Influence of organic additives on electrocrystallization mechanism and structure of zinc deposits

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Electrodeposited zinc and zinc alloys coatings are widely used in the field of corrosion resistance as sacrificial materials for the protection of steel [1]. Homogeneity, brightness as well as anti-corrosion behavior, paintability and mechanical properties of zinc deposits strongly depend on the texture and morphology of the films. Since zinc often gives rise to dendritic growth, organic additives are usually added in the electrolyte [1, 2]. In the present work, we investigate the influence of two additives, sodium dodecyl sulfate (SDS) and Poly(4-styrenesulfonic acid-co-maleic acid) sodium salt, denoted P, on the kinetics of electrocrystallization and on the morphology and texture of the layers.

Experimental

The solutions were made of 150 g/L $ZnSO_4$, $7H_2O$ and Na_2SO_4 40 g/L. They were maintained at 40°C and pH=4.8. Solution S1 was additive-free, solution S2 contained 4 g/L of P and solution S3 contained 0.6 g/L of SDS. Zinc deposits were carried out under galvanostatic conditions using a copper disc electrode rotating up to 1500 rpm as working electrode, a saturated calomel electrode (SCE) as reference and platinum sheet as counter-electrode for the determination of polarization curves and impedance diagrams. A voltammetric investigation using an electrochemical quartz-crystal microbalance was carried out. For SEM, XRD and internal stress analysis, zinc was deposited potentiostatically on XC38 steel and zinc sheet as counter-electrode. The morphology of the deposits was investigated by SEM. X-ray diffractograms enabled us to determine the texture of the films. Internal stresses were determined using the $\sin^2\Psi$ method.

Results and discussion

The steady-state polarization curves for the three solutions are shown in fig.1. Curves S1 and S3 exhibit the characteristic S shape, already observed in slightly acidified electrolytes [3]. Such a behavior has been attributed to the presence of an autocatalytic step during the multistep electrocrystallization of zinc [3]. In the presence of P, the S-shape disappears. In the presence of organic additives the curves are shifted to less negative potentials, contrary to what is generally observed.

Impedance plots exhibit, in addition to the high-frequency capacitive loop, two or three inductive loops. The Rt.i, product of the charge transfer resistance and the current density, is smaller in the presence of the additives.

The comparison of the experimental data with a theoretical model close to that proposed by Epelboin et al. [3] and Cachet et al. [4], is in progress in order to understand the kinetics of zinc electrocrystallization in the presence of the additives and to correlate these mechanisms with the morphology of the deposits.

The morphologies and textures of the deposits vary with the potential deposition (-1800 mV<E<-1300 mV) and the nature of the additive. Fig. 2 illustrates the influence of the additives on the morphology. At –1800 mV, in the absence of additive the deposit is facetted (a), in the presence of SDS, it is coarse-grained (b). With P, the morphology depends strongly on the deposition potential: at –1300 mV it is spongy, typical of dendritic growth, whereas at –1800mV, it shows fine grains (c).

Relatively low tensile stresses are observed compared to those measured for zinc deposited at for high current density [5]. They do not excess 30 MPa except for films deposited in the presence of P additive. In the latter case, low stresses (30MPa) are associated with spongy or dendritic growth and higher stresses (70 MPa) with fine grained structure as shown in Fig.2c.

References

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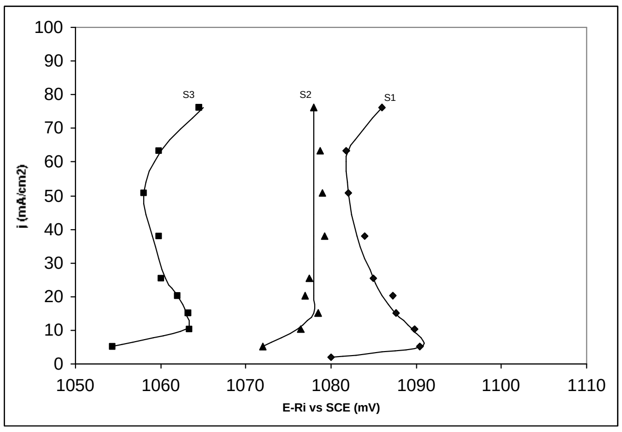
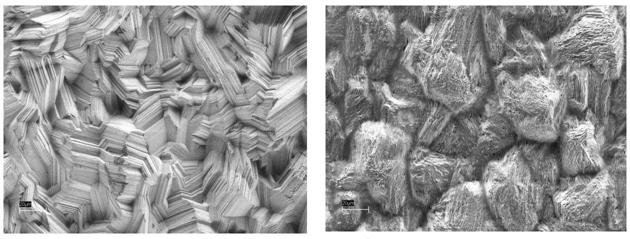
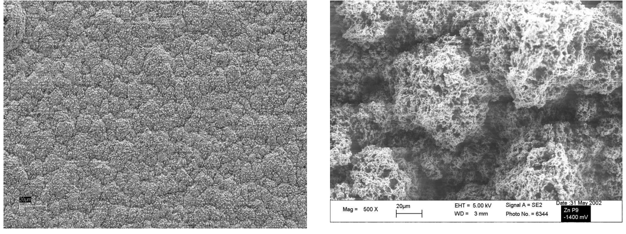


Figure 1: Steady-state polarization curves for the three solutions S1, S2 and S3 (1000 rpm)



a) S1(E =-1800mV) b) S3 (E =-1800mV)



c) S2 (E =-1800mV) d) S2 (E = -1400 mV)

Figure 2 : S.E.M. micrographs