Electrochemical Growth of Iron Arborescences under In-Plane Magnetic Field: Morphology Symmetry Breaking

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Pattern formation in the electrochemical deposition of iron from a thin layer of $Fe(SO_4)$ aqueous solution was investigated in a circular geometry under a magnetic field applied in the plane of growth. Arborescent aggregates were obtained whose macroscopic morphology changes from circular in zero field to rectangular in finite field, one edge of the rectangle being parallel to the field. This field-induced symmetry breaking is explained as resulting from a selection at the microscopic scale of the orientation of the branches with respect to the field, associated with a minimization of the magnetic dipolar energy of the growing branches.

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Complex patterns emerge in nonequilibrium and irreversible phenomena which, either physical, chemical, or biological, abound in nature and are actively studied [1]. One of the challenges is to understand the origin of the morphology of these patterns, generated by different microscopic mechanisms, with a small number of basic parameters and to look for possible universalities. Growth phenomena were in this respect among those investigated in depth [2,3] and continue to raise up a strong interest.

A model growth phenomenon is the electrochemical deposition (ECD) of metals in thin gap geometry: it has the great advantage of allowing, with the same experimental setup, the generation of a number of patterns with different morphologies, fractal or nonfractal, which were empirically termed dense radial, dendritic, needlelike, stringy, open, etc. [4,5]. What explains this diversity is that several processes are involved, related either to the chemical aspects of the metal reduction or to the transport under an electric field of cations and anions, namely diffusion, migration, and transport induced by the fluid motion [6].

Quantitative analysis of stationary growth with diffusion and migration showed that ramified growths are triggered by an off-equilibrium space charge which develops in the vicinity of the growing front upon anion depletion and that the growth speed of the deposit is fixed by the anion recession [7]. A strong electric field is associated with this charge space which can induce local electroconvection [8]. A gravity-induced convection can come out as well, which can modify the distribution of ions within the fluid thickness when the shear motion dominates over the diffusion [9]. Although these transport processes are now well understood, the full interpretation of the experimental ECD patterns is still challenging. Stationary growths can be materialized only on average, with parallel electrodes and constant currents, and to explain the texture of some fractal aggregates at the fractal cutoff scale an oscillatory nucleation-growth mechanism must be invoked [10]. On the other hand, chemical aspects come often into play through drastic effects of surface active impurities [6]. Alternating transitions between dendritic and tip splitting growths were for instance observed in the ECD of iron from a layer of $Fe(SO_4)$ aqueous solution, interpreted as arising from the periodic accumulation and depletion of H^+ impurities in front of the growing interface [11].

Additional environmental parameters can provide further insights. The impurity effects are thus best investigated by mixing appropriate molecules with the initial salt, in a concentration ratio that can be reproducibly tuned up [6]. A magnetic field is also relevant because, owing to the Lorentz force, it is expected to act on the migration of ions and to induce convection. Silver and zinc ECD experiments in thin gap geometry performed under a magnetic field perpendicular to the plane of growth show field-induced changes of morphology and spiraling geometry [12]. When the field is applied in the plane of growth, the Lorentz forces associated with most of the transport processes are perpendicular to this plane and, except through the effects associated with the gravity-induced convection, no drastic changes on the growth are *a priori* expected. On the other hand, if the deposit gets magnetized as with iron, then magnetic dipolar forces are induced, which should influence the growth. We report in this Letter an experimental study which shows that spectacular effects can come out.

The experiments were performed without a supporting electrolyte and at constant voltage applied between a circular anode and a central cathode. The anode is a copper ring of diameter 4 cm and thickness 0.5 mm and the cathode is a copper wire of thickness 0.05 mm. A thin film (about 500 μm thick) of an aqueous $Fe(SO_4)$ solution is spread on a glass plate, edged by the anode. The cell is analogous to the ones used in [4] and [5], but is left open to reduce the destroying effect on the deposits of the H_2 bubbles generated during the growth. Unfortunately, only a narrow range of external parameters is found for which the growth is not altered by the H_2 bubbles: concentration between 3.10^{-2} and 7.10^{-2} mole/l and voltage between 4

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and 7 V. A microscope coverslip is put under the cathode in order to reduce locally the thickness of the liquid film and to allow removal of the deposit out of the solution after the growth. To insure the reproducibility of the growth, the entire setup is temperature regulated and placed in a transparent Plexiglas box isolating the growth from external perturbations. Each growth is done at 20 °C and takes a few minutes.

Two different devices are used to generate the magnetic field: a "magnetic mangle" and an electromagnet. The magnetic mangle consists of four cylindrical magnets, each one magnetized perpendicular to its axis, disposed in such a way that a uniform magnetic field is obtained in a volume of about $2 \times 2 \times 2$ cm^3. By rotating the magnets, the amplitude of the magnetic field can be varied from -0.2 to 0.2 T. The electromagnet has a distance of 4 cm between the pole pieces and can generate magnetic fields up to 1.6 T. The cell used in this case is smaller, with an anode of diameter 2.8 cm. The electromagnet allows higher and more uniform fields, while the magnetic mangle, a compact system easy to handle, allows *in situ* microscopic observations. Both devices show the same effects of the magnetic field on the growth.

All the growths presented here were done with an initial solution of pH $= 7$, a concentration of 6.10^{-2} mole/l, a voltage of 5 V, and a magnetic field applied in the plane of growth. *In situ* observations are performed during the growth process, at different scales using an optical microscope, a CCD camera, and a video recorder. The deposits are floating in the aqueous solution and are very fragile so that removing them out of the solution may lead to a destruction of the very small branches as well as an oxidization. Post-deposited analyses are then more delicate than *in situ* analyses.

Without magnetic field, in the available range of control parameters in the experiments, the deposits show the "dense branching morphology" (DBM) [4,5,13,14], isotropic with a circular envelope and dense branches going outward from the central cathode [Fig. 1(a)].

When an in-plane magnetic field is applied during the growth process, the main result, at the macroscopic scale, is that the shape of the aggregate is no longer circular but rectangular, one edge of the rectangle being along the field direction [Fig. 1(b)]. The branches seem to grow straight along the diagonals of the rectangle, building a straight front in the directions parallel and perpendicular to the field. An absence of growth from the cathode in the direction perpendicular to the field is often observed.

The rectangular shape is achieved almost at the beginning of the growth and the growth proceeds homothetically, with straight fronts propagation (Fig. 2).

With respect to the field strength, the shape changes progressively from circular in zero field [Fig. 1(a)], to rectangular with rounded corners in low field up to fully rectangular in stronger field [Fig. 1(b)]. The aspect ratio of the rectangular shape is not field dependent, but can show slight changes from one experiment to the other.

The growth process leading to the rectangular shape does not depend on the initial conditions, as shown in Fig. 3 where the shape of the aggregate changes from circular to rectangular when the field is applied after about a minute of growth under zero field.

In situ observations during the growth process, at a scale down to a few μm, were performed to understand the origin of the observed change of the macroscopic shapes: it was found that the main effect of the in-plane magnetic field is to induce a growth of the branches of the aggregates along well-defined directions.

Under zero field the DBM is obtained, as already mentioned, but to be more precise the microscopic structure of the aggregate evolves during the growth: in the first stage of the growth, the aggregate is radial, dense, isotropic, but too dense to allow a clear *in situ* observation of the structure of the branches [Fig. 4(a)]. As the growth proceeds the aggregate becomes less dense and more dendritic, owing probably to the gradual change of the concentration and electric field during the growth, leading in turn

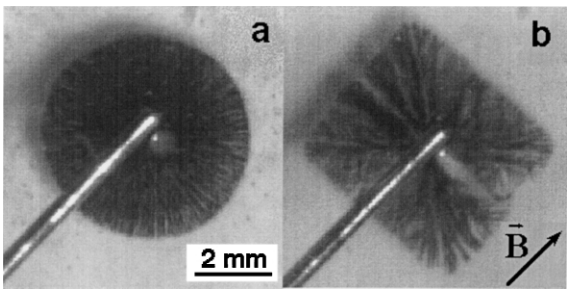

FIG. 1. Iron electrodeposit grown under (a) zero field and (b) an in-plane field **B** of 0.2 T.

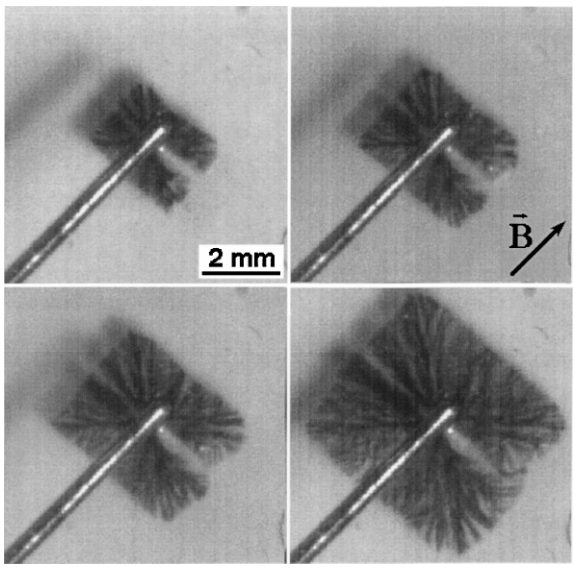

FIG. 2. Iron electrodeposit grown under an in-plane field **B** of 0.2 T viewed at different times during the growth.

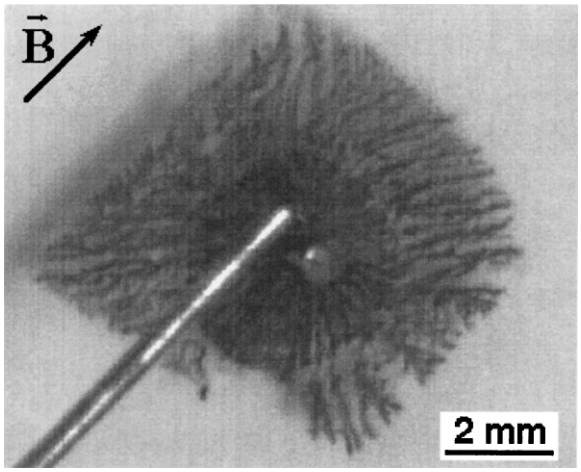

FIG. 3. Iron electrodeposit obtained by starting the growth in zero field and applying an in-plane field **B** of 0.2 T at an intermediate stage of the growth.

to an evolving velocity of the growing branches [15,16]. A well-defined angle is then observed between the main branches and the sided branches of the dendrites [Fig. 4(b)]. Nevertheless, the orientation of the branches is only local, with no long range correlation and its distribution in all the directions results in a radial isotropic pattern maintaining a circular envelope.

When the in-plane field is applied, the branches grow along a few well-defined directions. As in the zero-field experiments, the aggregate is more dense and the branches thicker at the beginning of the growth than at the end, but it is not clear if one can speak of a change in the morphology during the growth process. The branches look more needlelike or dendritic, even at the beginning of the growth, than in zero magnetic field. There are differences between the growth around the field direction and the growth around the perpendicular to the field direction. The diagonals of the rectangular aggregate separate the space in four regions associated with these two directions. Along the field direction, the branches look thicker and with a tendency to grow on average along the field direction, but always at an angle of about 30° from the field [Fig. 5(a)]. Perpendicular to the field, the branches are thinner and grow again at a definite angle from this direction [Figs. 5(b) and 5(c)], but the angle now increases slightly during the growth as well as with the field strength from about 30° at low field to about 40° at high field. Close to the diagonals these angles increase, up to a maximum of about 45°.

In order to check whether the observed pattern change could be induced by Lorentz forces associated with the in-plane field, zinc ECD experiments under the same conditions (magnetic field, initial concentration, and voltage) as those generating the iron rectangular aggregate were performed up to 0.2 T: no effect was found.

The basic difference between zinc and iron is that the Fe^{2+} ions have a magnetic moment and that the aggregate is ferromagnetic so that growing under an applied field it acquires a macroscopic magnetization which in turn generates a magnetic field $\mathbf{B}_d$ of dipolar origin.

Magnetization measurements confirmed that the iron aggregates are ferromagnetic at 20 °C. For in-plane fields a magnetic hysteresis was measured, which ends around 0.2 T. At this field the magnetization is not fully oriented along the field. Above it and up to 0.6 T the magnetization processes consist in reversible nonuniform rotations to overcome the shape anisotropy of the branches. For all values of the in-plane field the magnetization lies in the plane of growth, owing to the planar morphology of the aggregate. So will the field $\mathbf{B}_d$ it creates. Consequently, in-plane ionic diffusion, electric-field induced migration, and electroconvection will give rise to Lorentz forces perpendicular to the plane of growth and are no longer expected to generate the observed pattern change. An in-plane Lorentz force can emerge ahead of the growing branches from the motion within the fluid thickness associated with the gravity-induced convection, but the inherent symmetries of the rectangle at high in-plane fields tell us that it is irrelevant: the two edges of the rectangle parallel to the in-plane field grow indeed at the same

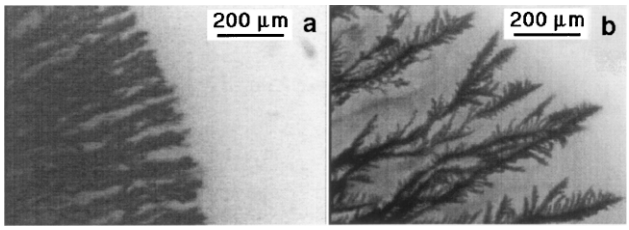

FIG. 4. Microscope view of the growing iron electrodeposit in zero magnetic field (a) at the beginning of the growth and (b) at the end of the growth.

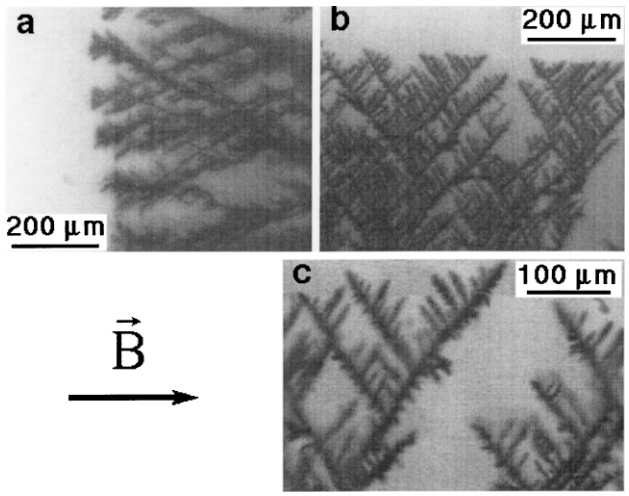

FIG. 5. Microscope view of the growing iron electrodeposit under an in-plane magnetic field **B** (a) around the field direction and [(b), (c)] around the direction perpendicular to the field.

speed in opposite directions while the magnetization being aligned to the in-plane field would lead via $\mathbf{B}_d$ to forces in the same direction on these two edges.

As a matter of fact, the crucial feature of $\mathbf{B}_d$ is that it is not uniform. A field gradient then exists leading to a force given as $\Delta\mathcal{M} \cdot \mathbf{B}_d$ where $\mathcal{M}$ is any magnetic moment induced by the sum of the applied and dipolar field. At 20 °C, the gain in energy $\mathcal{M} \cdot \mathbf{B}_d$ when a free Fe^{2+} ion comes into contact with the aggregate from a far distance is estimated to be about 4 orders of magnitude smaller than the energy of a moving charge under the electric field in ECD. Considering, on the other hand, a grain of a few hundred atoms, a much larger magnetic dipolar energy is calculated, about a hundred times per Fe atom, owing to the increase of the magnetic moments via the exchange interactions within the grain. As a consequence, the magnetic dipolar forces are not expected to play a role at the level of individual ions in the aqueous solution, but rather at the level of grains, to induce preferential nucleation or growth processes. A detailed analysis of magnetic dipolar effects is complex and challenging, as it requires taking into account the evolving magnetization distribution of the growing aggregate. Nevertheless, one can say from the experiments that these effects tend to favor branch orientations with respect to an absolute direction, the one of the applied field. Whether magnetic dipolar effects alone can impose an angle selection is, however, unclear.

As suggested by the *in situ* observation of the aggregates grown in zero field [Fig. 4(b)] the existence of a well-defined angle between two branches seems to be of crystalline origin. Preliminary transmission electron microscopy (TEM) observations revealed small single crystals of pure iron, consisting of dendrites of about 2 μm long, with side branches as small as 50 nm, at 60° with respect to the main branches. Electron diffractions indicate a growth of branches along the twofold axes, perpendicular to the [111] axis of the iron bcc structure. The interaction of the magnetized branches with the applied and dipolar field can force definite orientations of these dendrites with respect to the applied field and lead to a textured polycrystal displaying angles close to those defined by the crystalline anisotropy. One would then expect to observe a polycrystal with the same morphology as the artificial snowflake shown in Fig. 3 of Ref. [17]. Our aggregates are quite similar to this ice crystal, at least around the direction perpendicular to the applied field [Fig. 5(c)], but we do not observe a dendrite with a main branch growing along the field direction and side branches at 60°. A simple estimate of the magnetic dipolar energy of such a dendrite along the field direction compared to that of two needles at 60°, growing symmetrically with respect to the field direction, indicates that this later situation is favored: the observed aggregate results from a minimization of the magnetic dipolar energy under the constraints of the crystalline anisotropy. It consists of a textured polycrystal reflecting the symmetry of two single crystals oriented perpendicular to each other. The fact that the macroscopic shape is rectangular instead of square may be related to slight differences in the growth processes along and perpendicular to the field, leading to branches a little thicker along the field, and then to a larger straight front speed perpendicular to the field.

In conclusion, even if several aspects of the growth processes are still unclear, the main effect of the magnetic field is a selection of the orientations of the growing branches with respect to it. The macroscopic rectangular shape simply results from this selection since branches growing at the same speed along two well-defined directions give a straight front. The effect of the in-plane magnetic field is somehow analogous to the surface tension anisotropy in crystal growth, leading to faceted crystals, or to the anisotropy imposed by engraving a grid on the glass plates in viscous fingering experiments [2]. The morphology symmetry breaking induced by the magnetic field in our experiment, associated with a diverging correlation length of the branch orientations bears a strong analogy with the symmetry breaking associated with an order-disorder phase transition, the disordered phase here being the isotropic aggregate grown in zero field.

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