Study of CoNi electrodeposition mechanism in a glycine bath using EQCM

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Although the anomalous codeposition, a recurring effect in iron-group metals alloys, in which the less noble metal is deposited preferentially over the more noble metal, an effect known since the beginning of XX century, little is yet known about its mechanism. Moreover, the effect of the presence of additives in the mechanism of such processes is still not established. A better understanding of the mechanism of electrodeposition processes or of the role of an additive in the bath is obtained if there is a possibility of direct access to the reactions occurring at the interface and/or species present, using *in-situ* techniques. The objective of this communication is to report some results of study of the anomalous codeposition of CoNi alloy from a sulfate bath in the presence of glycine as additive using the electrochemical quartz crystal microbalance (EQCM).

The experiments were run using an Au foil as working electrode, a Pt mesh as counter-electrode and Ag|AgCl(KCl$_{sat}$) as reference electrode. The plating bath was constituted of 0.10 mol L^{-1} CoSO$_4$ + 0.10 mol L^{-1} NiSO$_4$ + 0.50 mol L^{-1} Na$_2$SO$_4$ + 0.2 mol L^{-1} glycine (Gly). Media pH was kept constant in the range of 4.0 to 7.0.

The results are discussed in terms of the (M/z) ratio data, which is the slope of the Δf x ΔQ curve, obtained from the frequency-voltage curves. Preliminary studies done using a bath in the absence of Gly, independently of the bath pH, have shown that the initial step consists of the formation of hydroxide, characterized by an (M/z) value of 46.45 g mol^{-1}, value similar already reported by other authors [1,2], which is in accordance to the mechanism proposed by Bockris *et ali.* for iron-group metals reduction [3]. When glycine is added to the bath at a ratio of [M^{2+}]/[Gly] = 1, independently of the bath pH, there is no apparent change in the Co^{2+} reduction, whereas it changes Ni^{2+} in the sense that it reduces directly to Ni^{o}.

In the CoNi bath without Gly, for all the studied pH´s, the values of the (M/z) ratio at the onset of the reduction are around 29.40 g mol^{-1}. This differs from the obtained value for the deposition of the single metals from Gly-free baths, 46.45g mol^{-1}. Those (M/z) values are constant during the cathodic scan which suggests that the mechanism for alloy deposition differs from that one for the single metal deposition.

The model proposed by Podlaha and Landolt [4] suggests that the cause of the anomalous codeposition is the formation of an intermetallic species of both metals, (CoNi)$^{3+}$. Assuming that this species is not adsorbed on the surface, reduction of this species to the metallic state will be observed in a EQCM experiment a (M/z) value of 29.40 g mol^{-1}, as we observed in this study.

When Gly is added to the bath, the (M/z) ratios at the beginning of deposition are: lower than 29.40 g mol^{-1} when pH =4.0, near 29.40g mol^{-1} when pH=5.0 and 6.0, and higher than 29.40g mol^{-1} when pH=7.0.

The species distribution curves for a bath containing Co, Ni, Gly in a 1:1:2 ratio, reveals that the Ni(Gly)$_2$ species predominates when pH > 4.7, with its maximum quantity (60%) in pH = 7.0, with almost no formation of any Co-Gly complex. A reasonable explication for the observed results, at pH=4.0, is that the reduction occurs through the reduction of species from the (CoNi)$^{3+}$ intermetallic species, the same way as in the bath without Gly. When 5.0<pH<6.0, some Ni^{2+} is complexed with Gly, being deposited directly through this complex, whereas Co is mainly reduced from the intermetallic species. In the bath with pH=7.0, as the Ni-Gly complexes are more stable than Co, most, if not all, Ni is complexed with Gly, not alloying the formation of the intermetallic species. This leads to a bath where the reduction of Ni occur as in the Ni bath with Gly and Co reduction happens as in the Gly-free bath, giving an average (M/z) value of 37.9g mol^{-1}, the same values seem here.

Thus, as it can be seen, depending of the pH of the bath and Gly presence, we see changes in the mechanism of the deposition of the alloy. In a bath without Gly, both metals reduce differently from their respective baths, indicating the existence of interaction between them, most likely the one suggested by Landolt and Podlaha. When Gly is added to the bath, and its complexation with one of the metals is favored over the other, then both metals reduce as if there weren't any interactions between them.

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