Is electrodeposition indeed versatile? – A case of Al-Mg alloy deposition from organometallics

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Electrodeposition is often lauded as versatile in obtaining the desired composition, morphology and phases in the deposits. However, can all these features be achieved together to any desirable extent through electrodeposition? To address this question the dependencies among composition, morphology and phases need to be analysed meticulously; and the reasons for these dependencies must be understood. Electrodeposition is, primarily, driven by either applied potential or current. These parameters govern the concentrations of depositing ions in a multi-component system (i.e. two or more metals) from the electrolyte near the cathode. Eventually, how these ions settle on the cathode depends on various coupled kinetically and thermodynamically imposed effects. For instance, the rate of ion deposition, temperature, cathode etc. decide the phases (equilibrium or otherwise) and morphologies (via surface diffusion of ions). This offers an extremely complex scenario and renders it extremely difficult to answer the above mentioned, fundamentally, and industrially, important question.

Addressing the question is attempted through electrodeposition of Al-Mg alloys – an industrially important system. Al-Mg alloys were galvanostatically electrodeposited from $Na[AlEt_4]+2Na[Et_3Al–H–AlEt_3]+2.5AlEt_3+6$toluene at permissible ranges of current densities (60-150 mA cm^{-2}) and temperatures (60, 90 °C) using Mg anode on rotating Cu cathode in an inert atmosphere using a PAR 263 workstation [1]. Beyond these permissible ranges, either no deposit was obtained or the electrolyte evaporated. Within the permissible ranges, Surprisingly, higher current densities and temperatures encourage less noble-Mg deposition, falsely suggesting 'Regular' electrodeposition behaviour by Al-Mg system according to Brenner's categorisation. However, the plot between Mg/Al ratios in deposits vs those in electrolytes is always above the composition reference line (i.e. line of Mg/Al in deposit = Mg/Al in electrolyte, Figure 1(a)) [2,3]. This classifies this system as 'Anomalous' (Brenner's categorisation). This is because of the difficulty in extracting Al^{+3} from $[Et_3Al–H–AlEt_3]^-$ for its deposition. An almost unique relation can be seen between the obtained morphologies and composition ranges. Crystallographically consistent faceted/feather-like morphology always possesses 1-7 atom% Mg [4]; Smooth globules contain up to ~20 atom% Mg [5]; and rough globules always form over smooth ones and possess ~65-80 atom% Mg (Figure 1(b)) [5]. These relations are mostly due to the surface energy effects experienced by these morphologies. Moreover, irrespective of the morphology, the compositions below ~20 atom% Mg always yield metastable supersaturated Al-rich fcc solid solutions. Those within ~65-80 atom% Mg form metastable supersaturated Mg-rich hcp solid solutions. Compositions between 20-65 atom% Mg are always prohibited due to spatially drastic switchover from fcc to hcp phases – confirmed by extensive microstructural characterisation and supported by thermodynamic common tangent construction in ΔG-composition curves [6]. The results clearly indicate that only certain compositions, morphologies and phases are possible in the Al-Mg system. Hence, electrodeposition of Al-Mg is not versatile unlike, possibly, those of the well-established systems e.g. Ni-Co or Ni-Cu. Most probably this is because Al-Mg is not a thermodynamically isomorphous system the latter. Being non-isomorphous, accommodation of any concentration of Mg in Al or vice versa in the deposits is not possible, resulting in only certain composition ranges, morphologies and phases.

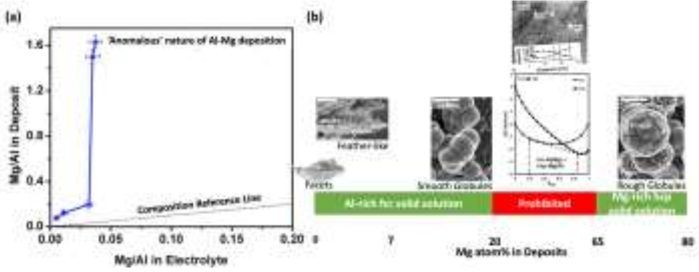

Figure 1. (a) Al-Mg composition line; (b) Feasible Mg compositions in deposits corresponding morphologies and phases.

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