Many transition metals and alloys are deposited with simultaneous evolution of hydrogen. This is accompanied by a pH rise near the cathode. The pH at the cathode significantly exceeds the bulk pH and affects the chemistry of nearby ions and the stability of intermediate products. Measurements of the pH at the surface during plating [1,2] help to understand mechanisms of alloy deposition. For instance, in plating of CoFe or NiFe alloys, it is of great interest to keep the surface pH, during plating, below the limit where oxides and hydroxides are formed and incorporated into the deposits. Incorporated oxides are lowering the magnetic moment and are leading to defects.

The Rotating Cylinder Hull (RCH) Cell [3] permits Hull-cell-type experiments under uniform and well-controlled mass-transport conditions. It is of great practical use in studying the effect of plating additives and to optimize the plating process.

A special cell allowing for surface pH measurements, identical with one described earlier [1], was built. A flat-bottomed pH electrode is brought in contact with the back of a very thin metal mesh containing small, uniform apertures. If the apertures of the mesh, used as cathode, are very small compared to the diffusion layer thickness of H\textsuperscript{+}, the measured pH as an average within the apertures is very close to the actual pH at the cathode during electroplating. The actual pH value at the cathode can be arrived at by using several electrodes with different aperture and then extrapolating the curve to show the true pH at the cathode. Neither the mass transport nor the electrical field is disturbed by the pH electrode. Since the measurement occurs over hundreds of apertures, the signal to noise ratio is large.

An in-situ surface pH measurement during electroplating of CoFe alloys showed that it takes several tens of seconds to build up a steady state pH (Fig. 1). Due to the buffer agents in the plating bath, we found a limiting pH, which was not exceeded even at higher current densities. Bath additives such as sulfur bearing compounds were found to lower the cathode pH. The compositional analysis of plated RCH Cell samples showed that additives, which are capable of lowering the pH over a certain range of current densities, lead to a decreased Fe content in the alloy over the same range of current densities (Fig. 2). This underlines the importance of knowing the surface pH in order to understand the alloy deposition mechanism. It also demonstrates that combining the two separate experimental techniques provides very useful information on the electrodeposition process control of iron group metals and alloys.

References