

Materials Science and Engineering Doctoral Defense

Morphology Evolution during Dealloying at High Homologous Temperature

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abstract

Dealloying, the selective electrochemical dissolution of an active component from an alloy, often results in nanoscale bi-continuous solid/void morphologies. These structures are attracting attention for a wide range of applications including catalysis, sensing and actuation. The evolution of these nanoporous structures has been widely studied for the case at low homologous temperature, TH, such as in Ag-Au, Cu-Au, Cu-Pt, etc. Since at low TH the solid-state mobility of the components is of order 10^{-30} cm²s⁻¹ or less, percolation dissolution is the only mechanism available to support dealloying over technologically relevant time scales. Without the necessity of solid-state mass transport, percolation dissolution involves sharp transitions based on two key features, parting limit and critical potential. Dealloying under conditions of high TH, (or high intrinsic diffusivity of the more electrochemically reactive component) is considerably more complicated than at low TH. Since solid-state mass transport is available to support this process, a rich set of morphologies, including negative or void dendrites, Kirkendall voids and bi-continuous porous structures, can evolve. In order to study dealloying at high TH we have examined the behavior of Li-Sn and Li-Pb alloys. The intrinsic diffusivities of Li were measured in these alloys using electrochemical titration and time of flight measurements. Morphology evolution was studied with varying alloy composition, host dimension and imposed electrochemical conditions. Owing to diffusive transport, there is no parting limit for dealloying, however, there is a compositional threshold (pPD) as well as a critical potential for the operation of percolation dissolution and the formation of bi-continuous structures. Negative or void dendrite morphologies evolve at compositions below pPD and at large values of the applied electrochemical potential when the rate of dealloying is limited by solid-state mass transport. This process is isomorphic to dendrite formation in electrodeposition. Kirkendall voiding morphologies evolve below the critical potential over the entire range of alloy compositions. We summarize our results by introducing dealloying morphology diagrams that we use to graphically illustrate the electrochemical conditions resulting in various morphologies that can form under conditions of low and high TH.