Galvanic Deposition of Mo atop Al 6061 Alloy

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Technological applications of Mo thin films include back contacts for photovoltaic devices and corrosion-resistant coatings. Mo thin film deposition currently requires expensive vacuum methods, but electrochemical methods are often less expensive, easier to scale-up, and more amenable to high-volume manufacturing. Electrochemical deposition of refractory metals from aqueous electrolytes is often difficult due to their cathodic standard reduction potentials, multiple valence states, and complex oxy-anion solution chemistry.

We recently demonstrated galvanic deposition of Mo films onto 6061 Al alloy from aqueous solutions containing 1 mM HNO_3 and 10 mM $MoCl_5$. Deposition for 1hr yields an 11 µm thick Mo film, which appears to be elemental and amorphous, that also contains 18 atom% Al due to Al dissolution and transport through the growing Mo film. X-ray diffraction (XRD) of the Mo films after annealing in an oxidizing environment show a mixture of peaks arising from MoO_2 and MoO_3.

Before and after annealing/oxidation, the Mo/Mo oxide films were studied by linear voltammetry and electrochemical impedance spectroscopy in 0.5 M H_2SO_4 and in 3.5 wt% NaCl electrolyte at pH 2, 7 and 12 to ascertain their effectiveness for corrosion inhibition. Surprisingly, voltammetry studies of the original Mo film and the oxidized Mo film in these four electrolytes are quite similar. However, the impedance results are quite different.

The impedance results for the galvanic Mo film can be fit to a Randle's equivalent circuit, with the differential capacitance (C_d) replaced with a constant phase element. In all four electrolytes, the best-fit equivalent circuit parameters are similar to those expected for a bare metal electrode. For example, the charge transfer resistance (R_{ct}) ranges from 20-430 Ω-cm^2. On the other hand, the impedance results for the oxidized Mo film appear to be anomalous, and cannot be fit with a simple equivalent circuit. Taken together, the voltammetry and impedance results suggest that the original galvanic Mo films are covered with a Mo native oxide that is not an electrical insulator.

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