Electrodeposition of Sacrificial Tin-Manganese Alloy Coatings

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As a substitute for cadmium in the sacrificial protection of steel, electrodeposited coatings of manganese alloys potentially combine high corrosion protection performance, good tribological behavior and suitable mechanical properties(1).

On the basis of the development of sound manganese coatings(2), we present here a study of composition (EDAX), structure (XRD), morphology (SEM) and corrosion resistance (E_{corr} *vs.* time) of tin-manganese coatings electrodeposited from a sulfate bath with addition of ammonium sulfate. The effect of citrate, tartrate, EDTA and gluconate complexing agents on the above process has also been investigated.

Formulations of the electrolytes are given in Table 1. All solutions contain $[(NH_4)_2SO_4]$=1M and pH was between 2.5 and 3.0.

Table 1 - Electrolyte Formulation

	M_nSO_4	S_nSO_4	Other additives
Sn-1	/	0.01M	/
Mn-1	0.59M	/	/
SM-1	0.59M	0.01M	/
SMC-1	0.59M	0.01M	Citrate 0.01M
SMT-1	0.59M	0.01M	Tartrate 0.01M
SMED-1	0.59M	0.01M	EDTA 0.01M
SMG-1	0.59M	0.01M	Gluconate 0.01M

Potentiodynamic Behaviors

Potentiodynamic behavior of the solutions in Table 1 has been measured in a three electrode, two compartment prismatic cell at room temperature (25°C) without stirring. The results are shown in Figure 1. Manganese ion discharging ability could be enhanced by codeposition with tin at low current density to form Sn-Mn alloys.

Electrodeposition of Sn-Mn Alloy and properties

Tin-manganese alloys were electrodeposited galvanostatically at room temperature from the solutions in Table 1 with names starting with SM. Current density (CD) was varied from 30 to 330 mA/cm^2. No stirring was employed. With increasing CD, Sn content decreases and Mn content increases (Fig. 2); correspondingly, coating appearance gradually changes from gray to dark for each bath.

X-ray diffraction (Figure 3) shows that, for simple sulfate solution (SM-1), nearly pure β-Sn(tetragonal) is obtained at 10 mA/cm^2. Mn^{2+} can be codeposited at 20 mA/cm^2, which is not possible for pure Mn, yielding mainly $MnSn_2$ (tetragonal) and other Sn-rich intermetallics. With increasing Mn content (60%~70%), γ-Mn was also present. Higher CD can yield an amorphous structure, as indicated by the broadened diffraction peak in Fig. 3 at 330 mA/cm^2.

The evolution of E_{corr} with time for nominal 10μm thick films in sodium sulfate/borate solutions is shown in Figure 4, left. The existence of $MnSn_2$ phase and other intermetallics is thought to be the main reason for the improved corrosion resistance of tin-manganese alloy compared with pure Mn. With the addition of other substances such as EDTA and gluconate and carefully controlling CD, the deposits showed mainly the $MnSn_2$ intermetallic phase (Figure 4, right).

Acknowledgement

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References

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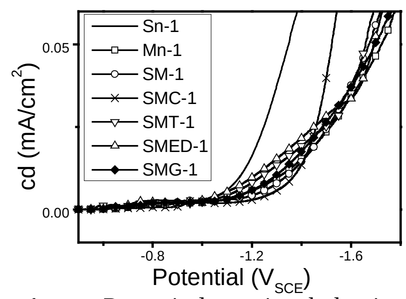

Figure 1 – Potentiodynamic behavior of Sn-Mn electrodeposition bath at room temperature

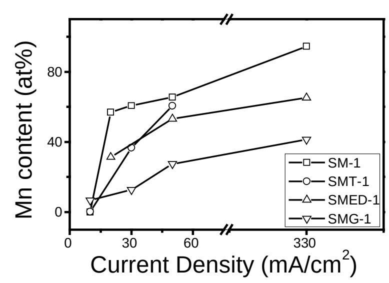

Figure 2 – Dependence of alloy composition on current density for alloy coatings obtained from various solutions

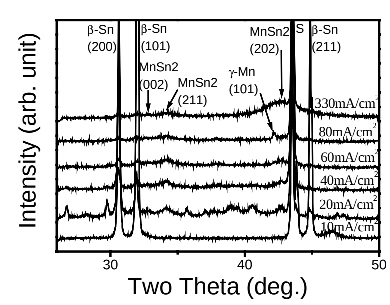

Figure 3 – XRD patterns of alloy coatings obtained from solution SM-1 at different current densities

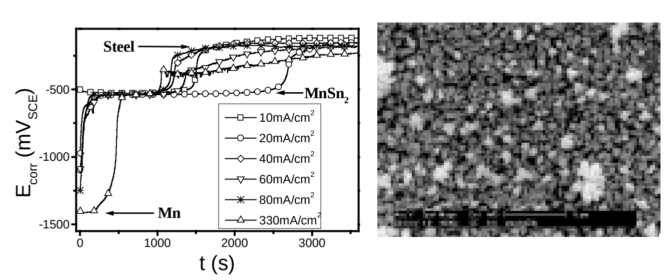

Figure 4 – Left – E_{corr} *vs.* time plots for Sn-Mn alloy coatings obtained from solution SM-1 immersed in 0.5M Na_2SO_4+0.5 M H_3BO_3 at pH 3.0. Right – SEM micrograph of Sn-Mn coating containing mainly $MnSn_2$ obtained from solution SMG-1