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Note

NOTE

Some aspects of nickel electrodeposition in the presence of a magnetic field

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Abstract: Nickel deposits obtained from a Watt solution both without and with a perpendicularly oriented magnetic field were examined by scanning electron microscopy (SEM). The nickel deposit obtained without an imposed magnetic field was very rough, with a clearly visible clustered structure. The nickel deposit obtained under a perpendicularly oriented magnetic field has a very developed dendritic structure, which can be denoted as arboreous – bead dendritic structure. The observed difference is essentially ascribed to the effect of a magnetic field on the magnetic properties of nickel.

Keywords: electrodeposition, magnetic field, nickel, copper.

The effect of an applied magnetic field on metal electrodeposition has been the 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. These effects on electrolytic processes and metal morphologies are usually ascribed to the Lorentz force.[5] During electrolysis, this force acts on the migration of ions and induces a convective flow of electrolyte close to the electrode surface. This effect on the electrodeposition process is known as the magnetohydrodynamic (MHD) effect.

The largest effect of the Lorentz force and, consequently, the largest effect on convective mass transport of the electrolyte, can be realized when the magnetic field is applied parallel to the electrode surface.[9] This expectation is generally observed in investigations which have been reported in the literature.[10–14]

On the other hand, when the 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] Meanwhile, there have been papers which report about possible large effects of a magnetic filed with perpendicular orientation to the electrode surface on the

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electrochemical process and the morphology of a metal deposit obtained by electrodeposition.[7,9]

The big difference between the morphologies of nickel obtained without, and with a perpendicular oriented magnetic field was also observed by Nikolić *et al.*[15,16] The nickel deposit obtained without a magnetic field was very rough, with a clearly visible clustered nickel structure. On the other hand, the nickel deposit obtained under a perpendicularly oriented magnetic field was a very developed dendritic structure, which was denoted as an arboreous-bean-dendritic structure (ABDS). These nickel deposits were obtained from a Watt solution with the addition of coumarin, at a cathodic potential of –1300 mV/SCE. However, when the expected magnetohydrodynamic (MHD) effect was zero, the obtained nickel morphologies were very different.

In order to establish whether the presence of coumarin in a Watt solution contributed to this unexpected change of the morphologies of the nickel, it was necessary to examine nickel deposits obtained from a pure Watt solution. Hence, the aim of this paper was to establish, whether the presence of coumarin in a Watt plating solution contributed to the unexpected change in the nickel morphology under a perpendicularly oriented magnetic field. These nickel deposits were compared with the corresponding copper deposits.

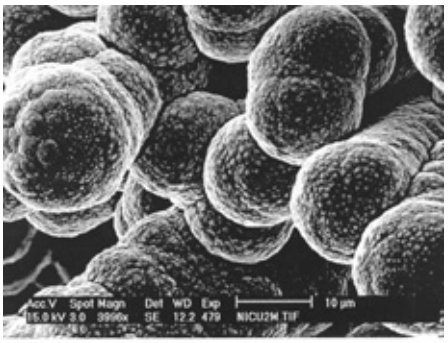
Nickel was electodeposited from a pure Watt solution of the following composition: $NiSO_4 \cdot 6\ H_2O$ – 262.5 g/l, $NiCl_2 \cdot 6\ H_2O$ – 45 g/l, H_3BO_3 – 37.5 g/l. The electrodepositions were performed potentiostatically, at room temperature, at a cathodic potential of –1300 mV/SCE (with respect to a saturated calomel reference electrode). The counter electrode was a nickel plate parallel to the cathode.

Copper was electrodeposited from 0.2 M $CuSO_4$ in 0.5 M H_2SO_4, at room temperature, at a cathodic potential of –500 mV/SCE. The counter electrode was a pure copper.

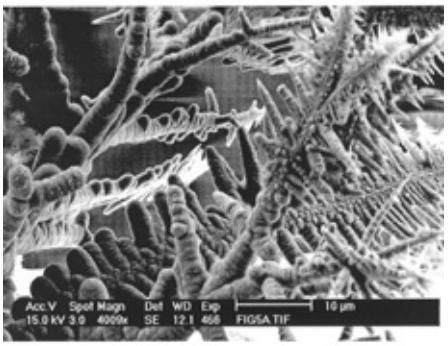
The electrodepositions were performed in photolithographically patterned thin film microstructures with a micrometer gap that was closed to form a nanocontact.[15,16] The cathodes, as well as the position of the electrodes in the electrochemical cell were the same in both cases.

The quantities of electricity were 16 mAh cm^{-2}. The deposition was performed by use of bipotentiostat – model AFCBP 1, Pine Instruments Company. The electrochemical cell was plunged in a uniform magnetic field of 500 Oe, which was perpendicular to the electrode surface. The magnetic system used was a model M – 50 MMR Technologies, Inc. The nickel and copper deposits were examined by scanning electron microscopy – model Philips SEM-FEG – XL 30. It should be pointed out that except for the solution used for nickel electrodeposition, the other experimental conditions were same as in Refs. 15 and 16.

The nickel deposits obtained from a pure Watt solution, at a cathodic potential of –1300 mV/SCE without and with a perpendicularly oriented magnetic field of 500 Oe are shown in Fig. 1a and b, respectively. It can be seen from Fig. 1a that the

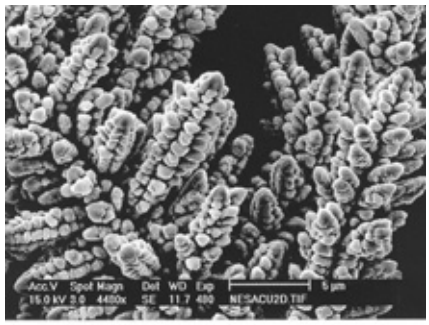


a)

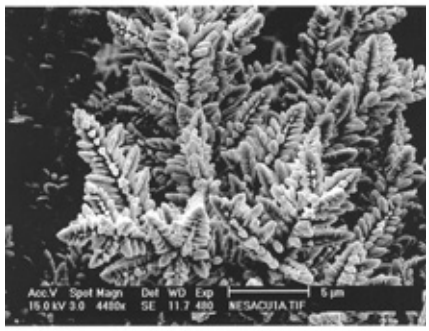


b)

Fig. 1. Nickel deposits obtained at a cathodic potential of –1300 mV/SCE from Watt plating solution ($NiSO_4 \cdot 6\ H_2O$ – 262.5 g/l, $NiCl_2 \cdot 6\ H_2O$ – 45 g/l, H_3BO_3 – 37.5 g/l): a) without, b) with imposed magnetic field (perpendicular orientation to the electrode surface) of 500 Oe.



a)



b)

Fig. 2. Copper deposits obtained at a cathodic potential of –500 mV/SCE from a sulfate solution (0.2 M $CuSO_4$ in 0.5 M H_2SO_4): a) without, and b) with a perpendicularly oriented magnetic field of 500 Oe.

nickel deposit obtained without an imposed magnetic field was very rough, with a clearly visible clustered structure. On the other hand, the nickel deposit obtained under a perpendicularly oriented magnetic field had a very developed dendritic structure, which can be denoted as arboreous – bead dendritic structure (or ABDS).

Hence, the presence of coumarin in the Watt solution did not contribute to the unexpected change of the nickel morphology under a perpendicularly oriented magnetic field. The explanation for this change of the nickel morphology should, therefore, be looked for in some other phenomena. The reason for this change of nickel morphology probably lies in the fact that nickel is a ferromagnetic metal. The change of morphology is not observed in the case of copper, which is a paramagnetic metal.

Figure 2 shows copper deposits obtained without and with a perpendicularly oriented magnetic field of 500 Oe. It can be seen from Fig. 2 that both copper deposits had a very developed arboreous bead dendritic structure (ABDS).

Hence, the cause for the change of the nickel morphology during electrodeposition with an imposed perpendicularly oriented magnetic field lies in the magnetic

characteristics of nickel. The unexpected change of the nickel morphology is probably the consequence of the effect of the magnetic field on the magnetic properties of nickel. The explanation can be given in terms of the resistance of the branched structure (*i.e.*, filaments of the deposits) due to domain wall scattering.[15,16] In the case of deposits with magnetic properties (as nickel), the resistance of these filaments depends on whether or not a magnetic field is applied. In order to grow a branched structure, it is necessary that the effective potential at the end of these branches is the same as the applied one. In the absence of a magnetic field, the resistance of the nickel filaments is too large, and the effective potential at their ends is much smaller than that needed for their further growth and branches, *i.e.*, for the electrodeposition of a very developed arboreous bead-dendritic structure. In the presence of a magnetic field, 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 arboreous bead-dendritic structure.[15,16]

Of course, as a possible cause for this unexpected change in the nickel morphology, it is also necessary to take into account the fact that at the employed potential the evolution of hydrogen was very intense. However, it can be assumed that the electrodeposition of a very developed ABDS nickel structure is the consequence of complex phenomena caused by the effect of the magnetic field and hydrogen evolution. Shannon *et al.*[4] also showed that when a low strength magnetic field is applied, a change of the nickel morphology is possible with both parallelly and perpendicularly oriented magnetic fields. This change is ascribed to the existence of a metastable hydrodynamic condition in the plating solution. This metastable conditions 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]

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ИЗВОД

НЕКИ АСПЕКТИ ТАЛОЖЕЊА НИКЛА У ПРИСУСТВУ МАГНЕТНОГ ПОЉА

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У овом раду, талози никла добијени из Ватовог раствора су испитани техником скенирајуће електронске микроскопије. Таложење је било изведено без присуства магнетног поља, као и у присуству вертикално оријентисаног магнетног поља. Талог никла добијен без присуства магнетног поља је био веома храпав, са јасно видљивим кластерима никла. Талог никла добијен под вертикално оријентисаним магнетним пољем је био веома развијене дендритичне структуре. Посматрана разлика између ових морфологија никла је првенствено приписана утицају магнетног поља на магнетне особине никла.

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