

MORPHOLOGICAL AND ELECTROCHEMICAL STUDY OF A ZINC-LEAF ELECTRODEPOSITED AT THE BUTYL ACETATE/ZINC SULFATE SOLUTION INTERFACE

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(Received 2 August 1979)

Abstract—Morphology and electrochemistry of zinc-leaves formed at the butyl acetate/ $\text{ZnSO}_4(\text{aq})$ interface were studied under various experimental conditions; the effects of ZnSO_4 concentration, temperature and cell-voltage being examined. The leaf obtained by controlled-voltage electrolysis generally consisted of the two types of deposits, *ie*, spoke-like and film-like; formation of the former was favored at higher current densities and that of the latter at lower current densities. Some factors governing the metal-leaf formation were discussed.

INTRODUCTION

Under certain experimental conditions, a two-dimensional metal deposit, so-called "Metallblätter (metal-leaf)", can be obtained by the cathodic reduction of the metal at the interface between an organic liquid and an aqueous solution of the metal salt. This interesting phenomenon was first reported by Mylius and Fromm[1] in 1894 and studied further by Freundlich and Novikow[2]; since then, however, very few studies have been carried out. Recently, Sukava *et al*[3] observed a similar phenomenon, *ie* a disk-like deposit of copper grew at the air/aqueous solution interface in the electrolysis of an acidified copper sulfate solution containing a small amount of norvaline.

The metal-leaf obtained under experimentally controlled conditions will be a useful model of analogous metal deposits often found in natural products. Physicochemical studies of the metal-leaf are considered to provide important information on the mechanism of crystal growth and on the texture and structure of minerals.

This paper presents a study of zinc-leaves obtained at the butyl acetate/ $\text{ZnSO}_4(\text{aq})$ interface under various experimental conditions, in an attempt to provide photographic and electrochemical evidences.

EXPERIMENTAL

The apparatus used in this study is illustrated in Fig. 1. The electrolytic cell was a glass beaker, about 5 cm in dia and 7.5 cm in height, with a water-jacket to circulate thermostated water. The cathode was a platinum wire, 0.5 mm dia; other materials, *eg* stainless steel and graphite, of a similar dimension could be

used as the cathode. In advance to each experimental run, the platinum cathode was cleaned in hydrochloric acid and washed with distilled water. In the case of zinc-leaves, the anode was a zinc plate of 99.99% purity, about 4×4 cm in size, placed at the bottom of the cell; a leading wire attached to the anode was insulated with a Teflon tape.

Analytical reagent grade chemicals were used without further purification. All solutions were in equilibrium with respect to atmospheric oxygen, because the metal-leaf formation was reported to be difficult in oxygen-free solutions[1, 2].

Each experiment was performed according to the following procedure. A small amount of organic liquid was added gently onto an aqueous solution of metal in the cell, so that the surface of the aqueous phase was completely covered by the organic liquid. After an

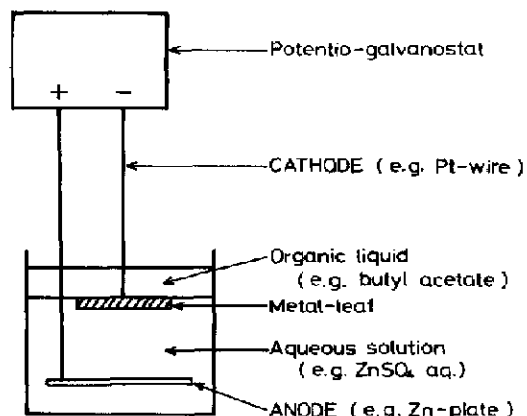


Fig. 1. Schematic illustration of the electrolytic apparatus.

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applied cell-voltage (or current) had been set on a potentiostat-galvanostat, the tip of the cathode was carefully positioned exactly at the interface by using a micro-manipulator. The proper positioning could be done by observing the electrolytic current which began to flow as soon as the cathode tip reached the aqueous phase. In order to obtain good interfacial deposits, it was essential not to insert the cathode tip into aqueous solutions; otherwise, the familiar three-dimensional growth of metal into the bulk of the aqueous phase was preferred to the interfacial formation of metal-leaves.

In order to follow the morphological change of a metal-leaf during the course of electrolysis, the leaf was photographed while still *in situ* in the electrolysis cell; a motor-driven camera was used for this purpose. Specimens of zinc-leaves were easily removed from the cathode and subjected to further studies, such as the determination of current efficiency, the chemical analysis and the observation using an optical microscope and scanning electron microscope (SEM).

RESULTS

Preliminary study

The preliminary investigation showed that zinc and cobalt gave leaf-like interfacial deposits under similar electrolysis conditions[1]. Leaves of copper and silver could also be obtained[1] when relatively dilute ammoniacal solutions of the metals were used as the aqueous phase.

Possibility of the zinc-leaf formation was studied with a variety of combination of organic liquids and aqueous solutions of zinc salts, the results being summarized in Table 1. Among these combinations the butyl acetate/ $\text{ZnSO}_4(\text{aq})$ system was found to give very good zinc-leaves and was extensively used in the present study.

The current efficiency of the zinc-leaf formation was calculated from the weight of the deposit obtained in $3 \text{ mol dm}^{-3} \text{ ZnSO}_4$ solutions at room temperature and at a cell-voltage $U_{\text{CELL}} = 4 \text{ V}$. It can be seen from the self-explanatory Table 2 that the current efficiency

Table 1. Possibility of the zinc-leaf formation under the controlled-voltage electrolysis at room temperature (preliminary observation)

Organic liquid	Concentrated aqueous solution of		
	ZnSO_4	ZnCl_2	$\text{Zn}(\text{Ac})_2$
l-propanol	no	*	*
l-pentanol	poor	*	*
l-decanol	good	*	good
diethyl ether	no	*	*
cyclohexanol	good	*	*
butyl acetate	good	poor	no
benzene	good	no	poor
petroleum ether	good	poor	no
liquid paraffin	no	*	*
silicone oil	no	*	*

* Not examined.

+ The chemical analysis was carried out by Dr. Y. Takahashi of the Institute of Physical and Chemical Research, to whom the authors' thanks are due.

Table 2. Current efficiency of the zinc-leaf formation under the controlled-voltage electrolysis at room temperature: system, butyl acetate/ $3 \text{ mol dm}^{-3} \text{ ZnSO}_4(\text{aq})$; $U_{\text{CELL}} = 4 \text{ V}$

Electricity consumed*	Weight of leaf	Theor. wt. of deposit†	Current efficiency
$Q(\text{C})$	$W(\text{mg})$	$W_{\text{theor.}}(\text{mg})$	$100W/W_{\text{theor.}}$
80.15‡	26.9	27.1	99.3
45.15	14.7	15.3	96.1
70.11	24.0	23.7	101.3
60.11	20.0	20.4	98.0
80.04‡	26.9	27.1	99.3
70.01‡	23.3	23.7	98.3
40.11	14.0	13.6	102.9

* Measured by using a Model 179 Digital Coulometer attached to a Model 173 Potentiostat/Galvanostat (Princeton Applied Research).

† Calculated by the Faraday law of electrolysis ($W_{\text{theor.}} = M_{\text{Zn}}Q/2F$, M_{Zn} being the molar mass of zinc).

‡ These samples were used for the chemical analysis.

is practically 100%. The chemical analysis of the leaves obtained under the above conditions gave the following results† Major component: Zn, 97–98%. Impurities: Cd, 6 ppm; Pb, 50 ppm; Cu, 4 ppm; Fe, 10 ppm; traces of Al, Ca, Mg, Mn and Si being detected by the spectrographic analysis.

Zinc-leaves obtained by the controlled-voltage electrolysis

Morphology of the zinc-leaf was affected by a slight change of experimental conditions, and it was not easy to obtain reproducible results. A typical example of the growth of a zinc-leaf was observed under the following conditions: ZnSO_4 -concentration $[\text{ZnSO}_4] = 3 \text{ mol dm}^{-3}$; $U_{\text{CELL}} = 3 \text{ V}$; and temperature $t = 25^\circ\text{C}$.

The morphological change of the leaf with time of electrolysis for several minutes and the corresponding current-time curve are shown in Figs 2 and 3. In the early period of electrolysis, the current gradually increased with time, and the interfacial deposit which looks like spokes of a wheel (photograph at 60 s in Fig. 2) grew radially from the cathode tip. The current sometimes reached a maximum and then became almost independent of time, as shown in Fig. 3. In many cases, the appearance of leaves changed with time of electrolysis: filmy deposits began to grow between each spoke in a concentric circle to give a petal-like deposit at the later stage of electrolysis (see photographs at 180, 210 and 240 s in Fig. 2).

Some surface movements or interfacial turbulence were observed at the organic liquid/aqueous solution interface, when a zinc-leaf was growing radially. This interfacial motion looked like ripples propagating outwards concentrically from the tip of the cathode.

The two surfaces of a leaf, one facing to the organic liquid (o-side) and the other to the aqueous solution (w-side), have different appearances. Figure 4 presents photomicrographs (a and b) and scanning electron micrographs (c and d) of both the o- and w-side of a petal-like zinc-leaf obtained at an electrolysis time of 180 s. Generally, the o-side (a and c) has metallic luster, and the w-side (b and d), initially being silver-grey, becomes darker, uneven and muddy with time.

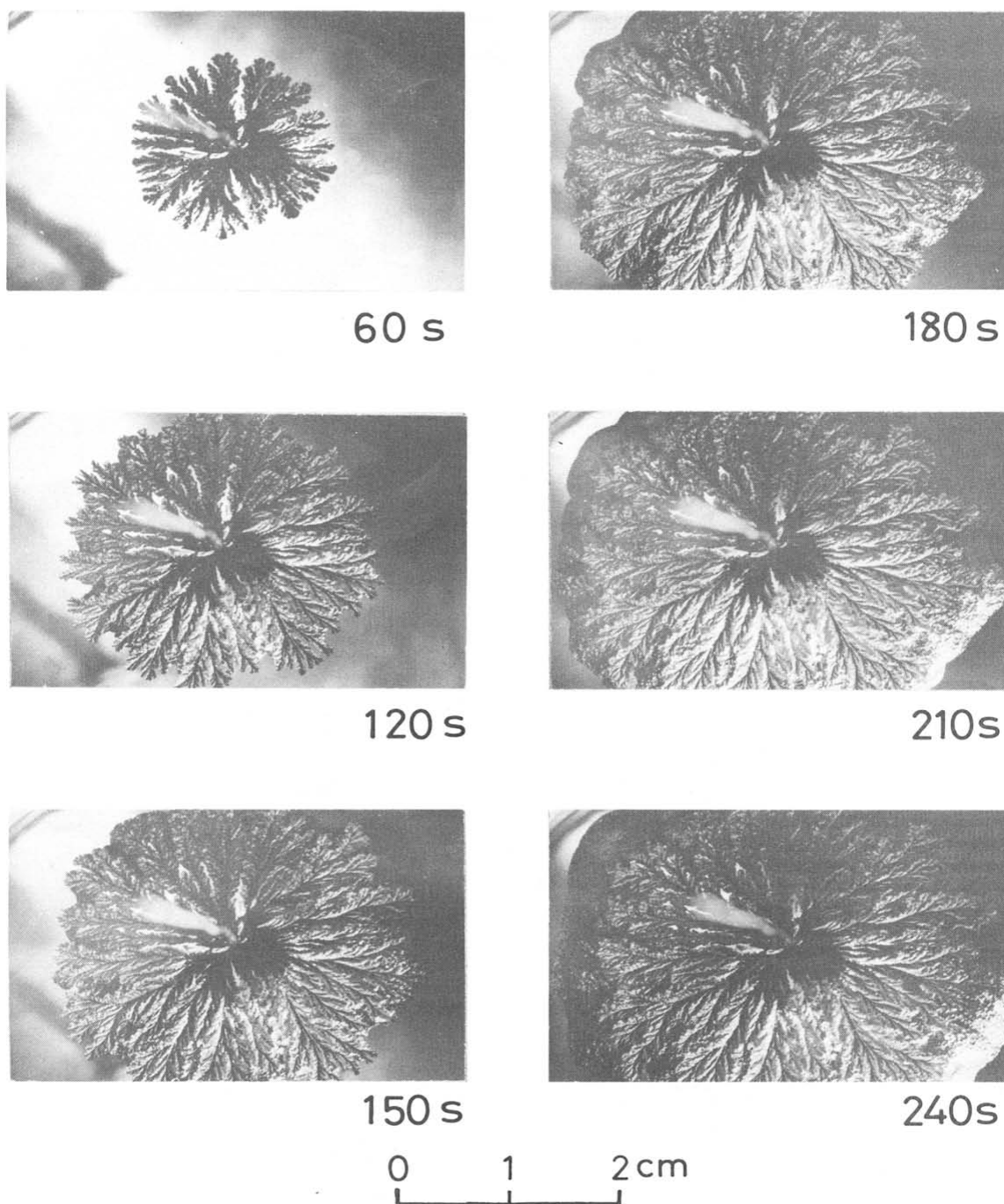


Fig. 2. Growth of a zinc-leaf under the controlled-voltage electrolysis: $[\text{ZnSO}_4] = 3 \text{ mol dm}^{-3}$; $U_{\text{CELL}} = 3 \text{ V}$; $t = 25^\circ\text{C}$. (A white, out-of-focus spot in the center of each photograph is a part of the cathode.)

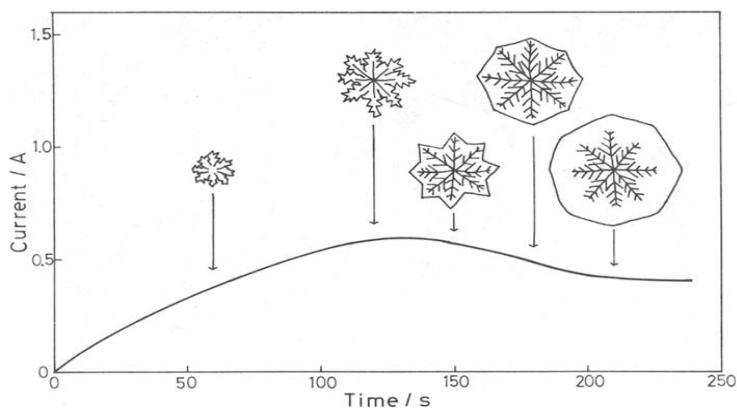
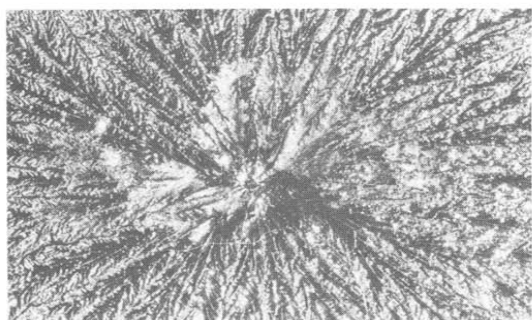
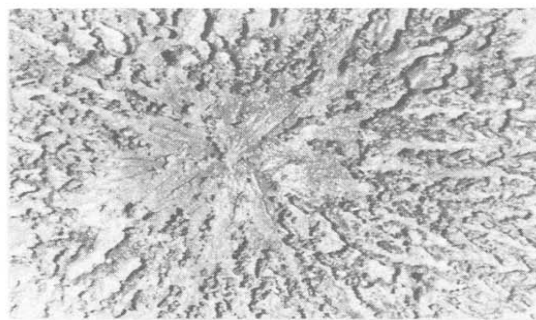


Fig. 3. Morphological change (schematic) of a zinc-leaf with electrolysis time and the corresponding current-time curve, observed under the same conditions as those in Fig. 2.



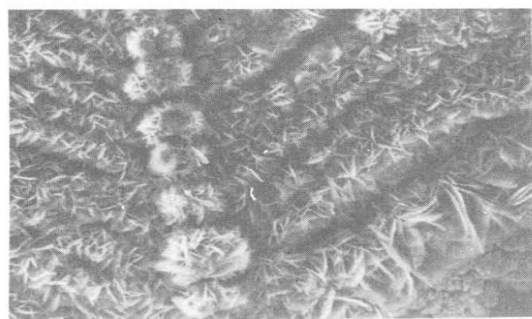
(a)

1 cm



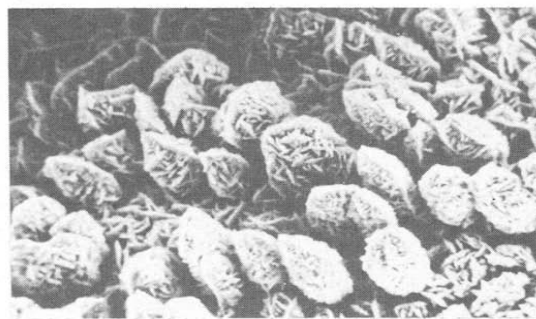
(b)

1 cm



(c)

20 μm



(d)

20 μm

Fig. 4. Photomicrographs (a and b) and scanning electron micrographs (c and d) of a zinc-leaf obtained under the following conditions: $[\text{ZnSO}_4] = 3 \text{ mol dm}^{-3}$; $U_{\text{CELL}} = 3 \text{ V}$; $t = 25^\circ\text{C}$; electrolysis time = 180 s. Photographs (a) and (c) for the o-side, and (b) and (d) for the w-side, respectively.

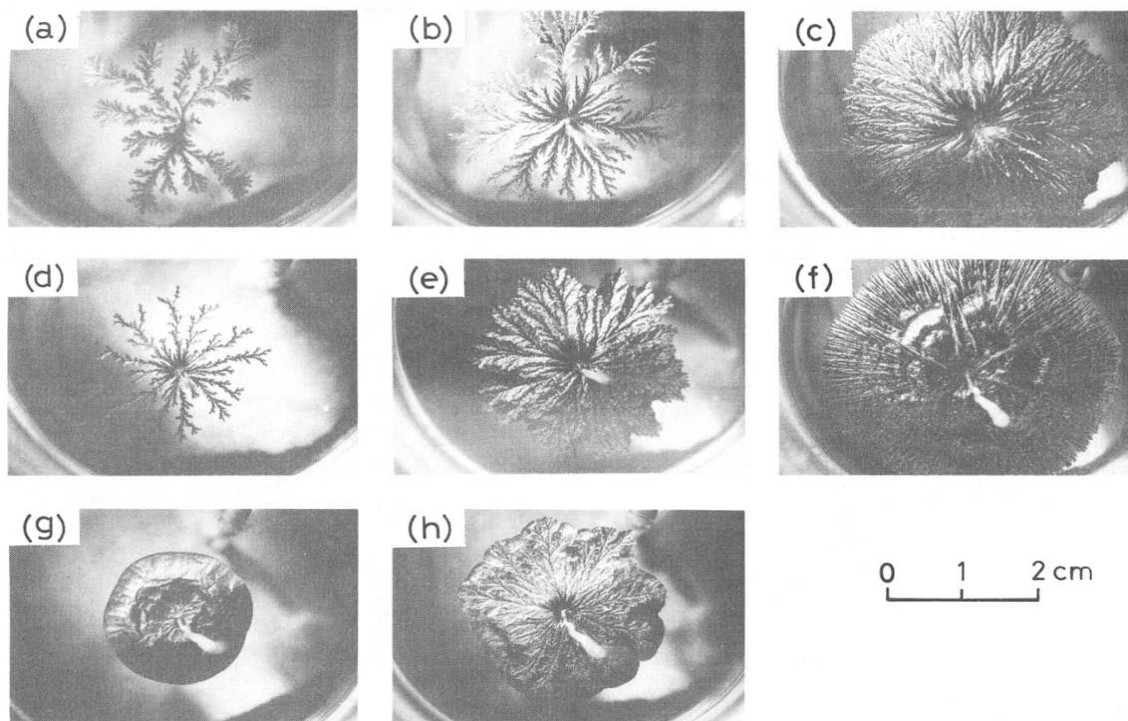


Fig. 5. Effects of ZnSO_4 -concentration (a, b and c), temperature (d, e, c and f) and cell-voltage (g, h and c) on the morphology of a zinc-leaf at electrolysis time = 180 s. (A white, out-of-focus spot in the center of each photograph is a part of the cathode.) Photo (a)–(c): $U_{\text{CELL}} = 3 \text{ V}$; $t = 25^\circ\text{C}$; $[\text{ZnSO}_4]/\text{mol dm}^{-3} = 1$ (a), 2(b), 3(c). Photo (d) (f): $[\text{ZnSO}_4] = 3 \text{ mol dm}^{-3}$; $U_{\text{CELL}} = 3 \text{ V}$; $t/^\circ\text{C} = 5$ (d), 15(e), 35(f). Photo (g), (h): $[\text{ZnSO}_4] = 3 \text{ mol dm}^{-3}$; $t = 25^\circ\text{C}$; $U_{\text{CELL}}/\text{V} = 1$ (g), 2(h).

The effect of ZnSO_4 -concentration on the morphology of a zinc-leaf was studied at $U_{\text{CELL}} = 3 \text{ V}$ and at 25°C (Figs 5a–c). At the concentrations below 1 mol dm^{-3} , it was difficult to obtain good leaves, and the current–time curve did not show a maximum. In a 1 mol dm^{-3} solution, the leaf consisted of delicate, dark spokes, each spoke being curved and branched, whereas in a 2 mol dm^{-3} solution the spokes were hard and lustrous. No filmy structure was observed at these concentrations.

The temperature effect was examined in saturated or 3 mol dm^{-3} ZnSO_4 solutions and at $U_{\text{CELL}} = 3 \text{ V}$; the result was of somewhat poor reproducibility. Photographs (d), (e), (c) and (f) in Fig. 5 compare the leaves obtained at 5, 15, 25 and 35°C . Because of larger electric conductivities of the aqueous solution at higher temperatures, the growth rate of leaves increased with increasing temperature. The leaf at 5°C consisted of stiff spokes only and had no filmy structure, and both o- and w-sides of the leaf had metallic luster. At higher temperatures (15 and 25°C) the filmy structure increased; at 35°C some small leaves appeared in the initial stage of electrolysis, which then joined together to give one big petal-like deposit.

The effect of the applied cell-voltage was studied in 3 mol dm^{-3} ZnSO_4 solutions at 25°C (Figs 5g, h and c). At $U_{\text{CELL}} = 1 \text{ V}$, the growth rate was very slow and

only the filmy structure was observed; the thickness of the leaf was a few μm . As the electrolysis time increased, the leaf grew to be a concentric circle. No maximum was observed on the current–time curve at low cell-voltages. When the cell-voltage was 2 V , the spoke-like structure appeared in the beginning and later the filmy structure followed; the spoke-like structure became more predominant with increasing cell-voltage.

Zinc-leaves obtained by the controlled-current electrolysis

Morphology of the leaves obtained under the galvanostatic controlled-current condition is different from that under the controlled-voltage electrolysis. In the case of the controlled-current electrolysis, the growth of usual dendrites into the bulk of the aqueous solution competed with the formation of a leaf at the interface; the dendrite formation was inevitable because of very high current densities in the beginning of electrolysis.

Figure 6 shows the leaves obtained under the following conditions: $[\text{ZnSO}_4] = 3 \text{ mol dm}^{-3}$; $t = 25^\circ\text{C}$; electrolytic current $I = 100 \text{ mA}$. The initial deposit at the interface consisted of a few broad leaves, which were then connected together by the filmy structure between the leaves. Further electrolysis caused the filmy structure to grow; its appearance

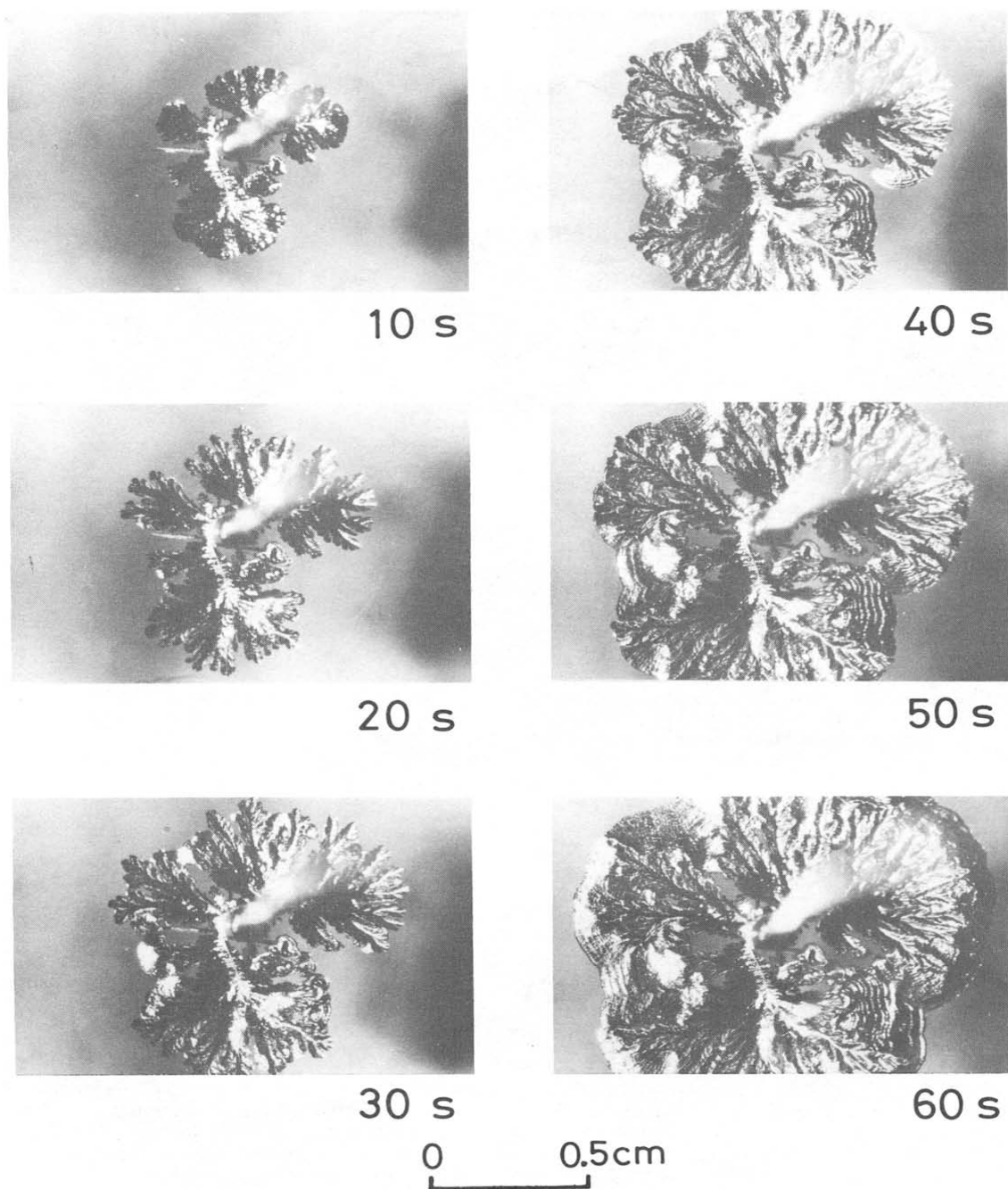


Fig. 6. Growth of a zinc-leaf under the controlled-current electrolysis: $[\text{ZnSO}_4] = 3 \text{ mol dm}^{-3}$; $I = 100 \text{ mA}$; $t = 25^\circ\text{C}$. (A white, out-of-focus spot in the center of each photograph is a part of the cathode.)

is similar to an annual ring of a tree and somewhat different from the filmy part obtained in the controlled-voltage electrolysis.

DISCUSSION

In order to obtain beautiful metal-leaves, it is necessary to avoid the growth of usual dendrites into the bulk of the aqueous solution. Higher current densities generally favor the dendrite formation in the bulk, and the formation of interfacial leaves is preferred at lower current densities.

The zinc-leaf generally consists of the two types of deposits; one is spoke-like and the other is filmy. The spoke-like deposit was found to be better formed at higher current densities, and may be corresponding to the lineage structure observed in conventional dendritic crystals. Similar morphology was reported by Tajima and Ogata[4] for the nickel dendrite which grows from the edge of a copper cathode by the electrodeposition in hot aqueous solutions of nickel sulfate. A preliminary SEM study showed that the spoke-like deposits at the butyl acetate/ $\text{ZnSO}_4(\text{aq})$ interface mainly consist of fine fragments, as can be seen from Figs 4c and d, whereas a zinc-leaf at the benzene/ $\text{ZnSO}_4(\text{aq})$ interface involves overlapping hexagonal plates. The latter structure is analogous to that observed by Noguchi *et al*[5] on zinc dendrites obtained in acidified ZnSO_4 solutions.

Formation of the filmy deposit was found to be favored at lower current densities. This type of deposit may be corresponding to the zonal structure in conventional dendritic crystals, and analogous to the layer deposit observed in electroplating. According to Wranglén[6], the growth layer of center type is formed at low current densities, whereas that of edge and corner type at high current densities. In our present experiments on zinc-leaves, the growth layer of center type was observed mainly at lower cell-voltages (*eq* 1 V), and that of edge and corner type was obtained typically under the galvanostatic controlled-current condition.

Although the factors which govern the metal-leaf formation have not yet been known in sufficient detail, it is considered that some kind of geometrical selection acts to favor the growth of a crystal structure similar to pseudo two-dimensional dendrites at the organic liquid/aqueous solution interface. Among some con-

ditions which must be fulfilled in order to give metal-leaves, the existence of capillary-active liquids and, in the case of zinc, for example, the existence of a small amount of zinc oxide, are supposed to be essential[1, 2, 7]. In the case of silver or copper, the leaves can be formed when the aqueous phase has a composition similar to that used in the chemical silvering process. This similarity between the formation of a metal-leaf and a silver mirror, which was suggested by Freundlich[7], is supposed to have an important significance in understanding the mechanism of the metal-leaf formation.

The interfacial movement of liquid observed while a zinc-leaf is growing should be remembered in discussing the mechanism of metal-leaf formation. Brimacombe and Weinberg[8] observed similar surface movements of liquid copper and tin, when the metal oxides grew radially by blowing a jet of oxygen vertically onto the liquid surface. This sort of a surface movement cannot be accounted for by the transfer of the oxygen jet momentum, and has been attributed to the local establishment of sufficiently large gradients of interfacial tension at the interface. In the case of zinc-leaf formation, it is highly probable that the gradient of interfacial tension can be established by local changes of electrical potential and zinc ion concentration around the tip of the cathode, and the resulting interfacial motion will contribute to the formation of metal-leaves.

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