ELECTROCHEMICAL DEPOSITION OF IRON IN THIN CELL UNDER IN-PLANE MAGNETIC FIELD

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Introduction. Electrochemical deposition (ECD) of a metal from an aqueous electrolyte in a thin cell and at a high current density is, among the physical prototypes of non-equilibrium growth phenomena, one of the easiest to set working while providing for the observation of a wealth of growth patterns [1, 2]. What explains this diversity is that a number of processes can be involved in the growths, contributing to the kinetic transfer, including chemical mechanisms and surface phenomena, or to the mass transport, by diffusion and migration or trough the electrolyte fluid motions (electro-convection, gravitoconvection, ...) [3]. Each of these acts at an own spatial scale, which in some instance lead to a decoupling of microscopic and macroscopic morphologies, and might become rate determining, either alone or together with others, according to many different control parameters, namely the electric voltage, the electric current, the electrolyte concentration, the cell thickness or the concentration of other active species within the electrolyte (H^3O^+, added impurities, ...). An additional fine-tunable control parameter that also modifies the ECD patterns or creates new ones is the magnetic field [4]–[7], which can be in- fluential through the magnetohydrodynamic forces associated with the moving charges and the non uniform magnetic fluxes and, when the growing aggregate is magnetic, through its magnetic interactions with the magnetic field and the magnetic dipolar interactions within it.

ECD of ferromagnetic Fe under magnetic field from $Fe(SO_4)$ aqueous solution were earlier performed, in thin cell circular geometry and at constant electric voltage [7]–[9]. In zero magnetic field and within the range of control parameters for which the growths are not thwarted by the hydrogen evolution, a dense morphology with many thin branches and a stable circular envelope, increasing uniformly in size as the growth proceed, is observed at low electrolyte concentration (Fig. 1*a*). When this gets larger, a sparse morphology with few thick branches and no well defined global shape is stabilized (Fig. 1*c*). Only slight changes in these macroscopic

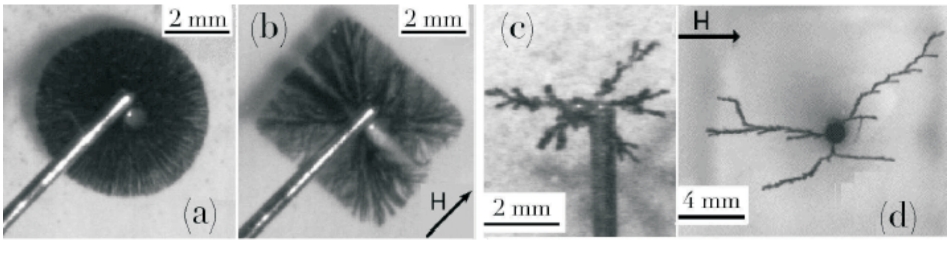

Fig. 1. Fe electrochemical deposits grown at constant electric voltage (5 V) from $Fe(SO_4)$ aqueous solution with initial concentration $6 \cdot 10^{-2}$ M (a, b) or $5 \cdot 10^{-1}$ M (c, d) in zero magnetic field (a, c) or under an in-plane magnetic field of 0.2 T (b, d).

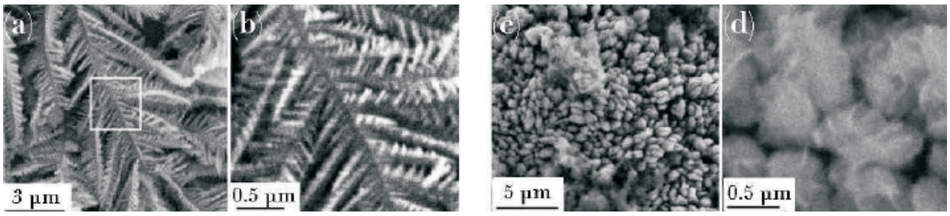

Fig. 2. SEM images at different scales of Fe electrochemical deposits grown in zero magnetic field and showing either the dense (a, b) or the sparse (c, d) macroscopic morphology.

morphologies occur under normal magnetic field. On the other hand, spectacular morphology transitions are induced when an in-plane magnetic is applied: the stable envelope of the dense morphology is transformed from circular to rectangular (Fig. 1*b*) and the sparse morphology shows stringy branches oriented along the magnetic field (Fig. 1*d*). While the latter effect is easily understood in terms of the minimization of magnetostatic energy, as for a compass needle in a magnetic field, the former effect was rather puzzling. According to the observations by transmission electron microscopy (TEM) [8] the growths at the nanometric scale would all be single crystalline dendrites, insensitive to the in-plane magnetic field. Coarse dendrites at scales about 100 m are also evidenced by optical microscopy in the deposits with the dense macroscopic morphology, but not in those with the sparse macroscopic morphology. A loss in branch orientation between the coarse dendrites occurs at larger scale owing to some noise effects [9], leading to the macroscopic circular envelope in zero magnetic field. A mutual ordering of the coarse dendrites takes place under in-plane magnetic field, transposing to a selection of growth directions at definite angles symmetrically with respect to either the magnetic field or its normal, which would geometrically explain the circle to rectangle morphology symmetry breaking [7]. Complementary experiments were desirable to get more insights about the mechanism of these in-plane magnetic field-induced branch orientation selection.

1. Scanning electron microscopy (SEM). As to determine the morphology of the deposits at intermediate scales, *ex situ* SEM on selected area of grown deposits were performed. As expected, dendrites are observed in the deposits with the dense macroscopic morphology (Fig. 2(a, b)). Apparently, these get disordered in zero magnetic field at scales above 1 m. A granular structure down to the lowest scales is evidenced in the deposits with the sparse macroscopic morphology (Fig. 2(c, d)), suggesting that the dendritic growth tendency observed at nanometer scales by TEM [8] is thwarted by some process. Under in-plane magnetic field the dendrites of the dense macroscopic morphology surprisingly do

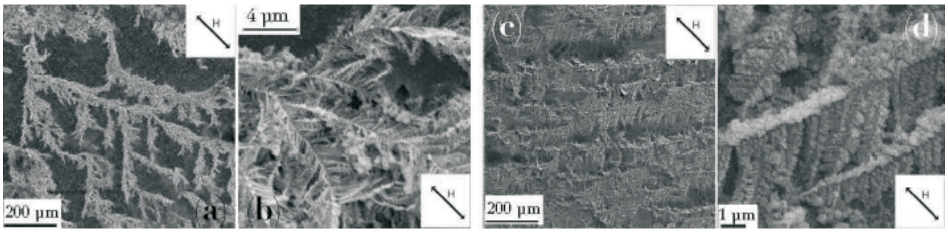

Fig. 3. SEM images at different scales of a Fe electrochemical deposit grown under an in-plane magnetic field, at proximity of the growth fronts normal (a, b) and parallel (c, d) to the magnetic field.

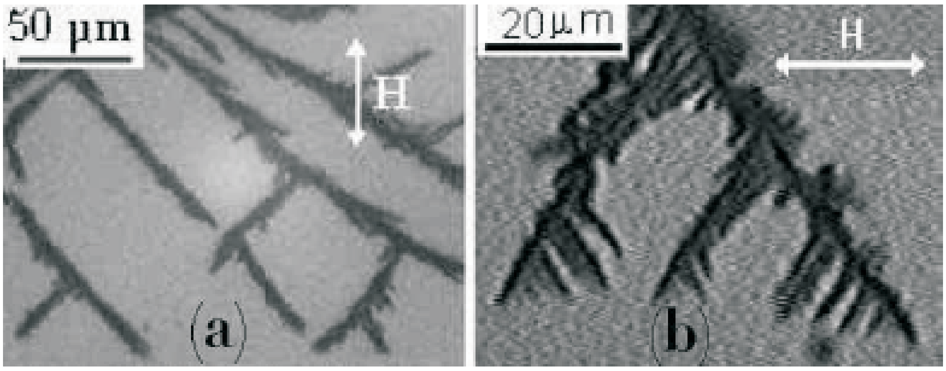

Fig. 4. Optical microscopy images of a Fe electrochemical deposit with the dense macroscopic morphology at proximity of the growth front normal (*a*) and parallel (*b*) to the in-plane magnetic field.

not order at the same scales according to the selected area on the deposits. At proximity of the growth fronts normal to the magnetic field the dendrites are still disordered at scales about 10 m and it would appear that only the coarse dendrites at scales about 100 m grow along the field at a definite angle from it (Fig. 3(a, b)). On the other hand, at proximity of the growth fronts parallel to the magnetic field long range correlations of branch orientation are already effective at scales about 1 m (Fig. 3(c, d)).

2. *In situ* **optical microscopy.** Observations by *in situ* optical microscopy revealed that at the growth front normal to the magnetic field (Fig. 4*a*), the average branching angle, which is twice that of the central nerve of a dendrite with the magnetic field, is larger than that expected from crystalline anisotropy [8, 9], while the opposite is observed at the growth front parallel to the magnetic field (Fig. 4*b*). Additionally, in this zone some of the sidebranches stick to each other during the growth. We understand these differences as arising from magnetic dipolar interactions between the branches. Owing to the magnetic shape anisotropy, a branch tend to be magnetized along its axis under magnetic field. At the growth front normal to the magnetic field, the two branches of a branching angle should show parallel magnetization components, so that will repel each other owing to the magnetic dipolar interactions. At the growth front parallel to the magnetic field (Fig. 4*b*), the magnetization of the two branches of a branching angle, which grow along the two different growth directions with respect to the normal to the magnetic field, should on the other hand show antiparallel magnetization components and will attract each other, owing to the magnetic dipolar interactions.

3. Growths in thin cell quasi-parallel geometry. Within a thin cell circular geometry, the electric field is radial and the magnetic field is axial so all the orientations of one field with respect to the other in the plane of growth exist simultaneously. As to fix a given orientation, the electric field must be axial, which is achieved in thin cell with parallel line electrodes. A line cathode with well separated transversal tips, at which the growths nucleated, was actually considered to preserve local semi-circular geometry. On gradually changing the orientation of the electric field with respect to the magnetic field, it was observed that the two growth directions were unchanged but the growth speed become larger along the direction closer to the electric field. A straight growth front parallel or perpendicular to the magnetic field is thus preserved (Fig. 5). At an intermediate orientation no straight growth front is observed, but instead quasi-linear branches growing fast along the electric field. It appears that the dendrites tend to make

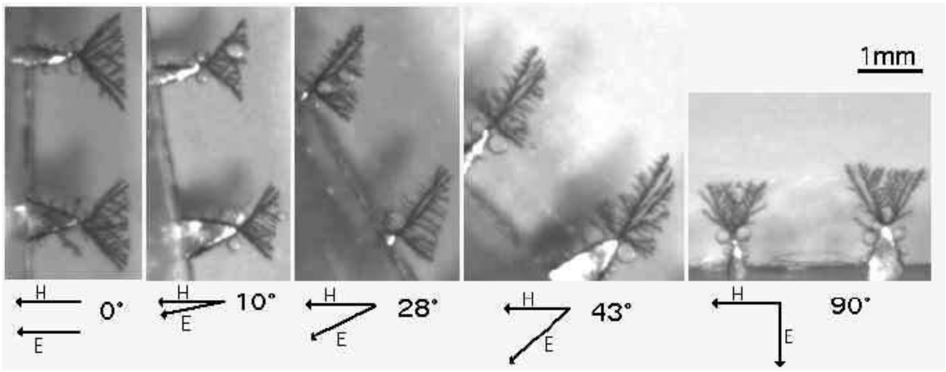

Fig. 5. Electrochemical growth of Fe in thin cell parallel geometry for different orientations of the magnetic field with respect to the electric field.

one single angle with the magnetic field.

4. Conclusion. As from the above experiments, it is deduced that the in-plane magnetic field-induced branch orientation selection, in the deposits with the dense macroscopic morphology, occurs primarily because of the interactions of the magnetized dendrite with the magnetic field. An isolated dendrite would tend to force its central nerve, provided it is suffciently thin, to align at 60° from the magnetic field so that one of the two series of side-branches get aligned along the magnetic field. Owing to magnetic dipolar interactions and distribution of the electric field orientation with respect to the magnetic field, the actual orientations deviate however from the ideal one.

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