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Electrodeposition of Ni-B and Ni-Co-B Alloys by Using Boric Acid as Boron Source

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In this letter, the formation of electrodeposited Ni-B and Ni-Co-B alloys by using boric acid as boron source was demonstrated. The estimated thickness of the films was 5 μm. By means of Cyclic voltammetry, X-ray diffractometry and energy dispersive X-ray spectroscopy analyzes, it was showed that Ni-B and Ni-Co-B alloys, with composition $Ni_{94}B_6$ and $Ni_{75}Co_{21}B_4$, can be easily formed onto glassy carbon when no complexing agents are employed in the electrodeposition bath. These results open the door to the production of electrodeposited boron-containing alloys by using boric acid as precursor due to its low cost and large-scale production.

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Electro- and electroless plated boron-containing alloys have attracted much attention in the last decades due to their uncommon properties such as high hardness and superior mechanical wear resistance.[1,2] Moreover, their application is so vast and includes several fields concerning aerospace, automotive, chemical and electrical industries.[3] Among them, binary and ternary alloys such as Ni-B, Co-B, Fe-B, Ni-W-B and Co-Ni-B have been studied with different purposes.[4–6]

In the case of electroless deposition, the use of strong boron-base reducing agents (borohydride, dimethylamine borane, trimethylamine borane, etc.) is mandatory to obtain boron-containing alloys. Besides the relatively high cost of these compounds, the electroless technique to produce boron alloys is limited to the use at high temperatures (70–90°C) and high pH values (13–14),[7] which in many cases restricts its broad utilization. In view of these facts, the conventional electrodeposition technique appears as an alternative to the boron alloys production. In addition, as reported by Bekish et al.,[2] the electrochemical method offers a number of considerable advantages when compared to the electroless one, e.g. operation at room temperature, high deposition rate, electrolyte stability, among others. However, studies concerning electrodeposition of boron-based alloys have only showed their production from baths containing the above-mentioned boron compounds.[4–6]

Here, we report, for the first time, the electrodeposition of Ni-B and Ni-Co-B alloys from a bath containing boric acid as boron source. By means of cyclic voltammetry, X-ray diffractometry and energy dispersive X-ray spectroscopy analyzes, it was demonstrated that Ni-B and Co-Ni-B alloys can be easily deposited from a simple bath.

Experimental

Ni-B and Ni-Co-B Alloys were potentiostatically deposited onto a glassy carbon disk (area = 0.075 cm^2). Glassy carbon was chosen as substrate due to its good electrical conductivity and long potential range of electrochemical inactivity. The electrolyte composition used for the alloys electrodeposition was: 0.05 M $NiCl_2$, 0.5 M NaCl, and 0.2 M H_3BO_3 for Ni-B alloy, and the same bath plus 0.025 M $CoCl_2$ for Ni-Co-B alloy. The bath pH for obtaining the electrodeposits was set to 5. In the case of the cyclic voltammetry (CV) experiments, a pH range 5–9 was employed, and the CVs showed that pH 5 was the best to produce the alloys. As reference electrode, it was utilized an $Ag|AgCl|KCl_{sat.}$ (0.199 V vs. SHE) connected to the working electrolyte by a Luggin capillary. The counter electrode was a Ti/Rh spiral (area = 5 cm^2). All measurements were performed in a BioLogic VSP potentiostat/galvanostat using the software EC-Lab V10.32. In all experiments, the total charge passed to obtain the electrodeposits was equal to 25 C. The thickness of the deposits was about 5 μm, estimated from the deposited mass. The composition of the alloys was estimated by energy dispersive X-ray spectrometry (EDXS) coupled to a scanning electron microscopy (SEM). X-ray diffractometry (XRD) was employed to characterize the alloy structure. The XRD experiments were performed utilizing a Siemens D 5000 X-ray generator using CuK_α radiation at 40 kV and 30 mA with monochromator at the diffracted beam. The XRD patterns were obtained using a 2θ range of 30–80° with a step size of 0.02° and a step time of 15 s; a slow scanning rate to avoid peak widening.

Results and Discussion

Fig. 1a shows the CVs obtained for the bath containing Ni ions plus H_3BO_3 in the pH range 5–9 onto a glassy carbon electrode. The cathodic branch shows that all CVs obtained in pH < 8 have a typical behavior of a nucleation/growth response due to the overlapping noticed in the cathodic part of CVs. In the anodic scan, at least two anodic current peaks are observed at around −0.3 and +0.8 $V/Ag|AgCl|KCl_{sat}$. The first one has evidently been assigned to the oxidation of metallic Ni to Ni^{2+} ($E^0 = -0.257$ V/SHE, -0.454 $V/Ag|AgCl|KCl_{sat.}$) while the second has been attributed to different compounds in alkaline and slightly acidic media. Such compounds include NiO,[8] $Ni(OH)_2$,[9] NiOOH,[10] Ni_3O_4,[11] and nonstoichiometric Ni oxides.[12] However, in our work this second anodic peak cannot be related to the formation of Ni oxides and/or hydroxides by the following reason: at pH 5, the current peak at ≈0.8 V is higher than those of more alkaline pHs. As an increase in the pH would increase the anodic current peak whether oxides and/or hydroxides species are formed, the formation of these compounds can be discarded. Therefore, if the current peak at ≈0.8 V is not related to oxides formation at pH 5, another species is contributing to the voltammetric response observed in the CV as an intense anodic peak (Fig. 1a E ≈0.8 V). As the electrochemical bath contains boron, we assume that boron is codeposited with Ni to form an alloy once boron has not been deposited by itself from aqueous solution. In this condition, it is supposed that Ni induces the deposition of B; a mechanism similar to what happens in the deposition of Ni with Mo or W, a so-called induced codeposition.[13,14] Hence, the anodic peak at ≈0.8 V (Fig. 1a) for different pHs is attributed to the oxidation of Ni-B alloy previously deposited during the cathodic scan.

In order to investigate the influence of boron on the Ni deposition at pH 5, CVs were recorded for 0 to 0.5 M H_3BO_3 solutions (Fig. 1b). In the insert of Fig. 1b, the CV for the solution containing nickel in the absence of H_3BO_3 (pH 5) shows a cathodic peak (≈−0.9 V) associated to the reduction (Ni^{2+} to Ni^0) and an anodic peak (≈−0.3 V) attributed to the oxidation (Ni^0 to Ni^{2+}) processes, respectively. The pair of reversible peaks observed at more positive potentials (E > 0.7) corresponds to some species of Ni(III) which is promptly reduced to Ni(II) species (see discussion above for possible Ni compounds) when the potential sweep is inverted. When H_3BO_3 is added to the solution containing Ni ions, the CV is completely changed as shown in Fig. 1b. It is observed now that the nickel

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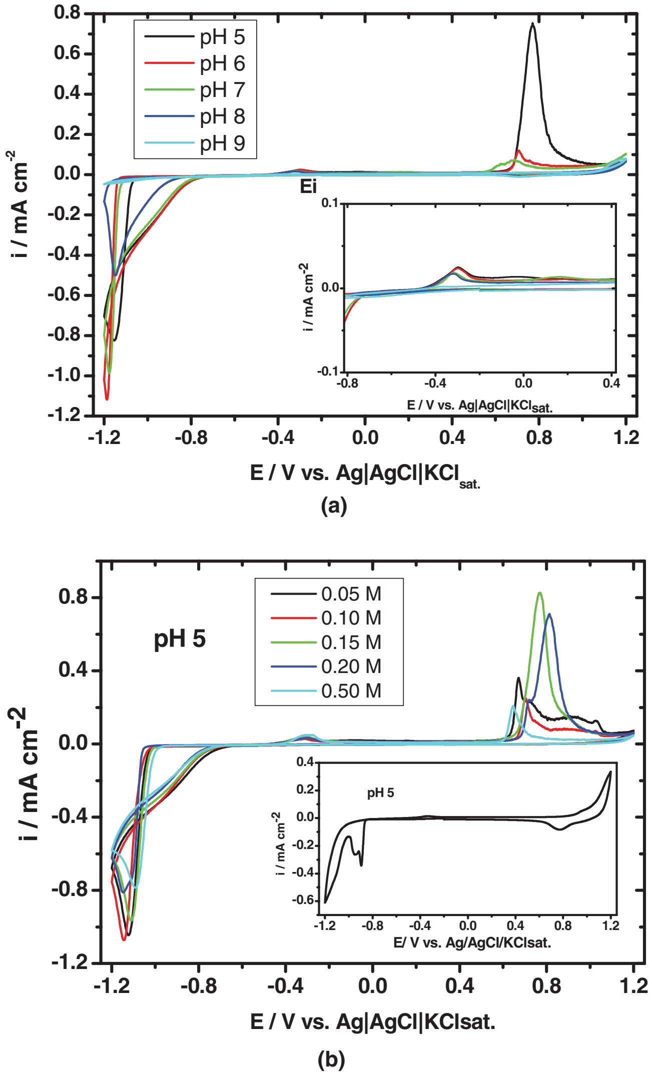

Figure 1. CVs obtained for the baths containing: (a) 0.05 M $NiCl_2$, 0.2 M H_3BO_3 and 0.5 M NaCl (the insert shows the first anodic peak region at ≈ -0.3 V); (b) 0.05 M $NiCl_2$ and 0.5 M NaCl in the absence (insert) and at different H_3BO_3 concentrations. CVs recorded onto a glassy carbon electrode and at 20 mV s^{-1}.

deposition starts at more negative potentials (≈ -1.1 V) possibly due to a complexing effect of H_3BO_3. The formation of a complex between Ni ions and boric acid has been previously reported,[15] even though its mechanism has not been elucidated so far. From the anodic branch, it can be inferred that the Ni oxidation takes place at about the same potential as in the case of H_3BO_3 absence; however, the presence of high intensity anodic peaks at higher potentials ($E > 0.6$ V) is now evidently noticed. These peaks at more positive potentials support the idea of a Ni-B alloy formation when H_3BO_3 is added to the bath for nickel deposition. Similar behavior was found when Co ions were added to the bath comprising Ni and H_3BO_3, with the formation of a Ni-Co-B ternary alloy.

To confirm this assumption X-ray diffractometry (XRD) was carried out for deposits obtained potentiostatically from the bath in the absence and presence of H_3BO_3, and also for the bath containing Co ions. Both Ni-B and Ni-Co-B deposits were obtained at the same conditions ($E = -1.2$ V/Ag|AgCl|KCl_{sat}, deposition time = 4 hours). This potential value was chosen based on the CVs that show the deposition process starting at ≈ -1.0 V. The XRD patterns are depicted in Fig. 2. The deposits obtained in the presence of H_3BO_3 were annealed at 500°C during 4 hours to ensure the crystallization of Ni-B compounds, if present, as suggested by Saito et al.[4]

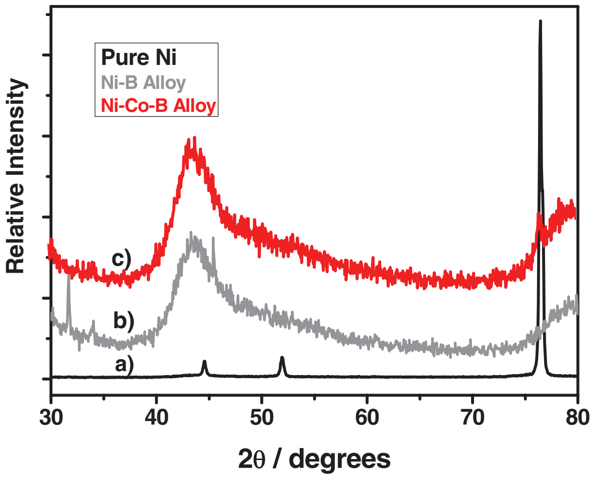

Figure 2. XRD patterns of deposits obtained from bath containing Ni ions: absence of H_3BO_3 (a), presence of H_3BO_3 (b), and presence of H_3BO_3 plus Co ions (c). Deposits obtained potentiostatically at -1.2 V/Ag|AgCl|KCl_{sat} with a charge of 25 C.

Fig. 2a displays the XRD pattern of pure Ni obtained from the bath containing Ni ions and no H_3BO_3. It is possible to see three crystalline peaks at 44.52°, 51.89° and 76.52° associated to Ni with FCC crystal structure. For the deposit obtained from the bath containing H_3BO_3 (Fig. (2b)), and after heat-treatment, the pattern is completely changed. A broad diffraction line, characteristic of an amorphous structure, is seen evidencing the formation of a Ni-B alloy as explained by Saito et al.[4] In their work, the formation of a Ni-B alloy was demonstrated. This alloy is amorphous in the as-deposited state and after heat-treatment it becomes crystalized due to the formation of a Ni_3B compound. A similar result is found for the deposit obtained from the bath containing Co ions (Fig. 2c), which also shows an amorphous state even after the annealing process. In summary, it can be inferred from the XRD data that the presence of boric acid in the baths containing pure Ni and Ni + Co ions leads to the formation of a Ni-B and Ni-Co-B alloys as previously suggested by the CVs results. Additionally, the EDXS analyzes revealed an alloy composition of $Ni_{94}B_6$ and $Ni_{75}Co_{21}B_4$, which also confirms the presence of boron in the deposits.

Conclusions

We have demonstrated the formation of electrodeposited Ni-B and Ni-Co-B alloys by using boric acid as boron source. By means of cyclic voltammetry, X-ray diffractometry and energy dispersive X-ray spectroscopy analyzes, it was showed that Ni-B and Ni-Co-B alloys, with composition $Ni_{94}B_6$ and $Ni_{75}Co_{21}B_4$, can be easily formed onto glassy carbon when no complexing agents are employed in the electrodeposition bath. It was assumed that B is codeposited with Ni by the induced codeposition mechanism. These results open the door to the production of electrodeposited boron-containing alloys by using boric acid as precursor due to its low cost and large-scale production.

Acknowledgments

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