JOURNAL OF APPLIED ELECTROCHEMISTRY 12 (1982) 359–367

Effect of growth parameters on the habit and morphology of silver crystals grown electrolytically in gels

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Received 9 September 1981

The interrelated effects of growth parameters on the electrocrystallization of silver in a silica gel medium have been investigated. The main parameters are current density, medium pH, concentration of the electrolyte and density of the gel. With suitable combinations of parameter values, the different growth forms obtained are: spongy dendritic growth, polycrystalline fibre-like growth, thick plates with overgrowth and rough surfaces, *2D* and *T3D* dendrites with well-facetted single crystals on the sides and edges of the dendrites. The conditions for obtaining different forms of the combinations of cube, octahedron and dodecahedron have been optimized. It has been observed that a slight variation of one of the parameters can change the growth forms profoundly. The dependence of the dedritic incubation time on the electrolyte concentration and current density is also discussed.

1. Introduction

Electrocrystallization of metals in aqueous and molten salt baths has been well described and reviewed [1–4]. The changes in habit and morphology of the metal crystals grown by electrocrystallization have been studied as a function of overpotential, current density, concentration and temperature [5, 6]. It has been shown recently by the authors that metallic crystals can also be grown electrolytically in gel media [7]. Dendrites with a variety of natures, habit and morphology can be grown by this new electrolytic technique. The effect of growth parameters on such out-growths has not been studied previously. The purpose of the present paper is to report the interrelated effects of the various growth parameters on the nature and morphology of silver dendrites and single crystals grown electrolytically in a silica gel medium. The main parameters employed here are current density, medium pH, concentration of the electrolyte and density of the gel medium.

2. Experimental details

The experimental method employed in the present investigation is described elsewhere [7]. $AgNO_3$ solution was used as the electrolyte which was incorporated in to the gel solution. A galvanostatic method was employed for growth. Details of the growth habit could be easily observed and photographed using optical microscopes.

The concentration of the electrolyte was varied from 0.01 to 0.2 mol dm^{-3}. The current density ranged from 5 to 60 $\mu A cm^{-2}$. The average current densities in the growth cell were obtained as in Wranglen's experiment [8]. The actual current density at the growing tips of a dendrite will be many orders of magnitude greater than the average current density. The pH of the medium was varied from 3.5 to 7.5. Glacial CH_3COOH was used to acidify the gel solution. Na_2SiO_3 solution, of specific gravity 1.03, was prepared as a stock solution. A solution of specific gravity below 1.03 was used if possible and this was adjusted by varying the quantity of $AgNO_3$ solution incorporated in the stock solution.

An electrochemical process may be investigated by holding either the current or the potential constant. As we have employed galvanostatic measurements only, the measurements of the current density were deemed sufficient, rather than the overpotential. Moreover, in the present investigation, as the current density employed is very low, the overpotential is insignificantly low and practically below the limit of easy identification by d.c. measurements. The general nature

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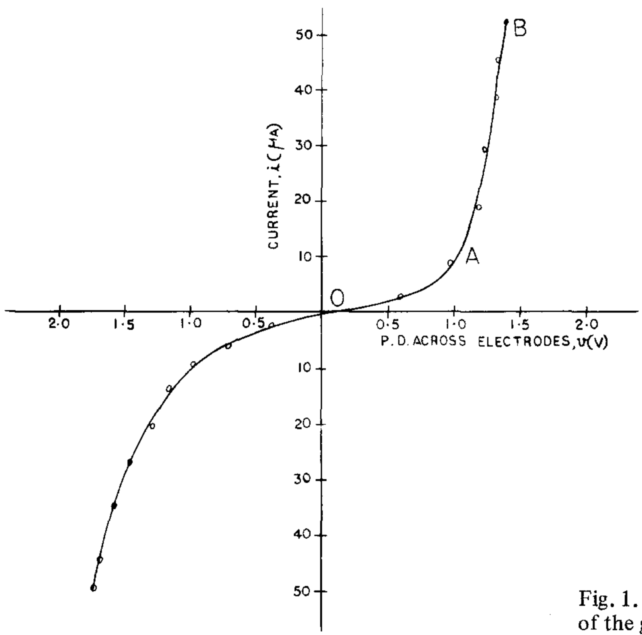

Fig. 1. The general nature of i–V characteristics of the gel medium.

of the current–voltage (i–V) curve for the gel medium is shown in Fig. 1. The growth experiments were conducted in the region OAB, which resembles the forward characteristics of a semiconductor diode.

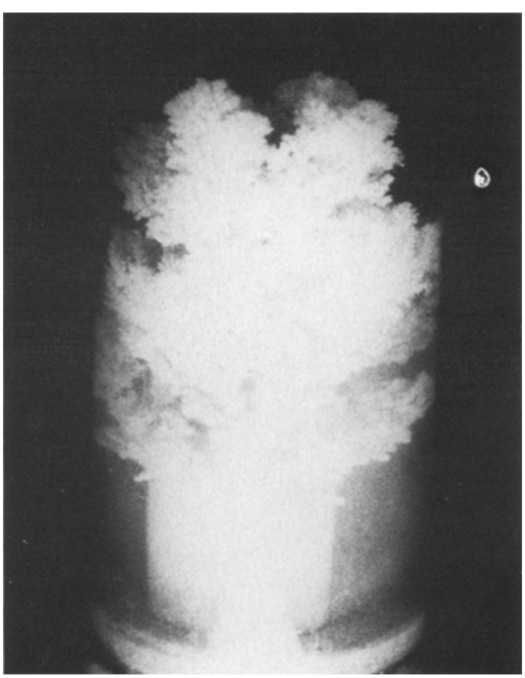

Fig. 2. Spongy dendritic growth up to a height of about 5 cm.

The time of growth varied from a few days to a few months. After a particular run was completed the cathode was carefully taken out and washed. The resulting growth was examined first under a low power microscope and then, if necessary, under a high power microscope or scanning electron microscope.

3. Results and discussion

The growth morphologies obtained can generally be classified into eight categories.

(a) Grey coloured spongy dendritic growth.

(b) White coloured spongy dendritic growth, fibre-like dendrites with little metallic lustre, irregularly shaped (Fig. 2).

(c) Large, thick, plate-like and round-edged dendrites with rough surfaces, branches not well-shaped and not at well-defined angles, thin round-edged plates with a rough surface, no facetted crystals (Fig. 3).

(d) Large polycrystalline dendrites with forward and backward branchings at well-defined angles, surface of dendrites rough, no facetted crystals (Fig. 4 a and b).

(e) Backward and forward branching dendrites developed above the spongy and fibre-like dendrites (Fig. 5).

(f) Small crystalline dendrites with forward and

Fig. 3. Thick, plate-like dendrites with irregular branches and rough surfaces (× 4).

backward branchings, plane, sharp-edged, smooth facetted and tabular crystals developed on dendrites (see Figs 2 and 3 of [7]).

(g) Large crystalline dendrites with primary, secondary and tertiary branches at well-defined angles and grown by the twin plane re-entrant edge (TPRE) mechanism, *T3D* dendrites with well-facetted single crystals on them (Figs 6 and 7).

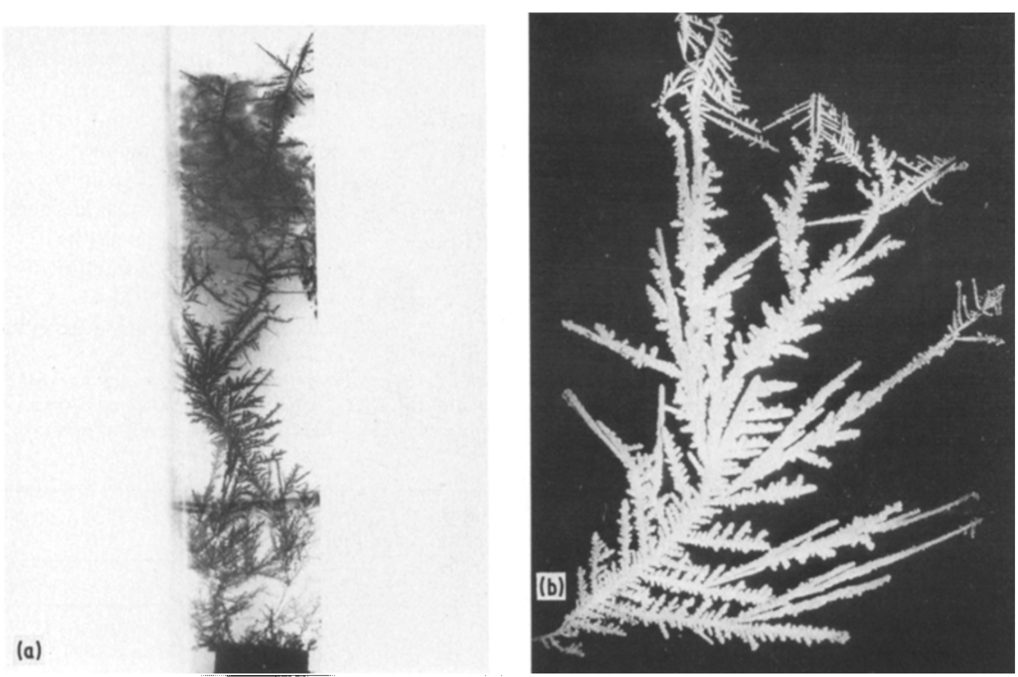

Fig. 4. (a) General appearance of large, forward and backward branching dendrites in the growth cell (× 1). (b) A portion of forward and backward branching dendrites separated from the growth cell (× 5).

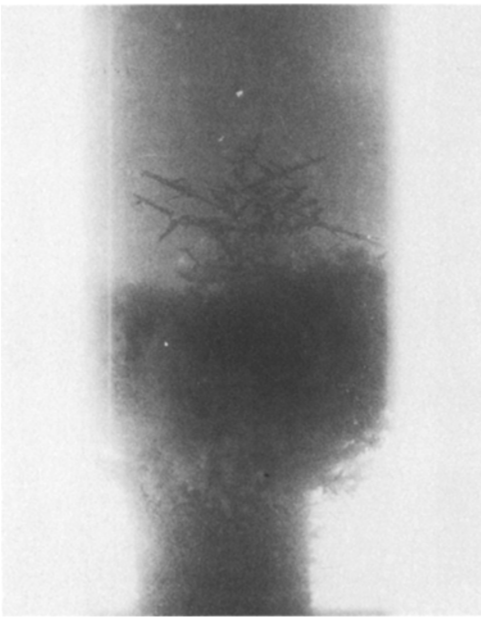

Fig. 5. Large crystalline dendrites grown at the top of spongy and fibre-like dendrites (X 1.5).

(h) No dendrites, polycrystalline aggregates, thin, small plates with sharp edges, hexagonal thin plates.

On close microscopic analysis each category can be divided further according to the mor-

Fig. 6. Dendrites with well-facetted crystals at the tips and edges. Primary, secondary and tertiary branches are developed (X 33).

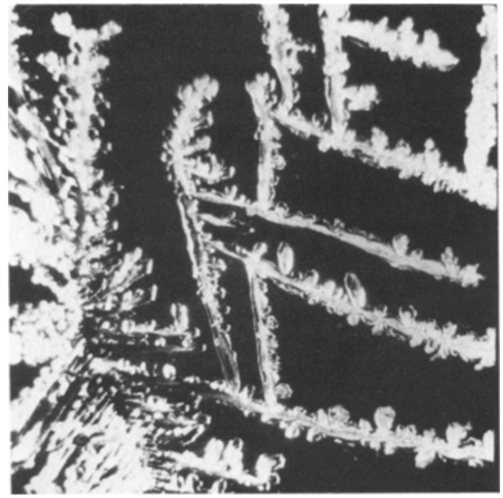

Fig. 7. A typical *T3D* dendrite with crystals of hexagonal facetted tops (X 66).

phological variations. Such analysis is beyond the scope of this paper. Tables 1 and 2 show the interrelated effects of different growth parameters on the nature and morphology of the deposited outgrowths as classified in (a) to (h). In many cases, more than one morphology is observed in the same growth cell, which is also shown in the tables. This is due to a morphological transformation when the growth is continued for a longer time. Often, almost the same external morphologies are obtained for different parameter combinations. But it is conjectured that although the general nature is the same, there may be differences in the composition and structure of the deposit.

In the present work spongy dendritic growth is

Table 1. Effect of current density and pH when the gel density and $AgNO_3$ concentration are kept constant: Volume of gel solution: Volume of $AgNO_3$ solution = 1:3. $AgNO_3$ concentration = 0.02 mol dm^{-3}

Current density (μA cm^{-2})	Nature and morphologies of the deposit for different pH values			
	4	5	6	7.5
8	b, d	g	d, e	a
15	b, h	g	d	a, b
26	b	f	b, c	a
52	a	f	b, c	a

Table 2. Effect of current density and concentration of $AgNO_3$ when pH and gel density are kept constant. pH = 5. Volume of gel solution: Volume of $AgNO_3$ solution = 1:2.5.

Current density ($\mu A\ cm^{-2}$)	Nature and morphologies of the deposit for different $AgNO_3$ concentrations ($mol\ dm^{-3}$)			
	0.01	0.03	0.05	0.07
8	a, b	d, g	d	h
15	a	c, g	c, h	h
26	a	c, f	c, f	c
52	a	b, f	a, b	a, c

observed for different growth conditions. Some scientists assign the formation of these deposits to the action of colloidal hydroxide particles which form during electrolysis [9, 10]. However, X-ray analysis of spongy deposits has disclosed the presence of metallic oxides rather than hydroxides [11]. Kudryavtsev [12] has demonstrated the essential part played by metallic colloidal particles in the formation of spongy deposits. In the conventional electrodeposition of metals the spongy growth is found as a layer on the cathode. But in silica gel medium, in addition to the spongy layer formation, the spongy dendrites are found to grow to a height of a few centimeters. The linear growth rate of these dendrites is greater than the well-shaped dendrite with good metallic lustre and facets. The conditions which favour the formation of spongy dendrites are: high pH, low electrolyte concentration, the presence of Ag anions (silver halide complexes) and the presence of oxidants (oxygenated water, nitrates, etc.). Hence, it is best observed with a current density greater than $30\,\mu A\,cm^{-2}$, a $AgNO_3$ concentration less than $0.01\ mol\,dm^{-3}$, a pH above 6 and a gel solution specific gravity greater than 1.03.

Another morphology observed is the thick plate-like dendrites with rough surfaces and irregular branches (Fig. 3). These brittle and semimetallic dendrites are found with and without branches depending upon the current density and concentration. The development of such dendrites is conjectured to be due to the incorporation of silica, as they are grown at moderately high pH values and current densities. An interesting phenomenon that is observed is the overgrowth of small plates of similar structure, normal to the plane of large parent plates. This is the *T3D* growth of plate-like dendrites.

If the growth is continued for a long time, say 2 to 5 months drastic and stage-by-stage morphological changes take place. These changes may be, to some extent, attributed to the aging of the gel, variation of pH, and variation of current density depending upon the tip radius of the parent dendrite. In certain growth cells, the growth starts as two-dimensional dendrites and on attaining a height of 1 or 2 cm *T3D* dendrites start developing on the *2D* dendrites. These *T3D* dendrites form single crystals in combinations of cubes, octahedra and dodecahedra (Figs 7 and 8). This stage-by-stage growth of silver dendrites and single crystals represents conceptually a suitable and simple example of self-organization found in the growth of crystals. Growth spirals are also observed on the (1 0 0) and (1 1 1) faces of such as-grown silver crystals developed on *T3D* dendrites [13]. It has been shown by the authors that the *2D* dendrites, under certain conditions, grow usually by a TPRE mechanism of growth whereas no sign of such a growth mechanism is observed in the growth of single crystals as shown in Figs 7 and 8. Hence in the same growth cell, by a self-organization process, dendrites grow with and without a TPRE mechanism [14].

Fig. 8. Different types of single crystals with combinations of cubes, octahedra and dodecahedra, developed on *T3D* dendrites (X 198).

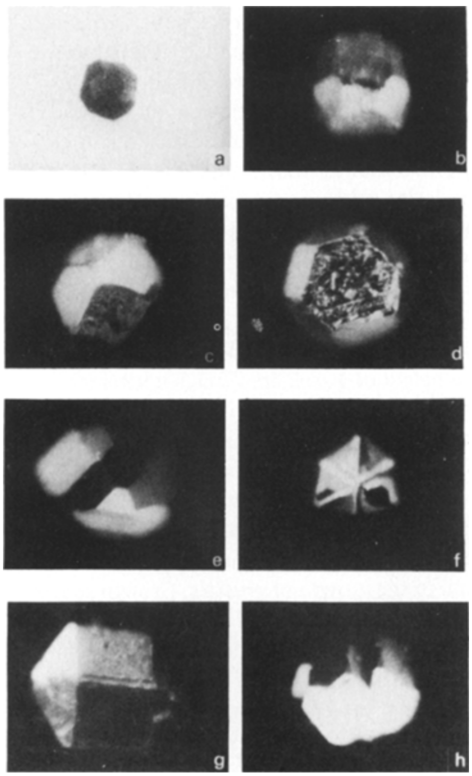

Fig. 9. Different types of facetted single crystals grown directly on the cathode without the formation of dendrites (× 40).

For a wide range of current density and other parameter values, polycrystalline aggregates are usually first formed on the cathode provided the pH and gel density are not very high. Almost all types of dendrites develop from these aggregates. For a particular combination of parameters, i.e. for gel density ~ 1.03, pH ~ 5 and current density ~ 10 μA cm^{-2}, single crystals in the form of combinations of cubes, octahedra and dodecahedra have been grown without the formation of dendrites. Fig. 9 shows different types of such facetted crystals. If the pH is decreased step-by-step without affecting the other parameters too much, the faces of the crystals become more and more smooth and atomically planar. Well-facetted single crystals and dendrites develop at low pH values because of the controlled dissolution and growth processes.

The dendrites of a specified nature and morphology grow linearly with time, at a rate depending mainly on current density and to a lesser degree on other parameters. A plot of dendrite length versus time shows two different types of growth characteristics. In the first system an almost continuous transition from spongy to 2*D* crystalline dendrites is observed (Fig. 10). In such cases the 2*D* dendrites which developed above the spongy deposit were too small. In the other system a discontinuous transition is observed

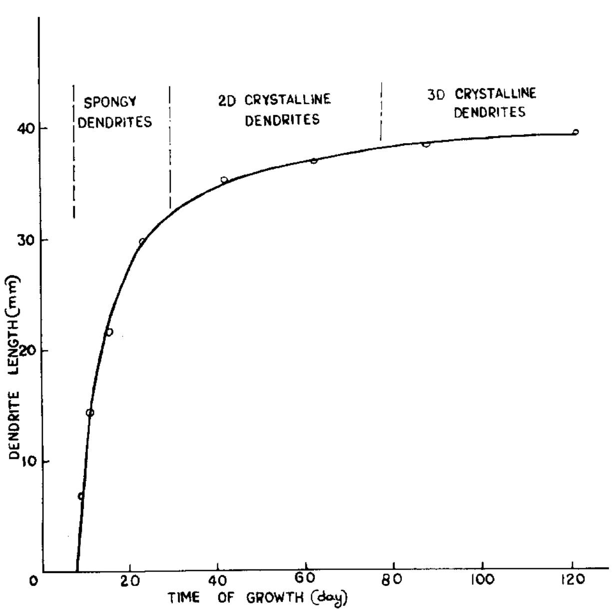

Fig. 10. A plot of dendrite length as a function of growth time showing continuous growth.

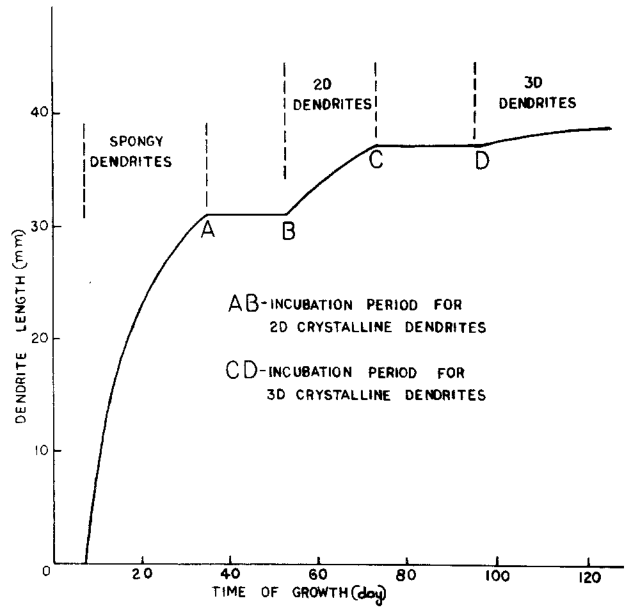

Fig. 11. A plot of dendrite length versus time, showing discontinuous growth.

(Fig. 11). But here, the 2*D* crystalline dendrites which formed above the spongy deposit had more branches and were larger in size (Fig. 5). The portions AB and CD shown in Fig. 11 may be said to be the incubation periods for 2*D* and 3*D* crystalline dendrites in a particular growth cell. The three stages of growth, namely, the spongy dendrites, 2*D* dendrites and *T*3*D* dendrites, with their characteristic inflections in their length–time curve are shown in the figures. For the same current density the linear growth rate changes only if the nature and morphology of the dendrite change. When the transition takes place from spongy to crystalline or polycrystalline dendrites, the linear growth rate decreases. The cessation of linear growth of a particular type of dendrite is usually accompanied by a change in the shape of the dendrite tip. A point was usually reached where the configuration of the dendrite tip changed, either to form polycrystalline masses or

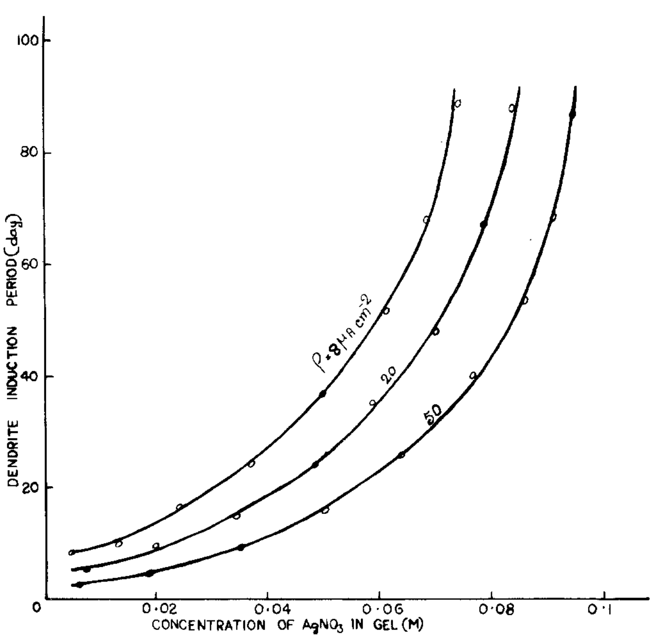

Fig. 12. Dendrite induction time versus concentration of electrolyte as a function of current density (ρ).

to split into $2D$ dendrites. In the case of polycrystalline masses the rate of advance was much less than that of the parent dendrite.

In earlier reports on electrocrystallization, measurements were made on the growth rate of metallic dendrites as a function of overpotential, concentration and temperature. The measurements of overpotential will be more meaningful if current densities of the order of hundreds of $mA\,cm^{-2}$ are used in such experiments. In the present investigation a current density less than $60\,\mu A\,cm^{-2}$ gave better results. Therefore, the overpotential is insignificantly low. The dependence of rate on temperature, and the problems associated with thermal gradients, are also avoided here as the experiments were carried out under ambient conditions.

After switching on the current there was an initiation time before the dendritic growth began. Diggle *et al.* [2] have shown that, at constant potential an initiation time of between 5 and 100 min is observed, depending on the values of overpotential, concentration and temperature. Barton and Bockris [1] studied the significance of induction time of the dendrites and their dependence on concentration and purity of the solution. They showed that dendrites are initiated up to 1 h after a constant current is switched on. In the present study the incubation time of the dendrites was found to depend on the nature of the outgrowth, current density, concentration of $AgNO_3$ and to a lesser degree on pH and density of the gel. Considering the nature of the growth in general, the dependence of initiation time on concentration as a function of current density is shown in Fig. 12. The dendrite initiation time for different types of growth is shown in Table 3. In some growth cells, for a particular combination of parameter values, say concentration about $0.025\,mol\,dm^{-3}$ and current density about $15\,\mu A\,cm^{-2}$, $2D$ crystalline dendrites develop first without the formation of spongy dendrites (Fig. 4a). In such cases more induction time was observed.

In gel media, dendrites are found to initiate even at current densities as low as $3\,\mu A\,cm^{-2}$, but only after about 100 days. A typical dendrite grown at such a low current density is shown in Fig. 13. Metallic dendrites of such a morphology have not been grown before at such a low current density. If the current density is increased the initiation time will be reduced but there are changes in morphology.

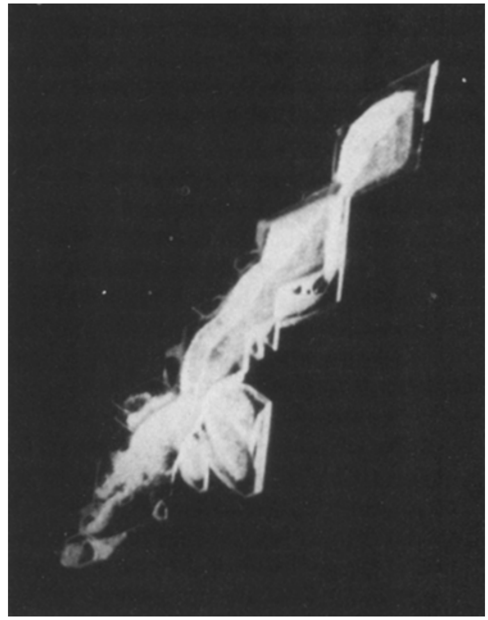

Fig. 13. A typcial dendrite grown by TPRE at very low current density (X 60).

From Table 3 it is clear that the quality of a grown crystal is controlled mainly by its growth rate, which in turn depends on current density, pH and diffusivity of the gel medium, concentration of $AgNO_3$ in the gel etc. A decrease in current density effectively reduces

Table 3. Nature of the dendrites and their initiation times

Nature of dendrite	Induction time-range, depending upon current density and other parameters (day)
Grey and white spongy dendrites	2–10
Plate-like, sharp-edged or round-edged dendrites with many small branches	10–30
Large $2D$ dendrites with well-facetted crystals on edges and tips	25–80 or more

the growth rate and consequently good quality crystals are expected to grow at low current densities. The experimental results are also in accordance with this (see Tables 1 and 2). When growth was continued for a longer time in a particular cell, more than one morphology was observed, the latter being crystallographically superior to the former. For a particular current density, assuming that the quantity of material supplied per unit time is a constant, the growth decreases with time so that such a change in morphology with time is expected. The addition of $AgNO_3$ in the gel effects the growth rate in two different ways, (a) by reducing the diffusion coefficient in the gel medium and (b) by supplying additional material to the growing crystals. At lower concentrations of $AgNO_3$ in the gel, the former effect predominates reducing the growth rate of the crystals. Thus, the quality of the crystals grown improves with $AgNO_3$ concentration up to a certain value. However, a further increase in the concentration of $AgNO_3$ causes the latter effect to predominate. This increases the growth rate of the crystals and the quality of the crystal deteriorates. Other parameters such as pH, density and age of the gel can also control the growth of crystals.

Acknowledgements

On of the authors (MTG) is grateful to the University Grants Commission, New Delhi for financial assistance.

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