

Short Communication

On the Anomalous Behavior of Zn/Ni UPD at Pt(111) Single Crystalline Electrode in Borate Containing Solution

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Underpotential deposition (UPD) of Zn²⁺ and/or Ni²⁺ ions at Pt(111) electrode was carried out in borate containing solution. The presence of borate in the solution was found to assist the appearance of sharp peak of Zn UPD at pH > 4, with consistency of our previous work. Zn UPD was found to occur at the so called butterfly wave potential range while Ni UPD occurs within the hydrogen adsorption/desorption region. In the case of electrolyte containing both Zn²⁺ and Ni²⁺ ions, the UPD of Zn, occurs at the most positive potential value and leads to suppression of Ni UPD process.

Keywords: Zn UPD, Ni UPD, Borate, Pt(111), Simultaneous UPD

1. INTRODUCTION

The electrodeposition of zinc alloys with Iron group, in particular, Zn-Ni alloy, has recently attracted interest because of their high corrosion resistance compared to that of pure zinc [1-3].

Mostly, the electrolytic co-deposition of Zn-Ni alloys is anomalous in nature since the less noble metal zinc deposits preferentially and its percentage in the deposit is higher than that in the electrolyte. Anomalous behavior has been recognized in spite of the composition of the deposition bath [4-7]. Two different theories have been proposed. In the first one, the anomalous co-deposition is attributed to the adsorbed layer of Zn(OH)₂ at the surface, which inhibits nickel discharge [8-11]. On the other hand, the second one [12, 13] assumes that anomalous co-deposition is due to the underpotential deposition (upd) of zinc.

Boric acid is mainly used as an additive in electroplating baths. Although the role of H₃BO₃ is not therefore quite correctly understood, many authors [14, 15] claimed that the boric acid was added

to the electroplating bath as a buffering agent. Hence, specific adsorption of borate was first studied on Pt(111) by cyclic voltammetry (CV) under the conditions of changes of pH's and borate concentrations, and we came to the conclusion that the specific adsorption of borate took place on Pt(111) by the release of H^+ [16]. These findings let us conclude that the role of boric acid is not limited just to act as a buffer [17]

According to Karwas and Hepel [18] boric acid inhibits zinc deposition shifting the nickel content in alloys toward Ni-rich phases. Increasing the boric acid concentration leads to the reduction of the anomalous co deposition [19].

We have recently reported the drastic change in Zn UPD at Pt(111) caused by borate adsorption/ desorption process [20]. In this work, we are going to give some insight on the role of both boric acid and UPD phenomena on the anomalous behavior during Ni-Zn alloy deposition.

2. EXPERIMENTAL

Experiments have been performed in a conventional three-electrode cell with a saturated calomel electrode (SCE) as the reference electrode and a platinum foil as the counter electrode [16]. The preparation of the Pt(111) electrode as well as cleaning of the electrode before each experiment has been done according to the Clavilier method [21]. The solutions were prepared from $HClO_4$ (Merck, suprapur), $KClO_4$ (Merck, pro-analysis), ZnO (Merck, suprapur), and H_3BO_3 (Merck, suprapur) with Milli-Q-Water ($> 18 M\Omega$). The pH was controlled by the change of the ratio of $HClO_4$ and $KClO_4$, where the value of pH was constant within experimental error before and after each measurement.

The electrolytic solution was kept oxygen-free during measurements by continuous bubbling of ultrapure Ar over the solution. The solution came in contact with the working electrode by hanging meniscus technique. The CV measurements were carried out at ambient temperature with potentiostat (Toho 2000) and function generator (Toho FG-01) connected to a computer for data acquisition and processing.

3. RESULTS AND DISCUSSION

3.1. Comparison between Zn UPD and Ni UPD in borate solution

Fig. 1. Shows CV's obtained at Pt(111) electrode in $10^{-2} M H_3BO_3 + 0.1 M XClO_4$, where X^+ is H^+ and/or K^+ in the absence (green curve) and presence of $1 \times 10^{-4} M Zn^{2+}$ (red curve) and $1 \times 10^{-4} M Ni^{2+}$ (black curve). $pH = 4.3$, Sweep rate was $5 mV s^{-1}$. As Zn ions are added in nickel electroplating bath for practical use, we observed Ni UPD at pH 4.3 in borate solution, as shown in Fig. 1 (green curve), where the curve due to the presence of Zn^{2+} ions is also included (red curve). The UPD shift of Zn on Pt was observed at 0.91 V, with which the Zn UPD occurs at more positive potentials than the standard potential of $\approx -0.47 V(SCE)$, of Ni^{2+}/Ni . As can be seen from Fig.1., in the presence of Ni^{2+}

ions, small negative and positive current increases at - 0.35 V and - 0.28 V(SCE), respectively, are attributed to Ni UPD on Pt(111), as previously found in the case of phosphate solution [22]. Zn UPD occurrence at more positive potential (-0.18 V) compared to Ni UPD, indicates that the amount of Zn deposition is expected to be higher than that of Ni. Zn UPD is expected to significantly suppress hydrogen evolution reaction as hydrogen electrode reaction rate at Zn metal is 3 to 4 orders of magnitude lower than that at Ni metal [23] so that the smooth and defect-free electroplating will be promised at least with Zn UPD covered surface.

3.2. Simultaneous Zn and Ni UPD at Pt(111) in borate solution

As UPD can be considered the starting key point in electrodeposition process, we have attempted to give some insight about the role of UPD on the anomalous behavior during the electrodeposition of Ni/Zn alloys. As Zn UPD occurs at more positive potential compared to Ni (See above), we try to find out the influence of Zn upd on Ni upd process.

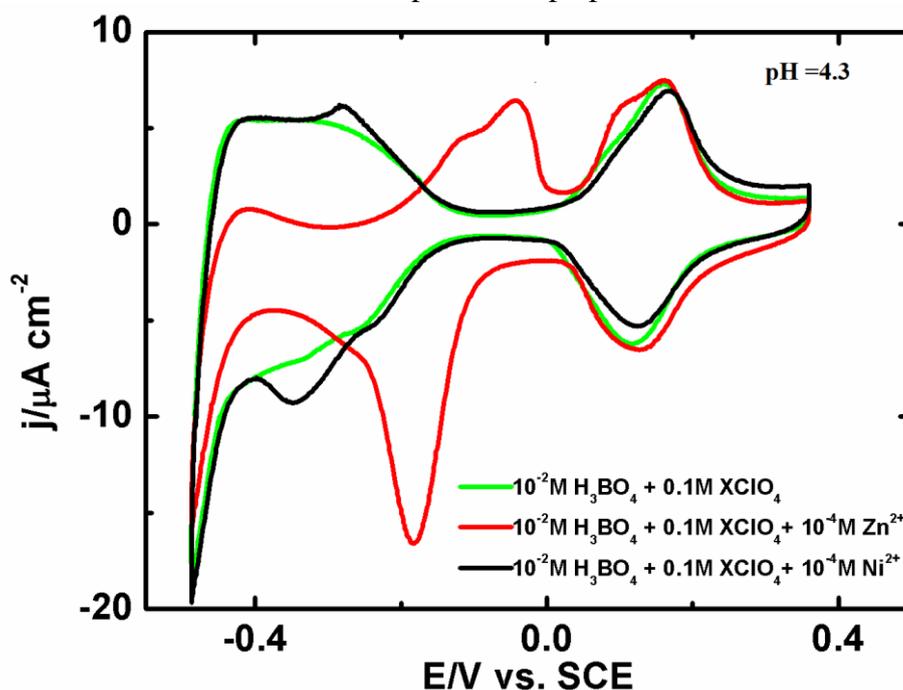


Figure 1. CV's obtained at Pt(111) electrode in 10^{-2} M H_3BO_3 + 0.1 M XClO_4 , where X^+ is H^+ and/or K^+ in the absence (green curve) and presence of 1×10^{-4} M Zn^{2+} (red curve) and 1×10^{-4} M Ni^{2+} (black curve). pH = 4.3, Sweep rate was 5 mV s^{-1} .

Fig. 2 shows the cyclic voltammogram for Pt(111) in borate solution containing Zn^{2+} and/or Ni^{2+} ions at pH = 4.8. As can be seen for the comparison of figs. 1 and 2, a small change in pH value leads to a drastic influence on Zn UPD process as reported previously [20], while no significant changes can be seen for Ni UPD. As can be shown from this figure, in the presence of Ni^{2+} ions, small negative and positive current increases at - 0.315 V and - 0.285 V(SCE), respectively, are attributed to Ni UPD on Pt(111). On the other hand, the presence of Zn^{2+} ions leads to suppression of the hydrogen adsorption-desorption process (see Fig. 2, red curve) with the appearance of sharp peak in the anodic

going sweep at 0.09 V for Zn desorption and a peak at 0.014 V in the reverse scan for Zn UPD. Both peaks coincident with the onset of borate adsorption desorption peak as described elsewhere [20]. In the presence of both ions, Zn^{2+} ions cause considerable suppression for peaks assigned to Ni UPD process. This indicates that in borate solution containing both ions, the main process occur is Zn UPD. This may be attributed to the formation of Zn UPD layer at more positive potential compared to Ni UPD.

It has been previously reported that, increasing the boric acid concentration leads to the shift of Zn UPD process to less positive potential [20]. This intern will leads to the decrease of Zn UPD process. This can explain the increase of Ni content in Ni-Zn alloy by raising the boric acid concentration in the deposition bath [19].

It is noteworthy to mention that the presence of Ni^{2+} ions in solution also decreases the Zn UPD peaks to some extent. This accompanied with the appearance of small shoulder for Ni adsorption in the negative going sweep at -0.3 V. This indicate that's small amount of Ni is also contributed in the upd process.

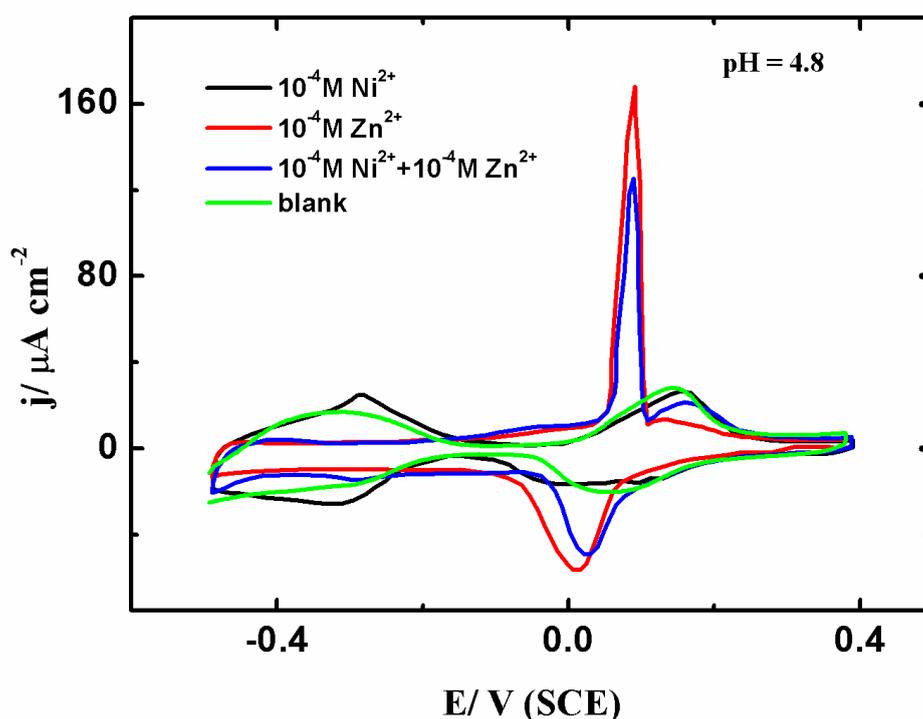


Figure 2. CV's obtained at Pt(111) electrode in 10^{-2} M H_3BO_3 + 0.1 M XClO_4 , where X^+ is H^+ and/or K^+ in the absence (green curve) and presence of 1×10^{-4} M Zn^{2+} (red curve), 1×10^{-4} M Ni^{2+} (black curve) and 1×10^{-4} M Zn^{2+} + 1×10^{-4} M Ni^{2+} (blue curve). pH =4.8, Sweep rate was 50 mV s^{-1} .

4. CONSLUSION

In the coexistence of Zn and Ni ions in borate, both ions can undergo UPD process at very

different potential range compared with their bulk deposition potentials. Zn upd occurs at more positive potential than Ni UPD. Accordingly, in the presence of both Zn^{2+} and Ni^{2+} ions, Zn UPD process is the predominant one and leads to suppression of both Ni UPD and hydrogen adsorption/desorption process. This can be the main reasons for the anomalous behaviour in Zn/Ni electroplating technology.

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