# Alloy Electrodeposition

by Kavita M. Jeerage and Daniel T. Schwartz

Alloy electrodeposition was first developed in the 1840s at nearly the same time as metal deposition, with brass coatings being an early commercial application. Despite this long history, alloy electrodeposition continues to attract attention; the majority of the electrodeposition-related articles published by The Electrochemical Society are on alloys. The enduring interest in alloy electrodeposition is tied to the wide range and tunability of physical properties one can achieve by varying alloy composition. As a result, most high-value-added applications of electrodeposition involve alloys, with the notable exception of copper interconnects for integrated circuits. For example, in the emerging field of nano- and microelectromechanical systems (NEMS/MEMS), alloying is key for achieving materials that are sufficiently strong to withstand grueling mechanical and environmental demands.[1] Other recent examples of alloy electrodeposition from the *Journal* and *Letters* include lithium-ion secondary battery anodes, magnetic recording materials, solder bumps, and catalysts for direct methanol fuel cells. The purpose of this tutorial is to provide non-expert practitioners of the art a flavor for the science, engineering, and issues that underpin and rationalize alloy electrodeposition.

Electrodeposition involves the reduction of precursor metal ions and/or metal ion complexes from solution at a conductive substrate. (Chemical reductants are used as the source of electrons in electroless deposition.) At a minimum, an alloy electrodeposition process requires an electrolyte with two or more reducible metal ions, a conductive substrate, a counter electrode, a power supply, and a container to hold the electrolyte and electrodes. This simplicity accounts for the appeal of electrodeposition, but may also lead one to neglect some basic controls needed to ensure reproducibility. As we describe below, good alloy electrodeposition also requires a means for reproducibly mixing the electrolyte, some consideration of cell geometry, and, like all electrodeposition processes, careful substrate preparation.

Figure 1 shows the polarization behavior for an ideal alloy codeposition system. In this ideal system, the deposition current for alloy AB is the sum of the pure metal partial currents from the independent reactions

$$A^{n+} + ne^- \rightarrow A$$

and

$$B^{m+} + me^- \rightarrow B$$
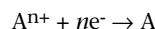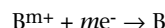
where the constants n and m are the number of electrons transferred. Deposition begins when the substrate potential is brought negative of the Nernst equilibrium potential for A, denoted E_A^{eq}. At this point, however, only A deposits since the substrate remains positive of the equilibrium potential for B, E_B^{eq}. Codeposition (*i.e.*, alloy formation) begins when the potential is negative of the equilibrium potential for B. The instantaneous composition of the resulting alloy is determined from Faraday's Law

$$X_A = \frac{I_A}{n} \left/ \left(\frac{I_A}{n} + \frac{I_B}{m} \right) \right.$$

where X_A is the mole fraction of A in the AB alloy, and I_A and I_B are the partial currents for each alloy species.

Certain details of the polarization curves may explain why surface preparation and electrolyte agitation are important. The partial current for a species normally rises exponentially as the electrode potential moves negative of the equilibrium potential (called Tafel behavior). In this exponential region, the species partial current is limited by charge transfer between the conductive substrate and the precursor ion in solution. Charge transfer processes are highly dependent on the nature of the surface; reproducible cleaning and preparation of the substrate is essential if either species is charge transfer limited. Moreover, surface preparation also impacts nucleation and growth on the substrate, which can affect the deposit grain size and roughness. As the potential of the substrate becomes even more negative compared to the species equilibrium potential, one normally reaches the mass transfer limited current for that species, denoted $I_{A,lim}$ and $I_{B,lim}$ for A and B, respectively, in Fig. 1. The mass transfer limited current is the maximum current achievable, and is proportional to the precursor ion concentration and diffusivity (the ease with which the precursor ion moves through the solvent), as well as how
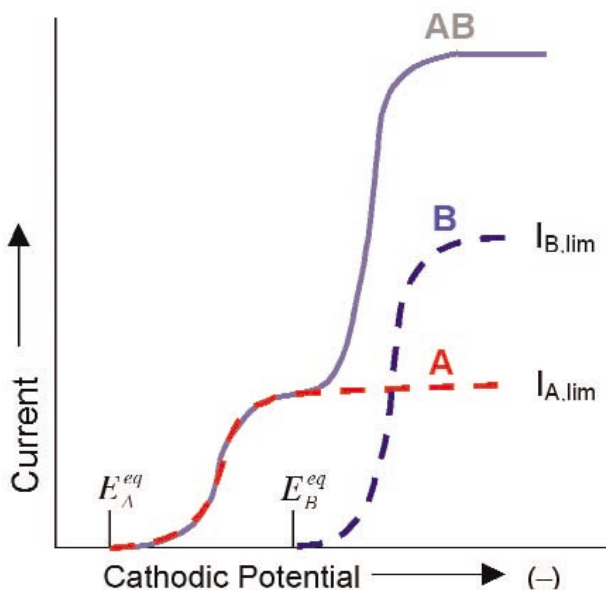

FIG. 1. *An ideal polarization curve for the electrodeposition of the binary alloy AB results from the sum of pure metal (A and B) polarization curves.*

strongly the electrolyte is agitated. Thus, if one or more species are mass transfer limited, how the electrolyte is mixed impacts the alloy composition.

In most real alloy electrodeposition systems, both mass transfer and charge transfer effects are important, meaning the surface preparation and mixing conditions must be controlled for reproducible results. Further, the influence of electrolyte resistance between the substrate and counter electrode must be recognized. How one arranges the two electrodes, therefore, may change the cell potential and affects how current is distributed to the substrate (current follows the path of least resistance through the electrolyte).

Alloy electrodeposition systems may have many further complexities, none of which undermines the lessons learned from an idealized system. Water electrolysis often obscures the alloy deposition behavior shown in Fig. 1 and also reduces the electrodeposition current efficiency. In anomalous codeposition systems, interactions between the depositing species cause the less easily reduced metal to inhibit deposition of the more easily reduced metal.[2] In induced codeposition systems, one species catalyzes the deposition of the other. For example, molybdenum and tungsten cannot be electrodeposited from aqueous electrolytes unless they are codeposited with iron-group elements.[3] We have also not discussed the nature of electrolytes and the use of various metal ion complexants like cyanide, citrate, sulfamate, fluoroborate, pyrophosphate, etc. to control the solubility, charge transfer kinetics, and equilibrium potentials of reducible metals. Abner Brenner's classic two volume handbook, *Electrodeposition of Alloys,* provides many electrolyte formulations for a wide array of alloys and is still a good starting point.[4]
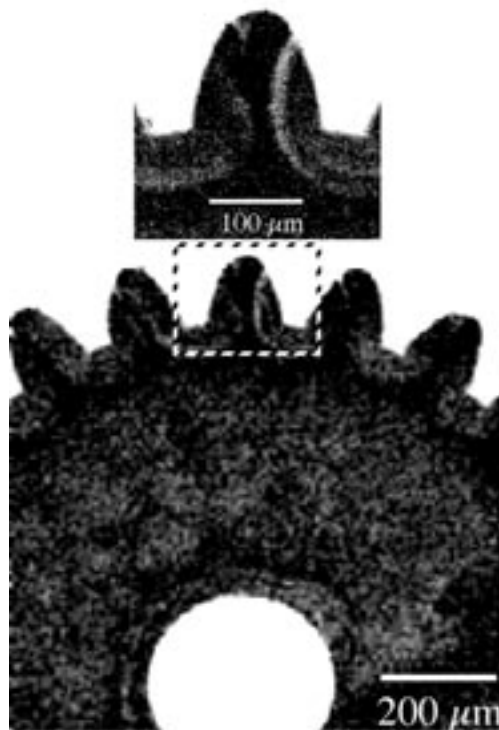

FIG. 2. *Composition map for half a Ni-Fe alloy microgear electrodeposited through a polymer mask. The upper image is a blow-up of the tooth shown in the dashed box.*

Finally, periodic variation of the current or potential may be used to produce multilayer alloys with nanometer features.[5]

Figure 2 shows how the basic principles discussed above can influence the uniformity of a deposit. The image is an energy dispersive X-ray composition map from the upper half of a Ni-Fe alloy microgear electrodeposited through a polymer mask, with one tooth blown-up to show additional details. The composition map shows that the gear has substantial variations in the ratio of Ni-to-Fe. Detailed analysis of the gear indicates that a combination of nonuniform mixing and nonuniform current distribution causes these composition variations in the microgear.[6] Changing the electrolyte formulation reduced the mass transfer sensitivity of the system, eliminating much of the observed variation. Generally, mixing and current distribution issues can cause alloy nonuniformities over a wide range of length scales.

To summarize, high-quality alloy electrodeposition requires more than a bucket, electrolyte recipe, substrate, counter electrode, and a power supply. It also requires attention to cell geometry, substrate preparation, and electrolyte mixing conditions. ∎

References

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