Local structure of pulse plated Ni:Zn alloys

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The materials in Ni-Zn system represent a model case of anomalous alloy growth [1]. The Ni:Zn alloys are in the interest of electrochemists due to the enhanced corrosion resistance (on the Zn rich end) [2] or enhanced electrocatalytic activity towards oxygen reduction (on the Ni rich end) [3]. The nature of the functionality improvement due to the alloying remains unknown mainly due to the missing information on the structure of these materials which give diffraction patterns conforming to amorphous materials[4].

Our experiments show that the local structure of the alloys reflects the plating conditions, namely the applied current density, deposition pulse time and film thickness. There are two principal regimes of the Ni:Zn alloy growth. In the first case the deposition process is controlled by transport of the Zn\(^{2+}\) to the electrode surface. In the second case it is the spontaneous dissolution of metal Zn which controls the alloy structure. The formed alloys are in both cases of a multiphase character.

The alloys grown in the first regime show little sensitivity of the Zn local environment to the deposition pulse duration. It suggests that the Zn in alloy samples is present most likely in one local environment regardless of the plating conditions. The Ni EXAFS shows pronounced decrease of the first coordination shell scattering amplitude with increasing plating pulse duration and/or film thickness. Such a behavior may be attributed to a disorder arising from presence of Ni in two local environments –one corresponding to a solid solution Ni-Zn phase (most likely of Ni\(_{0.85}\)Zn\(_{0.15}\) composition) and the other corresponding to Zn - free Ni phase. The Zn content in the solid solution phase slightly increases with increasing deposition pulse duration. The contribution of both phases changes in favor of Zn free phase as the plating time increases. This trend is accompanied with a slight shift of the Ni edge position by ca. 1 eV to lower energies which reflects increasing contribution of electrocatalytic hydrogen evolution and possible formation of corresponding hydride as a local inclusion.

The alloys plated in the second regime seem to show negligible variation of the Ni local environment(s) and significant variation of the Zn local structure. Also the positions of Ni and Zn absorption edges show inverse tendency than in alloys plated in the first regime. The Ni edge position is the same regardless of the deposition conditions, while the Zn edge shifts to more positive values (by ca. 1 eV) with increasing pulse duration. The gathered structural data suggest a two phase structural model when both phases contain both Ni and Zn. One of the phases is most likely the stable Ni\(_{0.85}\)Zn\(_{0.15}\) alloy, the other phase is rich in Zn, its composition is, however difficult to assess due to spontaneous dissolution of Zn. The fraction of Zn rich phase seems to increase decreasing pulse duration and decreasing film thickness.

The successfull application of the EXAFS technique to address the mechanism of the NiZn alloy formation in anomalous deposition mode still needs to be complemented by systematic investigation of the of the alloys grown under normal deposition mode. In similar manner the local structures reflected in the EXAFS spectra have to be matched to the actual electrocatalytic activity and structural changes triggered by the electrocatalytic oxygen reduction. These questions will be addressed in the experiments planned for the first half of the year 2010.
**Figure 1:** $k^2$ normalized EXAFS functions of the pulse plated NiZn alloys plated from sulphate bath in regime controlled by the Zn$^{2+}$ transport (left) and by Zn dissolution (right). The corresponding spectra were recorded in fluorescence mode and corrected for self-absorption. The actual plating bath compositions were 0.3M Ni$^{2+}$/0.015 M of Zn$^{2+}$ and 0.3M Ni$^{2+}$/0.03 M of Zn$^{2+}$, respectively. Figure legend shows plating pulse duration and alloy film thickness.

**References**


