# Electrodeposition and Characterization of Sacrificial Copper-Manganese Alloy coatings


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Electrodeposited coatings of manganese and its alloys potentially combine high corrosion protection performance, good tribological behavior and suitable mechanical properties. Therefore, they have been studied as a replacement for cadmium in the sacrificial protection of steel. Pure Mn coatings with good quality can be obtained by electrodeposition, but the as-deposited ductile γ-Mn (BCT) will gradually transform to brittle α-Mn (BCC) after aging for several days at room temperature. The codeposition of Cu, a FCC metal, with Mn can stabilize manganese in its ductile gamma form. Here we report on the electrodeposition of MnCu alloys, as well as their structural, microstructural, chemical, mechanical and corrosion properties.

MnCu electrodeposition was studied under different current densities (cds), at pH 6.4-6.6 and pH 2.6-2.8, and at different cupric ion concentrations. The basic solution contains $MnSO_4$ (0.59M), $(NH_4)_2SO_4$ (1M) and $CuSO_4$ (0.0025-0.02M). Electrochemical properties of these solutions were investigated by potentiodynamic polarization and cyclic voltammetry. Typical potentiodynamic curves are shown on Figure 1.

Electrodeposition was conducted galvanostatically. Three kinds of coatings were obtained: spongy Cu-rich films at low cd; compact, uniform and silvery matte films at intermediate cd (Type I), and glossy and compact coatings at high cd (Type II). The optimal current density ranges for different [$Cu^{2+}$] are shown in Figure 2. Current efficiency for plating Type I coating is between 70-80%. Typical microstructures are shown in Figure 3. Type I contain crystalline γ-Mn (BCT) and FCC Cu, while Type II shows an amorphous structure as determined by XRD. XPS shows that Type I films contain mainly Cu(0), Mn(0) as well as a little amount of Cu(I-II), Mn(II-IV) and O. Type II films contain mainly oxides of Cu and Mn, but also a considerable amount of Cu(0) and Mn(0). Cu:Mn atomic ratio in the coatings is rather stable in the current density range for each type of coatings, but varies with the cupric ion concentration in solutions. More [$Cu^{2+}$] can result in a higher Cu content in MnCu coatings, but the current range to obtain good quality Type I coating would increase correspondingly. The γ-Mn (BCT) structure can be greatly stabilized by the codeposition of even a very small amount of copper (1.5%), and no γ to α transformation could be detected after 7 months. Hardness, measured with a Hisitron nanomechanical properties system, was determined to be 0.11 and 0.54GPa for Type I and Type II coatings, respectively. Friction coefficients, measured with a Nano Indenter II system, were 0.68 (Type I) and 0.54 (Type II), respectively.

The corrosion resistance of both types of coatings was studied by anodic polarization in 3% NaCl, pH3 (Figure 4). The corrosion potential and current were calculated by fitting these curves with the Stern-Geary equation. Codeposition of copper causes a high corrosion rate and a more positive corrosion potential due to the galvanic coupling of Mn and Cu compared with pure manganese coatings, but it can also provide a barrier or passive layer at $-0.5 \sim 0.1V_{SCE}$.


**Acknowledgement**

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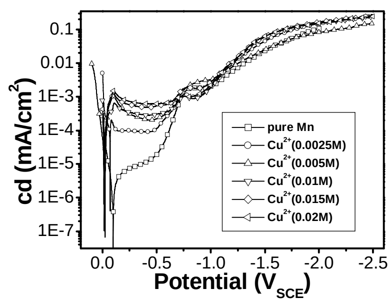



**Figure 1** – Potentiodynamic plots of solution $MnSO_4$ (0.59M), $(NH_4)_2SO_4$ (1M) and $CuSO_4$ (0-0.02M) at pH 2.6-2.8. The increase of $Cu^{2+}$ increases the discharge current of $Cu^{2+}$ at low cathodic voltage.

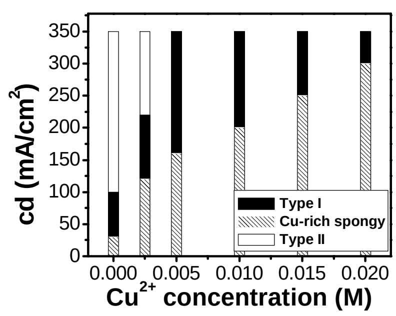
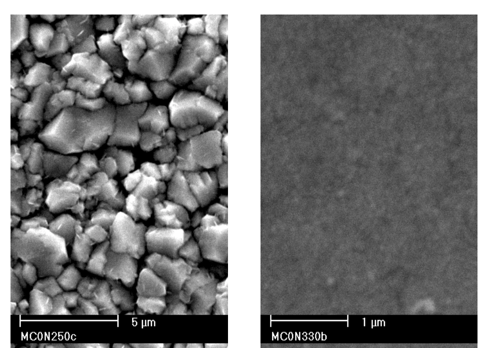



**Figure 2 -** Optimal cd condition of solutions containing different [$Cu^{2+}$].




Type I: 250mA/$cm^2$ Type II: 330mA/$cm^2$

**Figure 3** – Typical SEM micrographs of MnCu coatings obtained from basic solution containing 0.0025M $CuSO_4$ at pH 2.6-2.8.

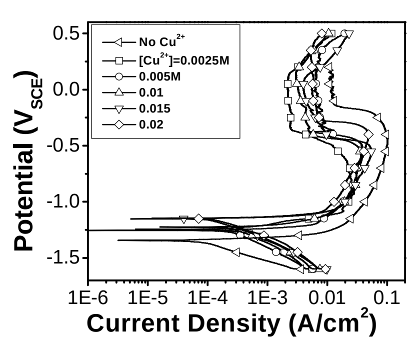



**Figure 4** – Anodic potentiodynamic behaviors of MnCu coatings obtained at different [$Cu^{2+}$].