregate immediately after it hits a growth site. After a perimeter site has been contacted m times, it is filled and the new perimeter sites are identified. Clearly, this procedure decreases the noise with increasing m, because probing the surface with many walks provides a better estimate of the expectation value of growth rate at the given point than a single walk.

However, the attempt to suppress noise or disturbance in a real experimental system does not seem very successful. In an electrodeposition system, even though thin-film geometry is used, disturbance and noise in the aqueous solution film, such as fluctuation of electrolyte concentration and convection of solvent near the growing interface, are still evident. To eliminate random noise in an electrodeposition system and especially to suppress convective solvent motion, Hibbert and Melrose [5] carried out the electrodeposition of copper sulfate on standard laboratory filter paper. However, from a microscopic point of view, fluctuation and noise still exist. Besides, the observed clusters on the filter paper were often inhomogeneous, on both macroscopic and microscopic scales. This effect may be caused by the inhomogeneity of the support media [5].

In this paper, we report on copper sulphate electrodeposition carried out in agarose gel medium. The typical character of this system is that the electrodeposition environment has been changed from an aqueous solution to a gel medium. In this way, noise in the system is sharply suppressed and convection is eliminated.

II. EXPERIMENTS

The noise-reduced electrodeposition is performed in an agarose gel medium. Agarose gel is a common biochem-

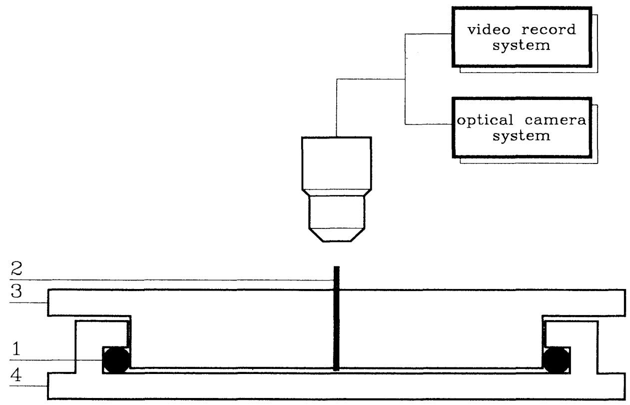

FIG. 1. Schematic diagram showing the experimental system: (1) anode, (2) cathode, (3) upper plate, (4) bottom plate.

istry supporter, which is transparent and in a jelly state. Agarose consists of 1,3-β-D galactose and 1,4-connected 3,6-α-L galactose. The molecules have a chain structure and form networks because of the double helix therein. Water molecules are enclosed in the networks of agarose molecules. The agarose gel is a porous medium with many small random holes (actually, channels). The size of these holes is of the order of 0.1 μm [6]. Therefore, convection is eliminated in this system and the diffusion coefficient is possibly decreased [7] because of the resistance of the jelly structure to the electrolyte movement. In this sense, this system is not only diffusion-limited, but noise-reduced as well.

A schematic diagram of the electrodeposition system is shown in Fig. 1. The agarose gel containing $CuSO_4$ solution is sandwiched between two glass plates. The thickness of the gel medium is controlled by mica spacers, which are the same in thickness and placed near the anode. The spacer thickness is 20 μm in this experiment. The cathode, which is made of a pencil core with a diameter of 0.5 mm, passes through the small hole on the center of the upper glass plate and gets in touch with the agarose gel. The anode is a copper ring with radius 1.2 cm, placed tightly in contact with the sidewall of the cell. Copper sulfate better than 99% pure is used in preparing the $CuSO_4$ agarose gel medium. The gel is prepared in the following way in this experiment: first, 0.15 g of agarose is dissolved in 100 ml deionized water by heating, then 2.34 g of $CuSO_4 \cdot 5\,H_2O$ is added and mixed. The pH value of the solution is usually adjusted to about 4 by adding drops of diluted sulfuric acid. Then, the electrodeposition cell is filled with the hot solution. The cell is fixed and cooled to room temperature ($\sim$20 °C) thereafter. When agarose gel becomes compact, a constant voltage of 4.00$\pm$0.01 V is applied across the electrodes. The morphology and the growing process of the deposit are observed under a microscope (Leitz, Orthoplan-pol) and recorded either on 35-mm film by a camera or on video tape by a video system.

To confirm the role of the agarose gel in the pattern formation, before carrying out a electrodeposition in gel medium, we first perform electrodeposition with regular

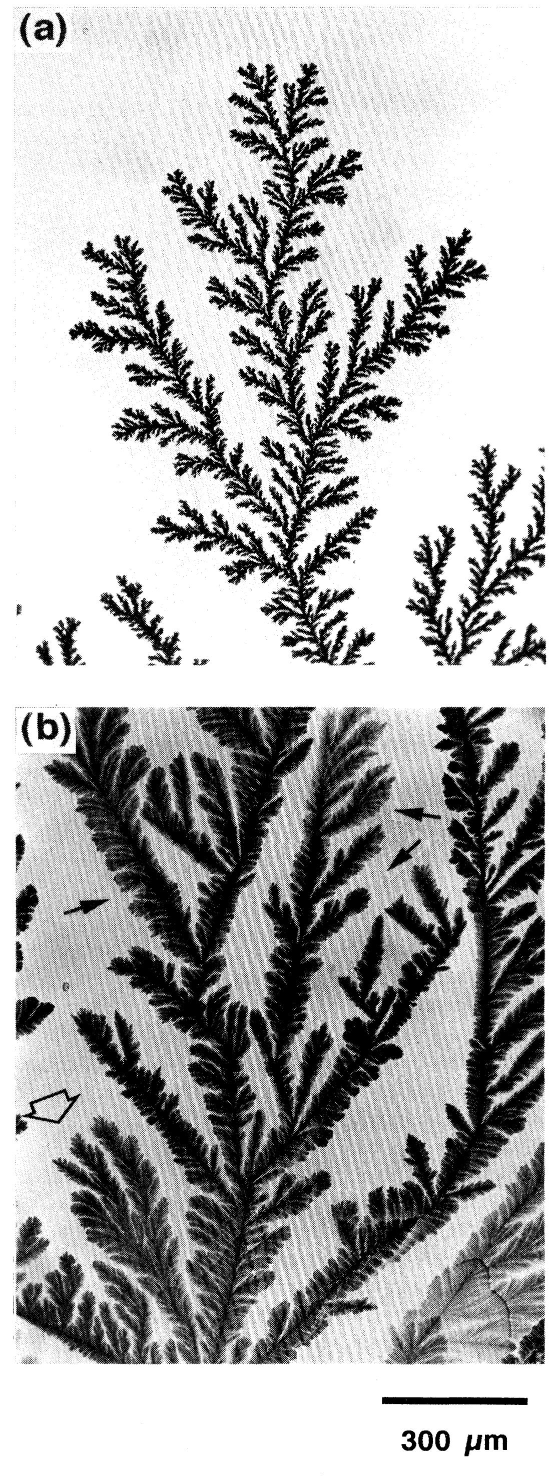

FIG. 2. (a) Fractal-like morphology generated in electrodeposition in regular $CuSO_4$ aqueous solution film; (b) the dendritic patterns observed when $CuSO_4$–gel-medium electrodeposition system is used. On the left side of the lower part of the picture, as indicated by the open arrow, one can find a typical dendritic pattern emerging from the dense-branching morphology. In both (a) and (b), the applied voltage across the electrodes, $CuSO_4$ concentration, and the thickness of spacers between the glass plates are the same.

$CuSO_4$ aqueous solution in the same growth cell. The $CuSO_4$ concentration, applied voltage across the electrodes, pH value of the solution, thickness of the spacers between the two glass plates, etc., are the same as used later in the agarose gel medium experiment. Figure 2(a) shows the typical pattern observed in the electrodeposition of a $CuSO_4$ aqueous solution film. Clearly, the tips of the branches of the deposit are not stable during their growth. Repeated random tip splitting is responsible for the generation of the observed fractal-like morphology. By contrast, when an agarose gel medium is used instead of a regular aqueous solution, a dendritic pattern which possesses an evident straight main stem and regular sidebranches can be observed, as shown in Fig. 2(b). In Fig. 2(b), densely spaced sidebranches occur on the two sides of the main stem of the dendritic. For a specific dendrite, in most cases, the orientation of the sidebranches corresponding to the main stem of the dendrite is fixed. One can also find examples where the sidebranches develop into a dendrite with an evident main stem (second generation of main stem). Occasionally, the third generation of stems can also be observed. The growth morphologies in Figs. 2(a) and 2(b) are quite different.

Some dark striations are observed on the stem of the deposit, which can be seen on the lower part of Fig. 2(b). As the deposit grows forward, the striation appears synchronously along the growing front, which marks the front evolution process. During the dendritic growth, the tip radius of the dendrite main stem is not always stable. With the help of striations, one can find the evolution of the tip radius on the branches marked by the filled arrows in Fig. 2(b). The tip was sharp at first, then became rounded. In some places, the alternating change of the tip radius can be observed. This process can be seen more clearly from *in situ* observations, as shown in Fig. 3. The time interval between each two successive pictures in Fig. 3 is about 3 s. Figures 3(b) and 3(c) show that the previously sharp dendritic tip becomes rounded. This happens when the growth rate of the main stem is slowing down and the sidebranches catch up with the main stem. Then the dendrite tip splits. A few seconds later, a sharp dendrite tip emerges again from the rounded tip.

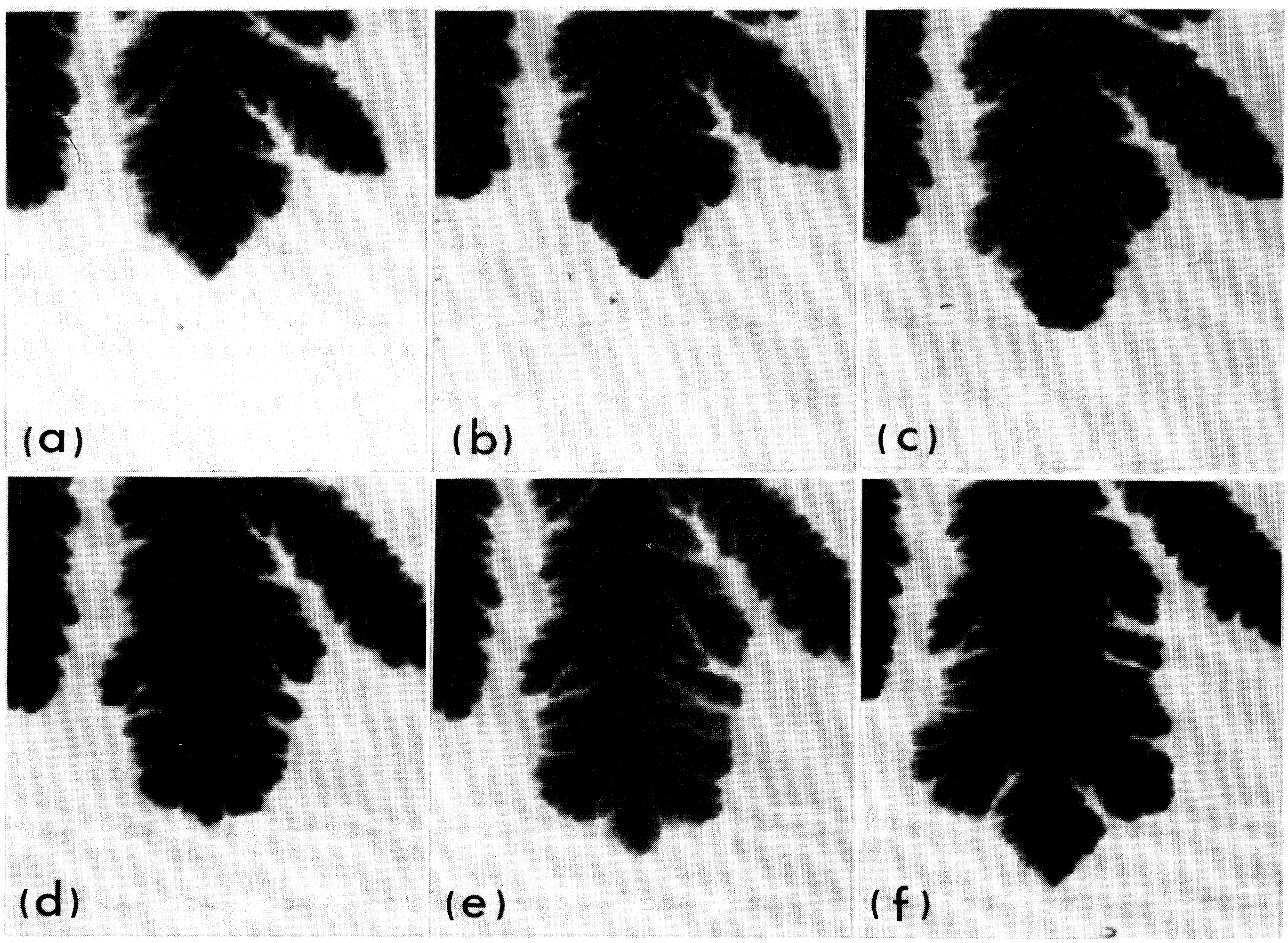

FIG. 3. Successive snapshots showing the evolution of the dendrite tip. At (a) the dendrite tip is sharp. As the dendrite grows, it becomes rounded (c), and then, it becomes sharp again (f). During this process, the applied voltage across the electrodes is kept constant. The time interval between the two successive pictures is about 3 s.

Meanwhile, the growth rate of the tip is higher than that of the sidebranches [Figs. 3(d)–3(f)]. In this way, the dendritic tip radius changes alternately. It is noteworthy that the evolution of the tip radius on the neighboring branches is independent. This means that when a branch is growing with a sharp dendrite tip, the tips on the neighboring branches may be growing simultaneously in a split way.

It should be mentioned that the sidebranches of the dendrite may grow in a dense-branching morphology (DBM), i.e., there are no stable sharp tips and dominant trunks on the sidebranches, as illustrated in Figs. 3(d)–3(f). Besides, as indicated by the open arrow in Fig. 2(b), one can find that a typical dendritic pattern emerges from the dense-branching morphology. These phenomena imply that dendritic pattern and DBM may coexist.

III. DISCUSSION

To explain the formation of dendritic pattern, we propose that noise in the agarose gel system (for example, convection) is greatly suppressed compared to the case when aqueous solution is used. It seems meaningful to use the concept of effective anisotropy of the growing interface. In a regular $CuSO_4$ aqueous solution electrodeposition system, the material anisotropy of copper may not be strong enough to overcome the influence of noise and fluctuations near the growing interface. Hence the effective anisotropy, which represents the total effects of material anisotropy and surrounding perturbations, is too weak to maintain dendritic growth. Consequently, a fractal-like pattern is formed. During electrodeposition in the $CuSO_4$–gel-medium system, however, the effective anisotropy may be increased because the convective disturbance is eliminated and fluctuations are suppressed. As a result, a dendritic pattern with a well-defined main stem, together with ordered-DBM in some cases, appears instead of random fractal-like morphology.

Recently, we noticed that analytical and experimental studies of the motion of fluid flow in electrodeposition given by Fleury, Chazalviel, and Rosso [8]. They found that convective vortices exist just beside the growing tips of the deposit. It is suggested that the average space between the deposit branches and, hence, the morphology of the deposit may be determined by the characteristic size of the vortices. Moreover, with the help of the interference contrast microscopy, we found that the electroconvection plays a very important role in pattern formation of the electrochemical deposition system [9]. In our gel-medium experiments, the appearance of the more ordered pattern instead of the random fractal-like shape may contribute to a sharp decrease in the characteristic size of the vortices. In other words, it can be stated that decreasing the size of the vortices may account for the decreasing strength of the disturbing noise. The weakening of the convective disturbance near the growing interface may lead to the appearance of a more ordered morphology.

It has been found that scratches on the substrate influence pattern formation. This holds especially when the gap between the two glass plates that sandwich the electrolyte solution film becomes very narrow, or in the ultraflat deposit growth on a substrate [10]. In our experiments, the influence of substrate scratches can also be observed. Sometimes we can find separated dendritic branches falling into the same line. However, further studies show that the scratch does not seem to be necessary to generate a dendritic pattern in this experiment. We intentionally use an upper glass plate of the growth cell, with straight polishing scratches in the same direction, to carry out the electrodeposition on the surface of a bulk agarose gel medium (the thickness of the agarose gel is more than 5 mm). The morphology of the deposit between the upper glass plate and the gel surface is investigated. Meanwhile, the scratches can be seen under the interference contrast microscope. *In situ* observation indicates that although there are some dendrites growing along the scratches, the dendrites growing in the radical direction (the direction of the electric field) do exist and the orientation of the main stems deviates considerably from the orientation of the scratches. In the latter case, no scratches have been detected in the dendrite growing direction.

The alternating changes of the dendrite tip radius (Fig. 3) possibly arise from the periodic changes of the microscopic interfacial dynamics, which originate from the alternating accumulation and depletion of impurities in front of the growing interface in this diffusion-limited growth system. It is generally believed that the interfacial growth dynamics and, hence, the growth morphology are very sensitive to impurities [11]. In our experiment, impurities may be other metallic ions in the chemical materials we used, or even protons in aqueous solution. The average concentration of impurity is much lower than the concentration of Cu^{2+} ions. So, as the deposit branch grows forward, the Cu^{2+} ion deposition rate will be higher than the deposition rate of impurities. Hence, impurity ions gradually accumulate in front of the growing interface. At the very beginning of the experiment, the local impurity concentration is low, so the morphology can maintain a dendritic shape due to the enhancement of the effective anisotropy by the gel medium. However, as the dendritic branch grows forward, impurity concentration in front of the growing interface increases. When the impurity concentration becomes sufficiently high, the deposition of the impurity becomes more evident. The incorporation of the impurity on the interfacial growth may change the interfacial growth dynamics and cause a decreasing of anisotropy. It is known that in case of insufficient anisotropy, the growing interface will become unstable. So tip splitting occurs, which is responsible for varying tip radius [Figs. 3(a)–3(c)]. As the growth of the deposit continues, the impurity ions in front of the growing interface are gradually consumed. This means that the local impurity concentration decreases. When the local impurity concentration decreases sufficiently, the anisotropy in interfacial growth may again be enhanced. Under the influence of diffusive instability, which encourages the growth of the most outward tip in the split tips, the dendritic pattern with one sharp tip will again emerge from the rounded-tip envelope [Figs. 3(d)–3(f)]. The process described above will be repeated during the growth of the deposit. The solute transfer is strongly limited in the gel-medium electrodeposition system, so the effect of accumulation and depletion of impurities in front of the growing interface may be more evident than in the other systems. Most recently, alternating morphology transitions between dendrite and DBM have been reported [12]. In that case, it is suggested that H^+ ions are the major impurities that change the anisotropy in interfacial growth and hence influence the morphology of the deposit. The real species of the impurities in the $CuSO_4$-gel system, however, are still unknown at this moment. Further studies are needed to find the most important impurities causing alternating tip splitting in the $CuSO_4$-gel system.

Dark striations on the deposit stems are possibly generated in a similar way. Actually, dark striations are regions where the branching rate is much higher than the other parts. The alternating appearance of the dark striations stands for the alternating changes of the branching rate of the deposit. Different impurity ions and impurity concentrations may result in different situations on the deposit development: alternating changes of the tip radius of the dendrite or the generation of dark striations. A detailed study about the formation of dark striations on the deposit stem and a comparison with the previously reported Hecker transition [11] will be discussed separately [13].

Up to now, oscillations of electric current (voltage) in electrochemical deposition of a salt solution of zinc have been studied by several authors [14–17]. Recently, we related this electric current oscillation to the interfacial growing process by studying the concentration field during electrodeposition in a $ZnSO_4$ solution film [17]. Corresponding to the electric current oscillation, we have observed the oscillation of the tip radius of the dendrite. However, high material anisotropy seems to be essential to observe the current (or voltage) oscillations. Actually, similar features are not observed during electrodeposition of the $CuSO_4$ aqueous solution. We have suggested that the oscillation phenomena observed in $ZnSO_4$ electrodeposition may result from the effect of faceted growth governed by a two-dimensional nucleation mechanism [17]. In our electrodeposition experiment in gel medium containing a $CuSO_4$ solution, we did not detect the evident electric-current oscillations in the gel system. Because a circular geometry is used in our experiment, there are many growing dendrite tips. Each one has contributed to the measured electric current. Besides, the evolution of the tip radius on the neighboring branches is not synchronous. So it is possible that the current fluctuations generated by the different dendrite branches are out of phase and are averaged out. On the other hand, our observation indicates that the typical distance between the neighboring branches of the deposit is about one hundred to several hundred micrometers, which is larger than the size of the diffusion boundary layer estimated from the growth rate of the deposit branches. So, it is possible that local accumulation and depletion of impurities may influence the growth of the dendrite branches independently. This means that the alternating tip splitting of the dendrite may be a local effect in this diffusion-limited growth system. We suppose that a detailed study of the local situations around the growing dendrite tip (for example, the concentration field) may provide more information.

The coexistence of DBM and dendrites in this gel electrodeposition system provides the possibility to study the pattern selection problem. If the growth rate of the main stem is not fast enough, the sidebranches may catch up with the dendrite tip, and the growth morphology may be changed. In this sense, we believe that the fastest-growing selection hypothesis [18], which is extended from the result of the microscopic solvability theory [19], may be correct. At the same time, it is intriguing to see that the dendritic pattern and the DBM coexist in such a small spatial area. Further studies in our system concerning the interfacial growth rate of the different morphologies and the local concentration field in front of the growing interface, as well as the investigations of the microscopic structures of the main stem and the sidebranches of the dendrite, should be helpful for a full understanding of this pattern formation mechanism.

In spite of the simplicity of the experimental system and the evident changes of morphology therein, there are still some uncertainties about this gel growth system. At this moment, we are not quite sure whether or not the agarose gel will influence the surface tension or surface energy of the aggregate. Surface tension is known to play an important role in pattern formation. Actually, an ideal way to study the noise-reduction effect on the electrodeposition is to use a system in which no additional chemicals are introduced while convection and noise are greatly suppressed. Research along this direction is now in progress.

In summary, we have studied the pattern formation in a gel-medium electrodeposition system. When $CuSO_4$ gel is used instead of regular $CuSO_4$ aqueous solution for electrodeposition, the deposit has a much ordered morphology instead of a fractal-like pattern. The suppression of convective noise near the growing interface might be responsible for the appearance of the dendritic pattern. The alternate splitting of the dendrite tip is interpreted as the result of alternating accumulation and depletion of impurities in front of the growing interface. The experiments also indicate that the dendritic pattern may coexist with the dense-branching morphology.

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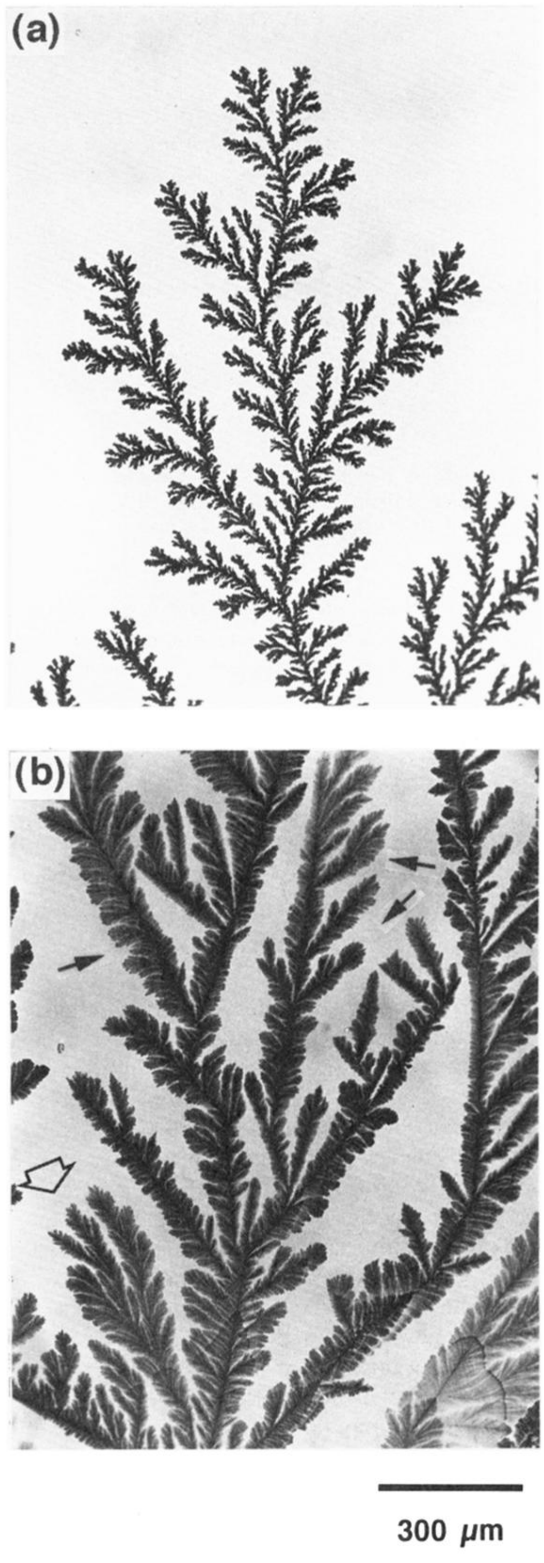

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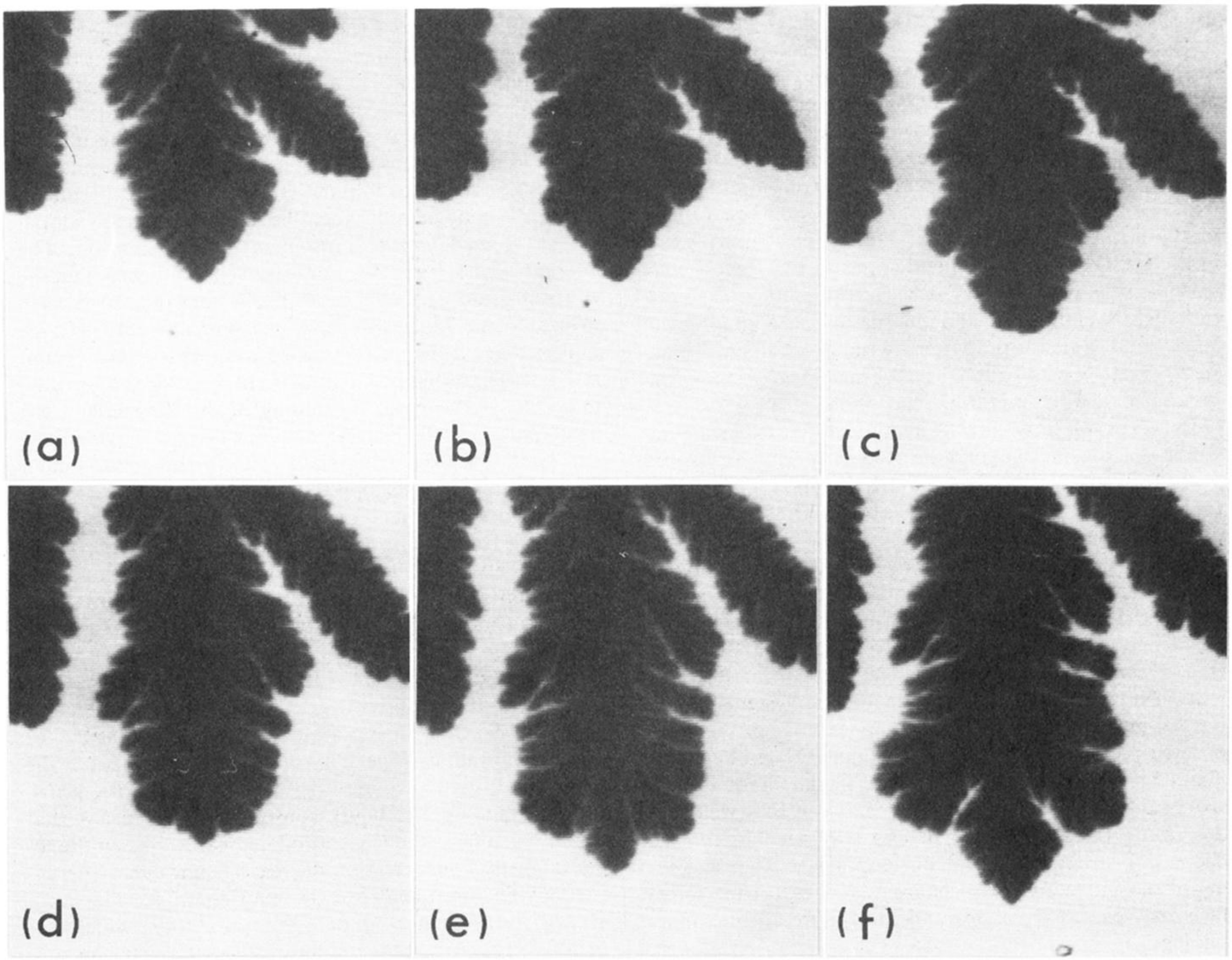

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