MAGNETIC FIELD EFFECTS ON Zn – Ni ELECTRODEPOSITION

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Introduction. The electrodeposition of Zn-Ni is mostly studied for its anticorrosion properties. For weak nickel contents, electrochemically obtained phases do not correspond to the thermodynamic diagram phases and change according to the thickness of the deposit [1, 2]. As part of studies on the magnetic field effects on alloy electroplating, these compounds are interesting to be studied because of their absence of magnetic features, contrarily to magnetic alloys such as Fe-Ni or Co-Fe.

1. Experimental. The used electrolytic solution contains H_3BO_3: 40 gL^{-1}, $ZnSO_4$, $7H_2O$: 172.5 gL^{-1}, $NiSO_4$, $7H_2O$: 56 gL^{-1}. After complete dissolution of the salts, the pH is adjusted to the desired value (2.5 or 3.5).

A conventional three-electrode cell has been used with a saturated mercury sulfate electrode (SSE) as reference and a $\oslash = 1$ cm working electrode. Classical electrochemical experiments were conducted by means of a Tacussel potentiostat-galvanostat PGZ 301. For the experiments under moderate magnetic fields, the cell was put into the gap of an electromagnet (Drusch EAM 20G) that imposed a uniform magnetic field, B. The latter was kept parallel to the upward horizontal electrode surface.

XRD experiments were performed with a BRUKER D8 diffractometer equipped with a copper anticathode ($\lambda_{\mathrm{CuK}\alpha} = 54056$ Å). SEM micrographies and quantitative analyses of the deposits were obtained by means of a JEOL JSM 6460LA miscroscope coupled with a EDS JEL 1300 microprobe.

2. Electrochemical investigations. Current-potential curves have been recorded for magnetic field amplitudes up to 1 T. No significant effects on the current intensity can be noticed for applied cathodic potentials up to – 2.5 V/SSE as a magnetic field is superimposed (Fig. 1). The modifications that can be seen

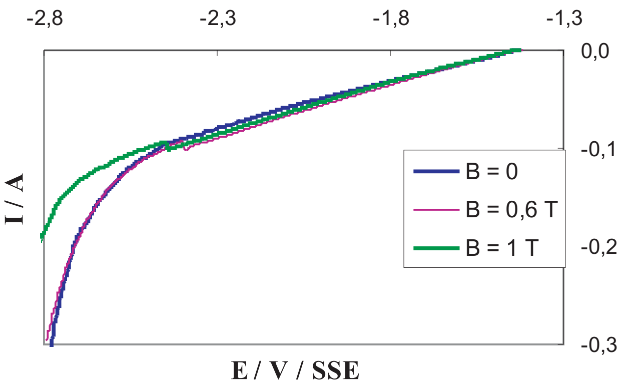


Fig. 1. Typical current-potential curve for different magnetic fields.

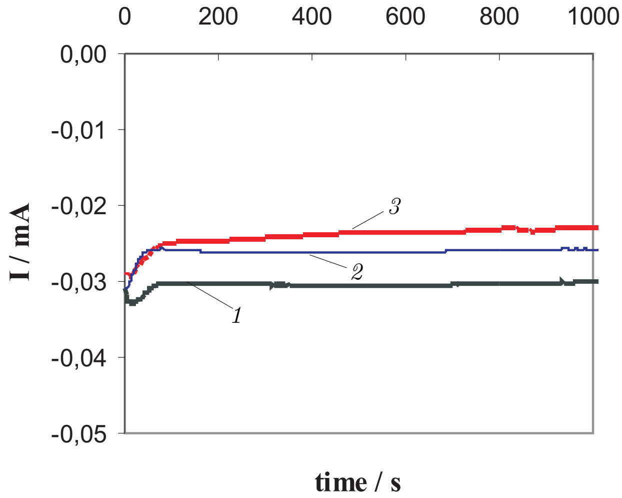
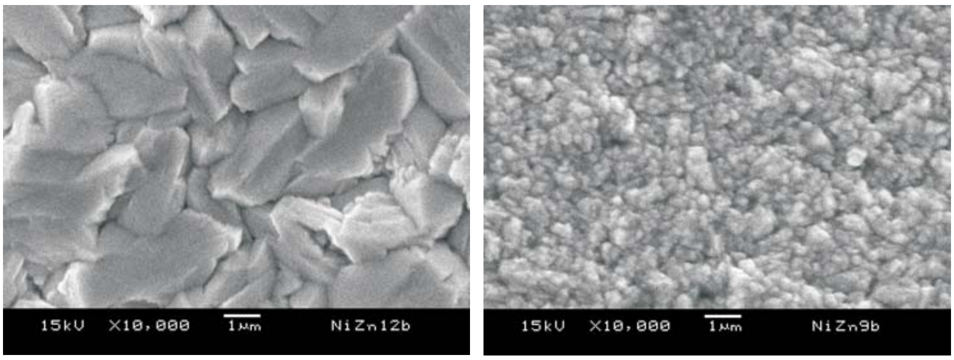


Fig. 2. Chronoamperometric curves for electrodeposition of Zn-Ni. Applied potential = −1.75 V/SSE. Line *1* pH = 3.5; $B = 0.6$ T; line *2* pH = 3.5; $B = 0$; line *3* pH = 2.5; $B = 0$.

for some curves and higher cathodic potentials on Fig. 1 are not correlated with magnetohydrodynamical convection, but with hydrogen evolution that is highly irreproducible under these conditions.

Alloys have been electrodeposited by a potentiostatic method for two different applied potentials (−1.75 and −2.0 V/SSE). The reported current transients (chronoamperometric curves) for these two applied potential values show that the final currents are not depending neither on the magnetic field superimposed nor on pH. When dendritic evolution, that can arise for long deposition times, is avoided, an average current density value for each potential can be calculated as 35 A/m^2 at −1.75 V/SSE and 75 A/m^2 at −2 V/SSE. These results are in accordance with the stationary results and point out the weakness of the MHD convection for these experimental conditions.

3. Physical investigations. By means of an EDS microprobe, composition of the alloys that have been obtained for various magnetic fields (up to 0.9 T) and for the two pH and the two applied potentials quoted above, have been determined. For all conditions, the atomic ratio of nickel can be regarded as constant and equal to 5%. On the other hand, SEM micrographies (Fig. 3) highlight



(1) (2)

Fig. 3. SEM micrographies of Zn-Ni alloys deposited at −1.75 V/SSE. pH = 3.5. Magnification × 10 000 (white line represents 1 μm) Photo 1: $B = 0$. Photo 2: $B = 0.6$ T.

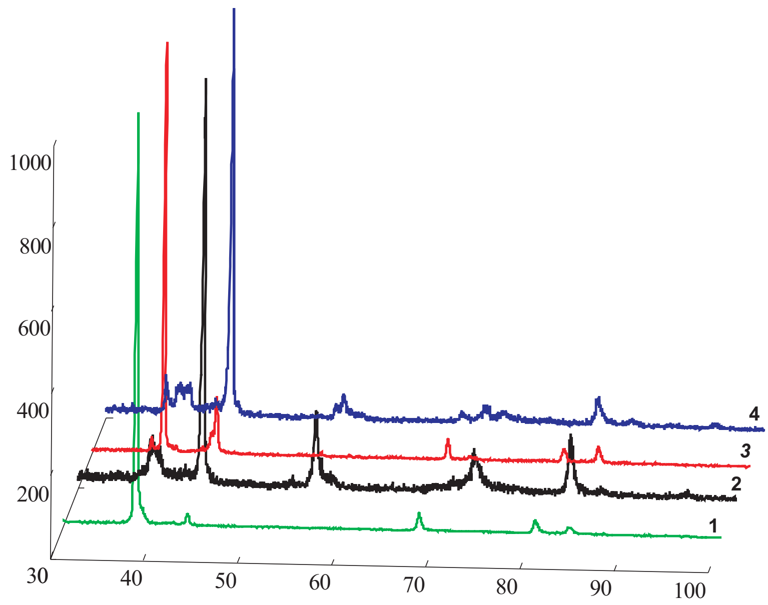


Fig. 4. XRD diagrams for Zn-Ni alloys. Electrodeposition has been realized at −1.75 V/SSE. The intensities have been normalized. Curve 1 pH = 3.5; $B = 0$. Curve 2 pH = 3.5; $B = 0.6$ T. Curve 3 pH = 2.5; $B = 0$. Curve 4 pH = 2.5; $B = 0.9$ T.

a very effective effect of the magnetic field on roughness of the electrodeposited alloys. As has been well established in many cases [3], the magnetic field acts as an inhibitor and reduces the size of pits.

But the most significant phenomenon that has to be noticed is highlighted by XRD diagrams. In Fig. 4 four diagrams are reported which are representative of the magnetic field effects.

In all deposits, the Zn (JCPDS (04-0831) data), Ni_5Zn_{21} (JCPDS (06-0653) data) and ZnNi (JCPDS (06-0672) data) phases can be identified, but the intensities of the peaks are very different depending on the superimposed magnetic field. For no magnetic field B, Ni_5Zn_{21} (321) peak has the highest amplitude, while (101) peak for the Zn phase is always predominant for the highest B amplitudes.

A typical widening can be noticed for many peaks highlighting the size spit decrease as has been observed by SEM micrographies. To get more relevant informations on the texture and preferred orientation, we have used the Muresan method [4] by calculating the texture coefficient $T_c(hkl)$:

$$T_c(hkl) = I(hkl) \times \Sigma I_0(hkl)/I_0(hkl) \times \Sigma I(hkl),$$

where $I(hkl)$ is the peak intensity, $\Sigma I(hkl)$ is the sum of the intensities of the independent peaks. The index 0 refers to the intensities for a ramdomly oriented pattern. By this way, it is obvious that Ni_5Zn_{21} is highly oriented whatever the magnetic field amplitude, the pH or the applied potential. The very low amplitude for NiZn peaks does not allow a significant analyze and it is not possible to discriminate between the lamellar (002) and dendritic (200) textures. On the other hand for the Zn phase, the magnetic field deeply modifies the orientation that is shifted from a (200) texture (which completely disappears) to a (101) one.

4. Conclusion. This preliminary study shows that the magnetic field effect under the used experimental conditions is quasi non-existent on currents both in stationary regime and in deposition regime. In all cases, the nickel atomic ratio remains quite identical. On the other hand, the magnetic field acts as a levelling agent and a refiner by lowering the deposit roughness and the spot size. More, it is highly visible on XRD diagrams that the magnetic field changes the texture of the majority Zn phase. It is interesting to carry on with this study that shows, despite a very weak convection MHD, magnetic field changes in deposition of non ferromagnetic materials.

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