Abstract #2342, 224th ECS Meeting, © 2013 The Electrochemical Society

Electrodeposition of Binary Alloys Immiscible in the Bulk

Defu Liang and Giovanni Zangari

Department of Materials Science and
Engineering, University of Virginia,
P.O. Box 400745, Charlottesville VA
22904-4745, USA
Phone: +1-434-243-5474, e-mail:
gz3e@virginia.edu

The phase structure of electrodeposited alloy films in some cases deviates from that of the corresponding bulk metallurgical alloys; this is due to the finite film growth rate, which may lead to the kinetic trapping of adsorbed atoms at metastable crystallographic positions. Changes in the deposition rate may therefore yield distinct alloy structures and micro-structures, resulting in different functional properties. Observation of metastable structures is particularly common with alloy systems having phase diagrams that exhibit miscibility gaps or eutectic structures; in particular, suitable deposition conditions may force solid solution formation. In this context, we have studied the electrodeposition of Au-Ni (a system that exhibits a miscibility gap) and Ag-Cu (an eutectic system) alloys.

Au-Ni alloys can be formed at underpotential conditions, despite thermodynamics predicting the formation of phase separated pure metal precipitates. We hypothesize that the net attractive interaction between Au and Ni results in the nucleation of solid solution phases where the strain energy is spontaneously minimized, followed by atomic rearrangements and freezing in metastable positions. Observation of a nanoscale alloy structure consisting of Au-rich grains of about 5 nm size surrounded by thick (2-3 nm) Ni-rich grain boundaries is consistent with the proposed model.

Ag-Cu alloys were deposited using both an acidic non-complexing electrolyte and a complexing thiourea-based electrolyte. It is found that film microstructure and physical properties are strongly dependent on the electrolyte chemistry: growth from non-complexing electrolytes results in the precipitation of pure Ag and Cu phases, in agreement with the bulk phase diagram; in contrast, the use of a complexing electrolyte leads to the formation of supersaturated solid solutions. Differences in deposition rates and in the potential at which the alloys are obtained may be responsible for such differences.