J. Serb. Chem. Soc. 71 (10) 1083–1089 (2006)
JSCS–3502

UDC 537.612:669.1+541.6:66.087
Original scientific paper

The effect of perpendicularly oriented magnetic field on the formation of very disperse iron structures

NEBOJŠA D. NIKOLIĆ[#]

ICTM – Department of Electrochemistry, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia (e-mail: nnikolic@tmf.bg.ac.yu)

(Received 17 November 2005, revised 2. March 2006)

Abstract: Iron deposits obtained without and with a perpendicularly oriented magnetic field were examined by scanning electron microscopy (SEM). It was found that the iron deposit obtained under a perpendicularly oriented magnetic field had a more highly branched structure than the iron deposit obtained without an applied magnetic field. Comparing the morphologies of these deposits with those of copper deposits, the branching of the iron deposits can essentially be ascribed to the effect of the magnetic field on the magnetic properties of iron.

Keywords: electrodeposition, magnetic field, branching, iron.

INTRODUCTION

For a long time, it was believed that a prependicularly oriented magnetic field has no effect on electrochemical processes and the morphologies of metal deposits obtained by electrodeposition. This was based on the fact that the effect of magnetic fields on electrochemical processes is associated with the effect of the Lorentz force.[1,2] During electrolysis, this force exerted by an electromagnetic field acts on the migration of ions and induces convective flow of the electrolyte close to the electrode surface. This effect on the electrodeposition process is known as the magnetohydrodynamic (MHD) effect. When a magnetic field is oriented perpendicular to the electrode surface, the Lorenz force is zero and, thus, changes in the morphologies of metal deposits are not to be expected.

Meanwhile, in the last few years, it was found that magnetic fields with a perpendicular orientation to the electrode surface can realize some effects on electrochemical processes and the morphologies of metal deposits obtained by electrodeposition.[3–6]

The differences between the morphologies of metal deposits obtained under perpendicularly applied magnetic fields and those obtained without applied mag-

---

[#] Serbian Chemical Society active member.

doi: 10.2298/JSC0610083N

netic fields has hitherto been largely observed during the electrodeposition of ferromagnetic metals, such as iron and nickel.[4–6] There is not any unique explanation for these unexpected changes of the morphologies of metal deposits. For example, according to Boda *et al.,*[4] the change of the macroscopic morphology of iron from circular in zero field to rectangular in the presence of a perpendicularly oriented magnetic field is associated with a minimization of the magnetic dipolar energy of the growing branches.

The change of the morphology of nickel deposits electrodeposited from a Watt solution containing coumarin under a perpendicularly oriented magnetic field of 500 Oe was associated with the magnetoresistance effect, which is one of the characteristics of magnetic materials.[6] The nickel deposit obtained under a perpendicularly oriented magnetic field had a very developed 3D dendritic structure completely different from the nickel deposit obtained without an applied magnetic field, which had a rough structure with clearly visible nickel clusters. It was shown that the presence of coumarin in the Watt plating solution did not cotribute to the change of the nickel deposit under the perpendicularly oriented magnetic field.[7] The explanation for this change of morphology of nickel deposits was also based on the comparison with copper deposits which do not have magnetic properties.[5–7] This explanation was based on the fact that copper deposits obtained without and with perpendicularly oriented magnetic fields had a very developed dendritic structure. A detailed analysis of the dendritic character of these copper deposits because of a fixation that they could be different was not performed.

Meanwhile, due to an idea obtained by inspection of new results of Rabah *et al.*[8] about a possible effect of perpendicularly oriented magnetic fields on paramagnetic species, a new analysis of the copper deposits obtained without and with a perpendicularly oriented magnetic fields was performed. It can be noticed by careful analysis of these copper deposits that there is a difference in the degree of branching between the copper deposits obtained without and with a perpendicularly oriented magnetic field of 500 Oe (see Fig. 2 in Ref.[7]). The copper deposit obtained with the perpendicularly oriented magnetic field was more disperse, *i.e.,* had a more highly branched structure than the one obtained without an applied magnetic field.[7]

Hence, on the basis of the previous analyses of the morphologies of nickel and copper deposits,[5–7] it follows that a magnetic field with perpendicular orientation to the electrode suface can effect the morphologies of both magnetic (nickel) and non-magnetic (copper) deposits. The effect was larger in the case of the electrodeposition of a magnetic metal (the change of the morphology of nickel from a very rough with a clearly visible clustered structure obtained without an applied magnetic field to a very developed dendritic structure obtained under a perpendicularly oriented magnetic field) than in the case of the electrodeposition of a non-magnetic metal (the copper deposit obtained under a perpendicularly oriented magnetic field had a more highly branched structure with respect to that obtained without an applied magnetic field).

However, it is very clear from the former consideration that the magnetic character of some metals is not the only factor which leads to a change of the morphology of metals deposited under a perpendicularly oriented magnetic field. It can be assumed that the existence of magnetic properties of some metals (in this case, nickel) only intensifies the change of the morphologies of metals deposited under a perpendicularly oriented magnetic field.

It order to confirm this assumption, it was necessary to compare the morphology of some metal from the iron group obtained without an imposed magnetic field in a very developed form (as was the case with copper) with the morphology of the same metal obtained under the same working conditions but under a perpendicularly applied magnetic field.

For this reason, iron deposits obtained without and with a perpendicularly oriented magnetic field under the same working conditions were examined by scanning electron microscopy (SEM).

EXPERIMENTAL

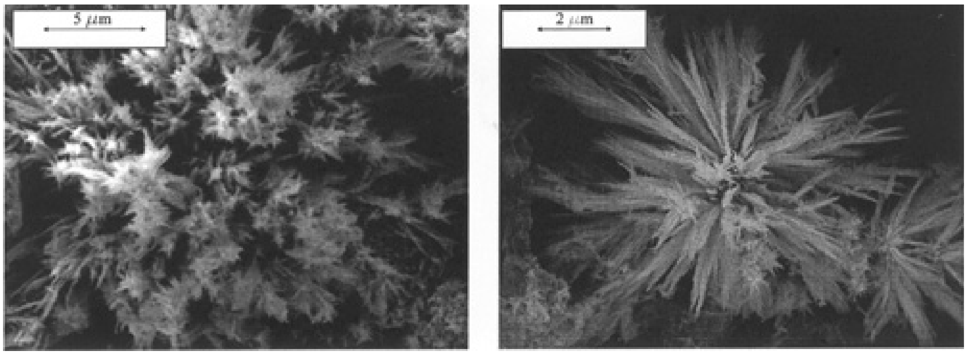
Iron was electrodeposited from a solution containing 225 g/l $FeSO_4 \cdot 7H_2O$ in 120 g/l $Na_2SO_4 \cdot 10H_2O$. The pH of the solution was 3. Iron was electrodeposited at a voltage of 5 V at room temperature. The electrodepositions were performed in photolithographically patterned thin film microstructures with a micrometer gap which was closed to form a nanocontact.[5–7] The anode was a platinum wire which was situated to be perpendicular with respect to cathode surface. The distance between the top of the platinum anode and the cathode was approximately 5 mm. The quantity of electricity was 16 mA h cm^{-2}. The deposition was performed by use of a bipotentiostat – model AFCBP 1, Pine Instruments Company. The electrochemical cell was plunged into an uniform magnetic field of 500 Oe, which was perpendicular to the electrode surface. The magnetic system employed was a model M – 50 MMR Technologies, Inc. The iron deposits were examined by scanning electron microscopy – model Philips SEM-FEG – XL 30.

RESULTS AND DISCUSSION

SEM Microphotographs showing iron deposits obtained at a voltage of 5 V without an applied magnetic field are shown in Fig. 1, from which the very developed spongy structure of this deposit (Fig. 1a), with flower – like iron elements (Fig. 1b) can be observed.

The iron deposit obtained under the same working conditions, but under a perpendicularly oriented magnetic field of 500 Oe, is shown in Fig. 2, from which can be observed that the iron deposit in this case had a cotton-like structure, with very small iron elements grouped in small aggregates (Fig. 2a). It can be estimated from Fig. 2b that the diameter of the needles, from which these iron aggregates were made, approached nano-size dimensions.

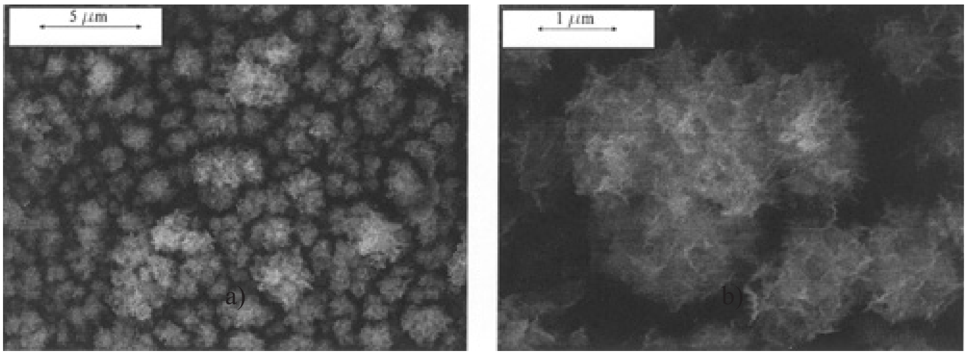
It can be concluded by comparison of the morphologies of the iron deposits shown in Figs. 1 and 2 that the presence of a magnetic field with perpendicular ori-



a) b)

Fig. 1. The iron deposit obtained at 5 V without an applied magnetic field.

entation led to an increase in the dispersity of the iron deposits. The iron elements which made very developed iron structures were much smaller for the iron deposit obtained with the perpendicularly oriented magnetic field than for the one obtained without an applied magnetic field.



a) b)

Fig. 2. The iron deposit obtained at 5 V with a perpendicularly oriented magnetic field of 500 Oe.

In order to explain this change in the morphology of the iron deposit under the perpendicularly oriented magnetic field, the concept of "effective overpotential", which was recently proposed for copper electrodeposition at high overpotentials when the hydrogen evolution was very intensive, will be applied.[9] According to this concept, at overpotentials at which the hydrogen evolution is competitive with metal electrodeposition, the hydrogen codeposition causes intensive stirring of the electrolyte and an increase of the limiting diffusion current density. As a consequence of this, at a specified overpotential, a deposit like that formed at the some lower overpotential, at which hydrogen codeposition does not occur, is obtained. This overpotential was denoted as "effective overpotential" of the electrodeposition process. However, this effect was caused by a change of the hydrodynamic conditions in the near-electrode layer generated by the evolving hydrogen.

This concept can be applied in other cases where there is a change of the hydrodynamic conditions in the plating solution. These changes can be caused by the effect of magnetic fields (MHD effect), ultrasound and stirring of the solutions by a rotating disc electrode (RDE). It is necessary to note that the concept of "effective overpotential" is associated with a change of the hydrodynamic conditions in plating solutions, and as opposed to the "magnetoresistance effect", it does not depend on the magnetic character of the electrodeposited metal.

The concept of "effective overpotential" when applied in this case of iron electrodeposition means that the overpotential at which the electrodeposition occured under the perpendicularly oriented magnetic field was effectively larger than the specified one. This was concluded on the basis of the more disperse structure of the iron deposit obtained under the perpendicularly oriented magnetic field with respect to the one obtained without an applied magnetic field. From the point of view of a change of the hydrodynamic conditions, this means that the change of hydrodynamic conditions caused by the perpendicularly oriented magnetic field was in the direction of a decrease of the limiting diffusion current density. It is known[3] that a uniform magnetic field oriented orthogonal to the microelectrode surface in order to induce rotational flow, causes either an increase or a decrease in the voltammetric limiting currents (– 37 to + 119 %) depending solely on the size of the electrode. For inlaid disc electrodes with radii less than ≈ 100 μm, the magnetic field driven flow results in a decrease in the transport limited current, a consequence of rotational solution flow adjacent to the surface preventing gravity driven natural convection. Some similar local effect on the deposition on a small scale profile can probably be expected in the case of deposition on the tips of iron dendrites, like the change of mass transfer conditions described by Bockris *et al.*[10,11] This can also explain the effect of the magnetic field on the morphologies of copper deposits.

However, electrodeposition of the more highly branched iron structure under a perpendicularly oriented magnetic field is associated with some additional energy caused by the imposed magnetic field with perpendicular orientation to the electrode surface. The morphology of the iron deposit obtained under a perpendicularly oriented magnetic field is, at the macro level, similar to that obtained at a higher overpotential (or voltage) without an applied magnetic field.

Also, it is necessary to note that the electrodeposition of iron, similar to nickel electrodeposition at a cathodic potential of – 1300 $\mathrm{mV_{SCE}}$, was accompanied by intensive evolution of hydrogen. For this reason, the effect of hydrogen evolution on the increase of dispersity of the iron deposit under a perpendicularly oriented magnetic field should not be neglected. It can be proposed that the increase of the dispersity of an iron deposit obtained under a perpendicularly oriented magnetic field with respect to an iron deposit obtained without an applied magnetic field is the consequence of a complex phenomenon caused by the effect of the magnetic field and hydrogen evolution, *i.e.,* the growth of the iron structure under a perpendicularly applied magnetic field is controlled by both a convective phenomenon caused by the magnetic field and a diffusion one.

On the other hand, it is necessary to take into consideration the fact that the electrodeposition of iron, similar to the electrodeposition of nickel, is performed from neutral solutions[12] and that there is a possible effect of local changes of the pH in the vicinity of the electrode due to the codeposition of the corresponding hydroxides with the electrodeposited metals. In the case of electrodeposition of metals from acid solutions (which is the case of copper from a sulphate solution), there is no effect of local changes of the pH on the morphology of the electrodeposited metals because hydrogen evolution causes only a small change of the pH in the vicinity of the electrode. Hence, the observed difference between the morphologies of copper deposits obtained without and with a perpendicularly oriented magnetic field cannot be ascribed to a local pH effect. On the other hand, in the case of iron electrodeposition, a possible effect of a local change of pH on the morphology of iron deposits can be expected during the electrodeposition both in the presence and absence of a perpendicularly oriented magnetic field and, thus, it can be assumed that this effect did not have a determinant effect on the change of the morphology of the iron deposit under the perpendicularly oriented magnetic field.

However, the change of the morphology of the iron deposit under the perpendicularly oriented magnetic field is associated with the effect of imposed magnetic fields and the concept of "effective overpotential" can represent one way of successfully explaining this change of the morphology of the iron deposit. The increase of the dispersity of metal deposits under the perpendicularly oriented magnetic field was larger in the case of iron (a ferromagnetic metal) than in the case of copper (a paramagnetic metal). This additional increase of the dispersity of the iron deposit can be ascribed to the effect of the perpendicularly oriented magnetic field on the magnetic character of iron. The change of the morphology of the iron deposit under the perpendicularly oriented magnetic field was less marked than in the case nickel, but it is necessary to note that the aim of this study was to obtain very developed dendritic structures of both, ferromagnetic and paramagnetic metals, without an applied magnetic field, and then, to compare the structures of these deposits after electrodeposition under an imposed perpendicularly oriented magnetic field. This was done in order to establish an eventual contibution of the magnetic character of an iron group metal to the increase of dispersity of deposits obtained under perpendicularly oriented magnetic fields.

This paper represents a part of investigations within the scope of the development of magnetic structures with very large magnetoresistance effects, which could potentially find application for magnetic reading heads.

Acknowledgement: The work was supported by the Ministry of Science and Environmental Protection of the Republic of Serbia under the research project: "Deposition of ultrafine powders of metals and alloys and nanostructured surfaces by electrochemical techniques" (No. 142032).

ИЗВОД

УТИЦАЈ ВЕРТИКАЛНО ОРИЈЕНТИСАНОГ МАГНЕТНОГ ПОЉА НА ФОРМИРАЊЕ ВЕОМА ДИСПЕРЗНИХ СТРУКТУРА ГВОЖЂА

НЕБОЈША Д. НИКОЛИЋ

ИХТМ – Центар за електрохемију, Његошева 12, 11000 Београд, Србија

Техником скенирајуће електронске микроскопије (SEM) су били испитани талози гвожђа добијени без примењеног, као и под вертикално оријентисаним магнетним пољем. Показано је да талог гвожђа добијен под вертикално оријентисаним магнетним пољем био разгранатије структуре од талога гвожђа добијеног без примењеног магнетног поља. Гранање талога гвожђа под вертикално оријентисаним магнетним пољем је првенствено приписано утицају магнетног поља на магнетне особине гвожђа.

(Примљено 17. новембра 2005, ревидирано 2. марта 2006)

REFERENCES

1. J. A. Shercliff, *A Textbook of Magnetohydrodynamics,* Pergamon Press, Oxford, 1965
2. O. Devos, A. Olivier, J. – P. Shopart, O. Aaboubi, G. Maurin, *J. Electrochem. Soc.* **145** (1998) 401
3. K. M. Grant, J. W. Hemmert, H. S. White, *J. Electroanal Chem.* **500** (2001) 95
4. S. Bodea, L. Vignon, R. Ballou, P. Malho, *Phys. Rev. Lett.* **83** (1999) 2612
5. N. D. Nikolic, Hai Wang, Hao Cheng, C. A. Guerrero, N. Garcia, *J. Magn. Magn. Mater.* **272**–**276** (2004) 2436
6. N. D. Nikolić, Hai Wang, Hao Cheng, C. Guerrero, E. V. Ponizovskaya, Genhua Pan, N. Garcia, *J. Electrochem. Soc.* **151** (2004) C577
7. N. D. Nikolić, *J. Serb. Chem. Soc.* **70** (2005) 1213
8. K. L. Rabah, J. – P. Chopart, H. Schloerb, S. Saulnier, O. Aaboubi, M. Ulemann, D. Elmi, J. Amblard, *J. Electroanal. Chem.* **571** (2004) 85
9. N. D. Nikolić, K. I. Popov, Lj. J. Pavlović, M. G. Pavlović, *J. Electroanal. Chem.* **588** (2006) 88
10. A. R. Despić, J. W. Diggle, J. O'M. Bockris, *J. Electrochem. Soc.* **115** (1968) 507
11. J. W. Diggle, A. R. Despić, J. O'M. Bockris, *J. Electrochem. Soc.* **116** (1969) 1503
12. S. Djordjević, M. Maksimović, M. Pavlović, K. Popov, *Galvanotehnika*, Tehnička knjiga, Beograd, 1997, p. 11 (in Serbian).