

Magnetoresistance Controls of Arborous Bead-Dendritic Growth of Magnetic Electrodeposits

Experimental and Theoretical Results

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The effect of magnetic fields applied on magnetic metals electrodeposition was examined. Nickel deposits obtained from a Watt solution with coumarin, at cathodic potentials of -1000, -1200, and -1300 mV/SCE, without and with, both, perpendicular and parallel oriented to the electrode surface low applied magnetic fields (up to 500 Oe) were examined by scanning electron microscopy (SEM) technique. At a potential of -1300 mV/SCE, a dramatic difference was observed between nickel morphologies obtained with a perpendicular oriented magnetic field (zero MHD effect) and those obtained in the absence of one. The nickel deposit obtained with perpendicular oriented magnetic fields was a very developed 3D arboreous-bead-dendritic structure. On the other hand, the nickel deposit obtained without the presence of magnetic field was very rough, with a clearly visible clustered structure. The obtained nickel morphologies are then compared with copper morphologies. Based on the fact that copper deposits obtained with and without a perpendicular oriented magnetic field were dendritic structures, the observed difference between nickel deposits, which are nonexistent in nonmagnetic materials. We also have done experiments with iron deposits. (© 2004 The Electrochemical Society. [DOI: 10.1149/1.1776591] All rights reserved.

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The effect of an applied magnetic field on metal electrodeposition has been a subject of many investigations.¹⁻⁸ It was shown that an imposed magnetic field realizes various effects on electrolytic processes and in particular on the morphology and structure of metals or alloys prepared by electrodeposition. Morphologies of electrochemically obtained metal deposits are often strongly changed if metal electrodeposition was performed in the presence of a magnetic field. For example, a dense and compact deposit can be obtained in the presence of a magnetic field instead of dendritic one obtained without a magnetic field.⁸

Changes in morphology of metal deposits were ascribed to the Lorentz force.⁵ This force, *F*, exerted by an electromagnetic field *B* on the ions of charge *q* moving at the velocity *v* within an electric field *E* can be presented by Eq. $1^{1,5}$

$$F = q(E + v \times B)$$
[1]

During electrolysis, this force acts on the migration of ions and induces convective flow of electrolyte close to the electrode surface. This effect on the electrodeposition process is known as the magnetohydrodynamic (MHD) effect. The magnetohydrodynamic flow in electrochemical systems is conveniently described by the force per unit volume acting on the solution, $F_{\rm MHD}$ (in N/m³), and which is given by Eq. 2,⁹ where J (in C/m²) is the local flux of ions

$$F_{\rm MHD} = J \times B$$
 [2]

The largest effect of this force, and consequently, the largest effect on convective mass transport of the electrolyte, can be realized when magnetic field *B* is applied parallel to the electrode surface (*i.e.*, an external magnetic field is oriented perpendicular to the direction of the ion flux).⁹ This expectation is generally observed in investigations that have been reported in the literature.¹⁰⁻¹⁴

On the other hand, when a magnetic field is applied perpendicular to the electrode surface, except through the effects associated with gradients and the gravity-induced convection, no drastic changes on the growth are *a priori* expected.⁷ Then, the applied magnetic field is parallel to the direction of the ion flux, what corresponds to $J \times B = 0$.

Meanwhile, there are papers which report possible large effects of magnetic field with perpendicular orientation to the electrode surface on electrochemical process and morphology of a metal deposit obtained by electrodeposition.^{7,9} This effect is ascribed to the change of electrode size (i.e., change from a transition from planar to radial diffusion as the electrode size is reduced).⁹ According to Bodea et al.,⁷ if the deposit gets magnetized as with iron, then magnetic dipolar forces are induced, which should influence the growth. The change of macroscopic morphology of iron electrodeposited from an aqueous FeSO₄ solution from a circular in a zero field to rectangular in the presence of perpendicular oriented of a magnetic field is associated with a minimization of the magnetic dipolar energy of the growing branches.7 Also, in this case, an arboreousneedle-dendritic structure (ANDS) was grown. We have tried to repeat these experiments but have not been successful. We obtain arboreous-bead-dendritic structures (ABDS) which are very different of those in Ref. 7. While in this reference, the arboreous branches were needle-like, in our experiments, the branches are bead-like, i.e., consisting of aggregations of spherical clusters forming branches like a rosary.

In this work, the effect of the magnetic field on the electrodeposition of nickel was examined. Nickel was electrodeposited from a Watt solution in the presence of coumarin as the leveling addition agent. Nickel deposits obtained without an imposed magnetic field, as well as with, both, perpendicular and parallel oriented magnetic fields were examined. Also, iron and copper deposits obtained from corresponding sulfate solutions were examined. These metal deposits were examined by the technique of scanning electron microscopy (SEM). It is shown that it is possible obtain a large change of the nickel morphology under an perpendicular-oriented magnetic field, and the explanation is given in terms of the resistance of the branched structure. Diffusion-limited aggregation (DLA) simulation of dendritic growth is also presented.

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Figure 1. (a) SEM microphotograph of the photolithographically patterned thin-film microstructures with a micrometer gap that is closed to form a nanocontact. (b) Schematic illustration of copper film sample and SEM microphotograph near-contact area.

Experimental

Working conditions.—Nickel was electrodeposited from the following solution: NiSO₄·6 H₂O, 262.5 g/L; NiCl₂·6 H₂O, 45 g/L; H₃BO₃, 37.5 g/L; and coumarin, 0.060 g/L, and pH 4.5.

Nickel was deposited potentiostatically, at room temperature, at the following cathodic potentials: -1000 mV/SCE (with respect to a saturated calomel reference electrode), -1200 and -1300 mV/SCE, respectively. The counter electrode was pure nickel.

Iron was electrodeposited from 225 g/L FeSO₄·7 H₂O in 120 g/L Na₂SO₄·10 H₂O; pH 3; at cathodic potentials between -1 and -5 V/SCE, and at room temperature. The anode was pure platinum.

Copper was electrodeposited from 0.2 M $CuSO_4$ in 0.5 M H_2SO_4 , (pH 1.5), at room temperature, at the cathodic potential of -500 mV/SCE. The counter electrode was pure copper.

The electrodepositions were performed in photolithographically patterned thin-film microstructures with a micrometer gap that is closed to form a nanocontact (Fig. 1a), in the T configuration of wires that has been used previously to form nanocontacts to measure ballistic magnetoresistance (BMR)¹⁵ or at special fabricated copper films (Fig. 1b). The procedure for preparation of these copper films was one of the traditional methods used to get printed circuit boards. It consists of drawing on the virgin board (20 µm of copper deposited in an epoxy resin) with a waterproof pen. Then, the board was put in a solution of chloridic acid and sodic perborate. This solution attacks the exposed parts (and does not attack the painted ones). After all the copper has been removed from the exposed parts, we take out the sample and wash it in water. The process is completed by taking off the paint with alcohol. No matter what substrate or electrode is used, in all cases the same structures are observed which are reported below.

Equipment.—The deposition of nickel, iron, and copper was performed using a bipotentiostat, model AFCBP 1, Pine Instruments Company. The electrochemical cell was plunged into a uniform magnetic field of 500 Oe, which was perpendicular or parallel to the



Figure 2. Schematic illustration of the electrochemical cell, the field directions, the ion velocity, v, and the flux ions J.

electrode surface. The magnetic system used was model M-50 MMR Technologies, Inc. Nickel, iron and copper deposits were examined by scanning electron microscopy, SEM, model Philips SEM-FEG-XL 30.

The electrochemical cell, including the field directions, the ion velocity, v, and the flux of ions, J, is illustrated in Fig. 2.

Results and Discussion

Nickel deposits obtained in the presence of coumarin, at a cathodic potential of -1000 mV/SCE without and with parallel oriented magnetic field are shown in Fig. 3a and b, respectively. It can be seen from this figure that both surfaces were relatively smooth. The nickel deposit obtained in the presence of a perpendicular oriented magnetic field was very similar to these mentioned above, and is not shown here. The fact that nickel surfaces obtained without and with both perpendicular and parallel oriented magnetic fields were very smooth and mutually similar can be ascribed to the good leveling characteristics of coumarin as an inhibitor of the deposition process in the electrocrystallization of nickel, and also to the fact that the applied fields were moderately weak (at most 500 Oe). We notice at this point that most of the effects due to magnetic fields, observed and existing in the literature, are for fields values of the order of 1000s of Oe and greater.

Figure 4 shows nickel surfaces obtained in the presence of coumarin at a cathodic potential of -1200 mV/SCE, correspondingly, without an imposed magnetic field (Fig. 4a), with a perpendicular oriented field (Fig. 4b), and with a parallel oriented (Fig. 4c) magnetic field. It can be observed from this figure that the nickel deposit obtained in the presence of a perpendicular-oriented magnetic field (Fig. 4b) was very similar to the nickel deposit obtained without any magnetic field applied (Fig. 4a). The latter nickel deposits were coarser than that obtained under an applied magnetic field with parallel orientation (Fig. 4c).

The obtained nickel morphologies can be explained through the influence of magnetic fields on the nickel electrodeposition process in the following way:

As mentioned earlier, the perpendicular orientation of a magnetic field should have an insignificant effect on metal electrodeposition processes, which is shown in our case as well. Nickel deposits obtained without and with perpendicular oriented magnetic field were very similar to each other (Fig. 4a and b, respectively). This result was in accordance with Eq. 2, that when the applied magnetic field is perpendicular to the electrode surface, then $J \times B = 0$, and a change in the structure of a metal deposit is not expected. On the other hand, it is known that parallel orientations of a magnetic field exhibit the largest effect on metal electrodeposition processes,





Figure 3. Nickel deposits obtained at a cathodic potential of -1000 mV/ SCE from a Watt plating solution (NiSO₄·6 H₂O, 262.5 g/L; NiCl₂·6 H₂O, 45 g/L; H₃BO₃, 37.5 g/L) with the addition of 0.060 g/L coumarin, (a) without and (b) with imposed magnetic field (parallel orientation to the electrode surface) of 500 Oe.

shown also in this case. The nickel deposit obtained in the presence of this magnetic field orientation had a more uniform structure than nickel deposits obtained without and with a perpendicular oriented magnetic field. This result was also in accordance with Eq. 2, so that when the applied magnetic field is parallel to the electrode surface, the product $J \times B$ is at its maximum, and then the effect of the magnetic field on the growth process is the largest. However, the change of the orientation of the magnetic field from perpendicular to parallel led to an expected change in nickel morphologies, *i.e.*, it led to a change that was consistent with the predictions of MHD theory.⁵

At this cathodic potential, the hydrogen evolution was more visible than at a cathodic potential of -1000 mV/SCE. The effect of hydrogen evolution on the morphology of a nickel deposit can be clearly observed from Fig. 5, which shows a part of the nickel deposit obtained at a potential of -1200 mV/SCE with a parallel oriented magnetic field. This part of the deposit consists of elliptical rings, formed by the attachment of bubbles resulting from hydrogen evolution and the effect of a parallel oriented magnetic field. Figure 5 also shows that the bubbles of hydrogen are deformed shapes, and that this part of the nickel surface represents a depression on the whole of that surface. A similar phenomenon is observed as well during nickel electrodeposition the in presence of

2-butyne-1,4-diol.⁵ These structural characteristics can be ascribed to the enhancement of the transport of the inhibitor toward the cathode by MHD convection.⁵

We should mention that for -1000 and -1200 mV/SCE the depicted current were 20 and 25 mA, respectively. When -1300 mV/SCE was applied, however, a large enhancement of the current was observed, up to 40 mA without applied field, and up to 80 mA with a 500 Oe perpendicular applied magnetic field. In all cases the electrodeposition surface area was same. This is very important since it already shows the strong influence of the magnetic field as well as a strong nonlinearity in the I-U/SCE characteristics as indicated in Fig. 6 for nickel electrodeposition. It is necessary to emphasize here that these I-U/SCE characteristics are not polarization curves for the electrodeposition of nickel. We take for every applied cathodic potential the current value at the end of electrodeposition, i.e., at the moment when a nanocontact is formed, and then, we plot the dependence of I-U/SCE. Based on this observation, we decided to perform a more detailed study of the structure of the deposits at the last cathodic potential.

Nickel deposits obtained at a cathodic potential of -1300 mV/SCE are shown in Fig. 7a and b (without a magnetic field), and Fig. 7c and d (perpendicular orientation of the magnetic field), respectively. The nickel deposit obtained in the absence of a magnetic field was very rough, with a clearly visible clustered nickel structure (Fig. 7a). In addition, every nickel cluster consisted of very small clusters of nanosized dimensions (Fig. 7b). On the other hand, the nickel deposit obtained in the presence of a magnetic field showed a very developed 3D arboreous-bead-dendritic structure (ABDS) (Fig. 7c). The structure of this deposit consisted of thin nickel branches which terminated in flower-like aggregates of nickel. The flower-like aggregates of nickel consisted of thin nickel branches (or filaments) made of small nanosized nickel clusters (Fig. 7d), like a rosary. It is noteworthy that these clusters of beads constituting the branches of the structure were connected by nanocontact-size junctions (as illustrated in Fig. 7e), which may exhibit very strong magnetoresistance, such as has been observed already in electrodeposited magnetic nanocontacts. $^{\rm 15\text{-}18}$

The large change in the morphology of nickel deposits, however, is obtained for an orientation of the magnetic field for which the expected MHD effect is zero $(J \times B = 0)$. At this cathodic potential, a magnetic field with a parallel orientation to the electrode surface showed an effect on the nickel electrodeposition process that was consistent with the predictions of MHD theory. The nickel deposit obtained in the presence of coumarin with a parallel-oriented magnetic field is shown in Fig. 8, where we observe that this deposit exhibited a more uniform structure than the nickel surface obtained without the presence of magnetic field (Fig. 7a and b). In order to establish whether having coumarin in the nickel plating bath contributed to unexpected changes in nickel morphologies under a perpendicular-oriented magnetic field, nickel deposits obtained from a pure Watt solution were also examined. The obtained nickel deposits were very similar to ones obtained in the presence of coumarin. Hence, at this cathodic potential, the presence of coumarin in the plating solution had no effect on the morphology of the nickel deposits. The big change of the nickel morphology under a perpendicular-oriented magnetic field is, therefore, unexpected; the reason being that the energy introduced by the field in the medium is only a paramagnetic term on the ions, SB, where S is the magnetic moment of the ion. At room temperature, however, this effect is completely negligible, as well as the possible gradient effect that has been observed for applied fields much larger than 500 Oe.

Our explanation for the perpendicular field effects are based on the ferromagnetic characteristics of nickel. At variance with nickel is the case of a nonmagnetic material such as copper, where changes of morphology with the application of perpendicular oriented magnetic fields are not observed, as can be seen from the analysis of Fig. 9. This figure shows copper deposits obtained without (Fig. 9a) and with a perpendicular oriented magnetic field (Fig. 9b). It can be observed that both Cu deposits showed a developed ABDS structure,



and were very similar to each other. As expected in this case, the magnetic field with a perpendicular orientation exhibited an insignificant influence on the morphology of the Cu deposit.



Figure 5. The nickel deposit obtained at a cathodic potential of -1200 mV/SCE from a Watt plating solution (NiSO₄·6 H₂O, 262.5 g/L; NiCl₂·6 H₂O, 45 g/L; H₃BO₃, 37.5 g/L) with the addition of coumarin, 0.060 g/L, with the imposed magnetic field (parallel orientation to the electrode surface) of 500 Oe.

tance of the nanocontacts that make up the filaments (Fig. 7d and e), due to removal of domain walls. This resistance changes with ap-

Therefore, when the perpendicular field is applied, the resistance

of the filamentary deposits should change due to the magnetoresis-



Figure 6. *I*-*U*/SCE characteristics for electrodeposition of nickel in the presence of coumarin, and iron. For every cathodic potential we take the value of the current at the end of electrodeposition, *i.e.*, at the moment when a nanocontact is formed.



Figure 7. Nickel deposits obtained at a cathodic potential of -1300 mV/ SCE from Watt plating solution (NiSO₄·6 H₂O, 262.5 g/L; NiCl₂·6 H₂O, 45 g/L; H₃BO₃, 37.5 g/L) with addition of coumarin, 0.060 g/L: (a) and (b) without, (c) and (d) with imposed magnetic field (perpendicular orientation to the electrode surface) of 500 Oe, (e) schematic illustration of the part of a surface from Fig. 7d with clearly denoted place of nanocontact.

plied fields in magnetic nanocontacts, and it has been observed with values up to ten times less than those without field. $^{\rm 15-17}$

Figure 10 shows a schematic illustration of nickel deposits obtained at a cathodic potential of -1300 mV/SCE, without (Fig. 10a) and with a perpendicular-oriented magnetic field of 500 Oe (Fig. 10b). The deposit consists of microwires or filaments of length *l*. The short lines within the branches (Fig. 10b) are indicative of mag-



Figure 8. The nickel deposit obtained at a cathodic potential of -1300 mV/SCE from a Watt plating solution (NiSO₄·6 H₂O, 262.5 g/L; NiCl₂·6 H₂O, 45 g/L; H₃BO₃, 37.5 g/L) with the addition of coumarin, 0.060 g/L, with the imposed magnetic field (parallel orientation to the electrode surface) of 500 Oe.



Figure 9. Copper deposits obtained at a cathodic potential of -500 mV/SCE from the sulfate solution (0.2 M CuSO₄ in 0.5 M H₂SO₄): (a) without and (b) with a perpendicular-oriented magnetic field of 500 Oe.

netic domain walls that exist at zero or low-field values. At 500 Oe field the domain walls will be removed, and the resistance lowered up to a factor of 10.

In order to grow branched structures, it is necessary for the effective potential at the end of these branches to be the same as the applied one. However, if the branches are very resistive, this potential will be reduced to one smaller than that needed for electrodeposition of Ni. In the case of magnetic deposits, with or without an applied field, the effective potential at the end of the wires or filaments will be

$$U_{\rm eff} = U_{\rm c} - IR(B = 0,l)$$
^[3]

for zero field, and

$$U_{\rm eff} = U_{\rm c} - IR(B = B_0, l)$$
^[4]

for a field $B = B_0$, where U_{eff} and U_c are the effective and the applied cathodic potentials, respectively, *I* is the current of deposition, and *R* the resistance of the filament *l* under a field or field-free, and is field-dependent in the case of magnetic materials. In other words, these materials are magnetoresistive. This resistance for magnetic materials may be very different without or with applied



Figure 10. Schematic illustration of different nickel deposits obtained at -1300 mV/SCE; (a) without and (b) with a perpendicular-oriented magnetic field.

magnetic fields. In fact, it was shown that when nanocontacts are formed, the differences due to domain wall scattering when no field is applied, can be up to factors of $10.^{15-17}$

In the absence of a magnetic field, the resistance of nickel filaments is too large and the effective potential on their ends is much smaller than that needed for their further growth and branches, *i.e.*, for the electrodeposition of a very developed ABDS structure. That is why a rough nickel structure is formed, with very large nickel clusters, consisting of small nanosized nickel clusters. In the presence of a sufficiently large magnetic field (500 Oe, fields smaller than 300 Oe have a much smaller effect), the resistance of these filaments is much smaller, because the domain walls are erased and the effective potential at the end of the branches is large enough for the electrodeposition of an ABDS structure.

The effect of the resistance creating a potential drop is enhanced by the nonlinear behavior of the current, which increases abruptly when the potential is -1300 mV/SCE (Fig. 6). This causes the potential drop at the filaments ($U_d = IR$) to be much larger due to the increase of current. As mentioned earlier, during nickel electrodeposition in the absence of a magnetic field the current response was up to 40.0 mA, while during nickel electrodeposition in the presence of a magnetic field the current response was up to 80.0 mA. On the other hand, current responses during nickel electrodeposition at cathodic potentials of -1000 and -1200 mV/SCE (20.0 and 25.0 mA, respectively), without and with a perpendicularoriented magnetic field were the same, as expected. This is because compact electrodeposits are formed at these potentials, and not ones with a filament formation.

The case of Ni is specially interesting because of the following: (*i*) the minimum potential for deposition of Ni is $U_{\rm m} \approx -700 \text{ mV/}$ SCE, (*ii*) the critical potential for the drastic increase of the current is $U_{\rm crit} \approx -1300 \text{ mV/SCE}$, therefore, (*iii*) a 600 mV drop in potential due to resistance of the filaments is enough to stop the filamentary growth of Ni, while the application of the magnetic field can change this potential due to magnetoresistance.

As a possible cause for this unexpected change in the nickel morphology, it is also necessary to take into account the fact that at this potential the evolution of hydrogen was very intense. However, it can be assumed that the electrodeposition of a very developed 3D ABDS structure of nickel is a consequence of a complex phenomenon caused by the effect of magnetic field and the hydrogen evolution. Having to view the values of currents during nickel electrodepositions at the examened cathodic potentials, as well as the obtained nickel morphologies, it can also be said that the growth of this structure is controlled by convective phenomenon caused by the magnetic field and diffusion one.

Shannon *et al.*⁴ also showed that for a small applied magnetic field value, a change of nickel morphology is possible with both parallel and perpendicular oriented magnetic fields. This change is ascribed to the existence of a metastable hydrodynamic condition in the plating solution. This metastable condition is subjected to local disturbances via the applied magnetic fields and gas evolution. The magnetic field, in addition to acting on the paramagnetic Ni ions, influences the flow dynamics and stability of the evolved gas bubbles.⁴

This behavior of Ni is at variance with that of the Fe electrodeposits because, in the case of Fe, there is no drastic increase of the current (Fig. 6) at investigated cathodic potentials between -1000and -5000 mV/SCE. At all investigated potentials, an ABDS structure appeared. Figure 11 shows the iron deposit obtained in the presence of a perpendicular-oriented magnetic field. From this figure we can easily observe the very developed ABDS structure of iron. However, the removal of the magnetic field does not change the structure. The reason is that, in the case of iron, there is no drastic increase of the electrodeposition current, that is to say, the ohmic drop is not enough to stop the electrodeposition of the ABDS structure of iron. At this point, we should say that we have tried to reproduce the data of Ref. 7 without success, even when the pH of our solution is practically the same as in Ref. 7 (pH 3). Although the







b)

Figure 11. (a), (b) The iron deposit obtained at cathodic potential of -4 V/SCE from 225 g/L FeSO₄·7 H₂O in 120 g/L Na₂SO₄·10 H₂O, with perpendicular-orientated magnetic field of 500 Oe.

branches are more needle-like, the direction of the branches does not depend on the direction of the applied magnetic field. In our case, however, the branches grow in all directions. Perhaps the differences are due to the shape and configuration of the electrolytic cell. In any case, we do not understand why the dipolar interaction should result in a preferential orientation of the growth with respect to the direction of the field. Our experiments shown in Fig. 7 and 11, furthermore indicate that Ni and Fe branches grow in all directions.

To simulate our experiments, we argue that the obtained ABDS structure represents a phenomenon known as laplacian growth in the far from equilibrium limit, such as the case when nickel is electrodeposited at -1300 mV/SCE (Fig. 7). In this scenario, the diffusionlimited aggregation (DLA) model¹⁹ can be applied (see Ref. 20, Chap. 10, for illustrative exposition), and it is a characteristic of many phenomena, not just in electrochemistry,²¹ but also regarding crystallization and viscous fingering,²² cracks,²³ etc.

DLA Simulations with Resistive Ferromagnetic Wires

We use the two-dimensional diffusion-limited aggregation model $(DLA)^{19,21}$ in our simulation. The growth rule in the model is as follows. We start with an immobile seed at a certain point or on the surface. A particle (walker) is then launched from a random position far away and is allowed to diffuse. If it touches the seed, it is immobilized instantly and becomes part of the aggregate. We launch



Figure 12. The result of simulation of a cluster growth on the point center of aggregation (a) and on the surface (b) with $k_1 = 0$, $k_3 = 0$, without potential reducing in the vicinity of long branches; the same for $k_1 = 1$ on the point seed (c) and on the surface (d); the same for $k_1 = 5$ on the point seed (e) and on the surface (f).

similar particle-walkers one-by-one and each of them stops upon hitting the cluster or walks away and disappears if it goes beyond a certain distance. After launching a few hundred particles, a cluster with intricate branch structures results as shown, correspondingly, in Fig. 12a and b, for the growth on a surface.

However, to simulate the process of electrodeposition we had to modify the DLA model. In electrodeposition the particles have a velocity towards the aggregation surface or center due to the cathodic potential applied. We introduced the parameter $k_1 = |V_p|/|V_d|$ that represents the ratio between the modulus of velocity towards the aggregation center V_p and the modulus of the random diffusion velocity V_d . For each step we assumed that the velocity of the particle was the sum of the two velocities V_p and V_d , which increased the probability of the particle maintaining a velocity towards the center of the aggregation. The arrows in Fig. 12a and b show the direction of V_p . The calculations have been done for $k_1 = 1$ and 5, Fig. 12c and d, respectively, for the growth around a center and Fig. 12e and f for the growth on the surface.

In addition, we simulated the influence of the magnetic field applied in the direction perpendicular the plane of growth and parallel to the surface of aggregation. In this case, the particles have an acceleration proportional to a product of the velocity vector of **V** the particle and the vector of the magnetic field **B**, directed perpendicular to the vectors **V** and **B**. Thus, in each step of the simulation, we have the additional increment of the velocity $\Delta \mathbf{V}$ whose modulus is proportional to $|\mathbf{V} \times \mathbf{B}|$. The other parameter of the simulation represents the value of the magnetic field **B**. We assumed $|\Delta \mathbf{V}| = k_2 |V|$, where k_2 is proportional to the magnetic field, and *V* is the modulus of the velocity of the particle, as well as being the sum of the vectors \mathbf{V}_p and \mathbf{V}_d .



Figure 13. The result of the simulation of a cluster growth on the point seed with $k_1 = 1$ (a) and $k_1 = 5$ (b), $k_3 = 0$, with potential reducing in the vicinity of long branches; the same on the surface for $k_1 = 1$ (c) and $k_1 = 5$ (d).

When we take ΔV into account, the direction with the greatest probability will shift clockwise from the direction toward the aggregation center. Finally, we simulated the resistive ferromagnetic wires. In this case, the potential will not be uniform, but will be reduced in the vicinity of the long branches of the growing structure. We assume that the probability of the particle to maintain a velocity toward the long branch is reduced by $k_3 l/r$, where l is the length of the branch, r is the radius of launching, and k_3 is a coefficient that represents the material properties. The longer the branch the higher is the reduction of the potential. Therefore, it is the potentialreducing effect that results in the more compact clusters. In the Fig. 13a and b, the cluster structures for $k_1 = 1$ and 5 are shown then the effect is taken into account. We attain the same result for growth on the surface (Fig. 13c and d), where the structures are more compact and the clusters have a smoother surface compared to the structures in Fig. 12 with the same parameter k_1 .

The calculations of the magnetic field parallel to the surface and perpendicular to the plane of growth are shown in Fig. 14. The resulting structures for the parameter $k_2 = 0.83$ are shown for growth at the center point. The branches of the structure are curved clockwise, and the structures are rougher and less dense. Figure 14a shows the result for $k_1 = 1$ and Fig. 14b for $k_1 = 5$, while the potential reducing effect was also taken into account. The same calculation was performed for the plane surface. The branches decline to the left, and the cluster structures become rougher and less dense with the increasing of the product modulus $|\mathbf{V} \times \mathbf{B}|$ or $k_1 \cdot k_3$ in the simulations. For big enough values of $k_1 \cdot k_3$ we have the separate long branches.

Figure 15 shows the different kinds of structures resulting with different values of k_1 and k_3 , without taking into account the potential-reducing effect in the vicinity of the long branches. Our calculations show that if the potential-reducing effect is less due to the magnetic field toward the aggregation surface, the structure is less compact and has long branches as it shown in Fig. 12f. At this point it should be mentioned that simulations made taking into account the drop of potential due to the resistance of the wires may be comparable to another proposal²⁴ based on the idea of screening. If there is a perfect screening of the potential, one should have a compact structure since that implies that the cathodic potential drops at the surface of the deposits. If, however, screening is not complete and the electric field penetrates and drops inside the deposits, then this points to an $U_{\rm eff}$ that is reduced from the $U_{\rm c}$ due to de potential drop in the deposits. One then obtains similar results to those expressed in Eq. 3 and shown in our simulations. There is a problem in this treatment, and this is that the effect should be independent of the

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Figure 14. The result of the simulation of a cluster growth on the point seed with $k_1 = 1$ (a) and $k_1 = 5$ (b), $k_3 = 0.83$, with potential reducing in the vicinity of long branches; the same on the surface for $k_1 = 1$ (c) and $k_1 = 5$ (d).

applied magnetic field. The reason is that the screening is due just to the metallic character or not of the deposits. In our experiments the applied magnetic field clearly plays a role.

Conclusions

The effect of a magnetic field, with both perpendicular and parallel orientation, on the morphology of nickel deposits from a Watt solution in the presence of coumarin was examined.



Figure 15. The result of the simulation of a cluster growth on the surface without potential reducing in the vicinity of long branches with $k_1 = 5$ and $k_3 = 1.1$ (a), 1.5 (b), 2.0 (c), and $k_1 = 1$ and $k_3 = 2.0$ (d), 10 (e), 20 (f).

At a cathodic potential of -1000 mV/SCE, there was no difference between nickel deposits obtained without and with a paralleloriented magnetic field. Both surfaces were relatively smooth, which is ascribed to the good leveling characteristics of coumarin.

At a cathodic potential of -1200 mV/SCE, the nickel deposit obtained with a parallel-oriented magnetic field had a more uniform structure than that obtained without and with a perpendicularoriented magnetic field. The obtained result was in accordance with predictions of MHD theory.

At a cathodic potential of -1300 mV/SCE, a great change in the morphology of the nickel deposit is obtained for an orientation of the magnetic field for which the expected MHD effect is zero. Furthermore, at this potential a large enhancement of the deposition current takes places that plays an important role in the developed structure. The nickel deposit obtained in the presence of a perpendicular-oriented magnetic field was a very developed 3D ABDS structure, with thin branches made of beads or clusters as in a rosary. On the other hand, the nickel deposit obtained without the presence of a magnetic field was a very rough and clustered structure. Based on the fact that copper (paramagnetic) deposits always exhibited a dendritic structure, we essentially ascribed the difference in morphologies of these nickel deposits to the influence of the magnetic field on magnetic properties of nickel. The explanation is given in terms of the resistance of the branched structure (i.e., filaments of deposits) due to magnetic domain wall scattering. Finally, for Fe at -4000 mV/SCE, we have obtained ABDS structures, but the branches of this deposit are oriented in all directions and are not much affected by the direction of the applied field.

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