

Electrodeposition of Binary Alloys from Complexes by Underpotential Codeposition of the Reactive Metal: Principles and Application to Magnetic Alloys

J. Mallett and G. Zangari

CESE, Department of Material Science and Engineering, University of Virginia.
Charlottesville, VA 22904-4745, USA

The electrodeposition of alloys which exhibit negative enthalpy of mixing occurs with a depolarization of the equilibrium potential of the reactive metal. In this case the reactive metal can be underpotentially co-deposited into an alloy with its atomic fraction thermodynamically limited by the deposition potential. The thermodynamic limit is achieved when the reactive metal deposition kinetics are fast and the overall alloy deposition rate is slow, allowing the reactive metal to be deposited close to equilibrium. These conditions have been realized for binary Pt alloy deposition by using a low concentration of Pt salt to limit the alloy deposition rate and a high concentration of reactive metal salt. Alloy compositions were found to be a well defined function of deposition potential, in accordance with a regular solution model of alloying. This method however presents restrictions when dealing with alloys of metals having widely different standard redox potentials; at the potentials required to co-deposit the reactive metal in fact Pt deposition may become diffusion limited, resulting in porous and cracked deposits. In addition, in the case of FePt, the deposition potential used was found to result in hydrogen generation, producing unwanted pH shifts leading to oxide incorporation.

We will discuss a general approach to the electrodeposition of noble metal/reactive metal alloys by using metal complexes to shift negatively the reduction potential of the noble metal while increasing the stability of the reactive metal against precipitation. We will focus in particular on the electrodeposition of Pt alloys with Fe or Co using the Pt amino-nitrite complex (Pt p-salt), which enables morphologically stable kinetically controlled Pt growth at alloy deposition potentials. The stability of this complex requires a slightly alkaline pH, which necessitates complexation of the reactive metal. However, operating in alkaline conditions reduces hydrogen evolution and suitable complexing agents for the reactive metal (citrate and glycine) also act as pH buffers. In contrast to previous studies from similar solutions, the deposition process is performed potentiostatically at potentials that are positive of the standard electrode potential of the reactive metal.

With the reactive metal deposited close to equilibrium, the Pt deposited under kinetic control and a deposition temperature of up to 95 °C, the prospects of achieving a higher than usual degree of chemical order in the as-deposited material are improved. This is particularly important for Fe-Pt and Co-Pt, which in bulk exhibit $L1_0$ tetragonal phases with high magnetic anisotropy. While direct electrodeposition of materials with long range $L1_0$ order is unlikely from aqueous solutions, the presence of a high degree of short range order in Fe-Pt and Co-Pt may provide the nucleation centers necessary for complete transformation at manageable annealing temperatures. This is especially true of nanoparticles, where it has been found that a small proportion of particles lacking the necessary nucleation sites remain untransformed, even after high temperature annealing for many hours. Similar considerations prevail in the case of nano-scale template deposition.