

Influence of Sulfate in Acid Tin Methanesulfonate Plating Solutions

In the development of E-PURE MSA® Arkema studied the effects of various impurities on the electroplating of tin in Methane Sulfonic Acid based plating solutions. The following article summarizes our research on the effect of sulfate in acid tin methanesulfonate plating solutions.

Methanesulfonic acid, $\text{CH}_3\text{SO}_3\text{H}$ (MSA), is often used as the acid electrolyte in the plating of electronic components. The popularity of MSA is due in large part to its ability to solubilize metals that may be insoluble in other mineral or organic acids. Tin and tin-lead plating electrolytes use MSA almost exclusively because MSA is a non-oxidizing acid and, as such, minimizes the formation of stannic sludge.

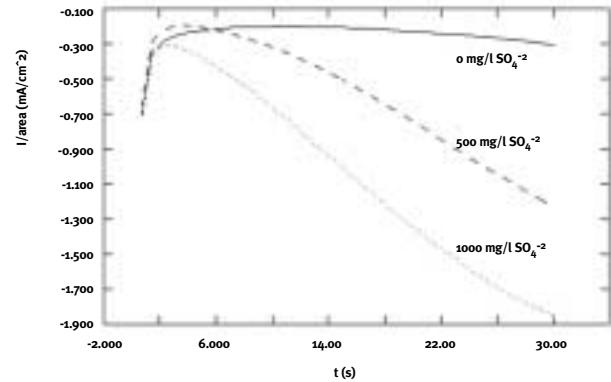
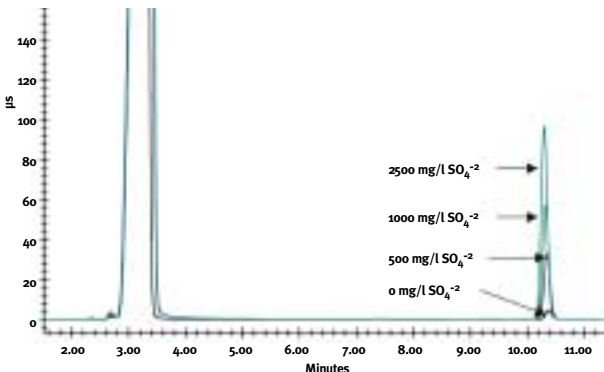
Several manufacturing routes are available to produce MSA, including the use of methyl mercaptan, CH_3SH , alkyl disulfides or polysulfides, RS-Sx-SR , or dimethylsulfate, $(\text{CH}_3)_2\text{SO}_4$ raw materials. Depending upon the precursor molecules and the oxidant used to produce MSA, sulfate may also be produced as a by-product of the oxidation reactions. The concentration of SO_4^{2-} in commercially available 70% MSA may range from ~20 mg/l to 100 mg/l.

As sulfate may be present in 70% MSA, some trace amount may also be added to a tin or lead-free tin plating solution. To address questions about the impact of sulfate on plating performance, Arkema scientists have recently studied the role of SO_4^{2-} in pure Sn-MSA plating solutions and its impact on matte tin deposit properties.

Effects of SO_4^{2-} on Tin Electrodeposition:

Sulfate is likely present in most tin and lead-free MSA electrolytes. Therefore, its role on the reduction of stannous to metallic tin was studied in detail. It was found that small amounts (< 2000 mg/l) may actually assist in depositing tin, particularly at low overpotentials.

Ion Chromatogram Showing SO_4^{2-} in Sn Solutions

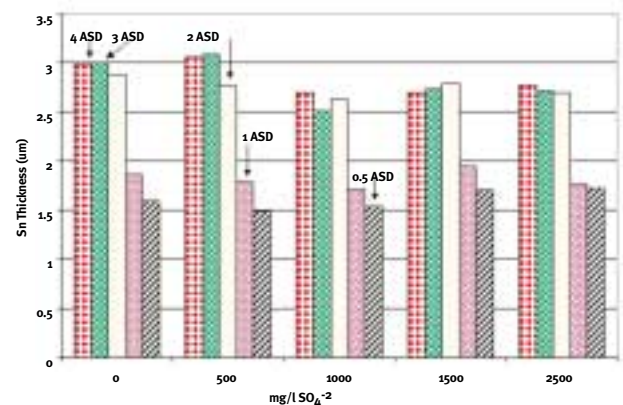


Potential Step Measurements Showing More Rapid Tin Deposition with Sulfate in the Plating Solution

Effects of SO_4^{2-} on Sn Thickness vs. Current Density:

Because electronic components can have different geometries, the current density will vary across the parts. X-ray fluorescence (XRF) studies show the tin thickness is not affected to any appreciable extent by SO_4^{2-} in the matte tin electrolytes:

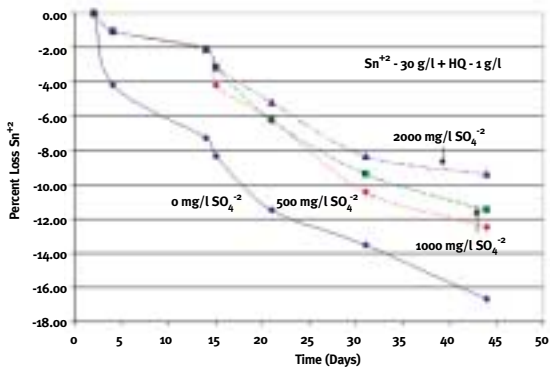
There is only a modest decrease in tin thickness below 3 ASD and 100 mg/l SO_4^{2-} . However, a typical sulfate concentration in a tin plating solution is ~25 mg/l, so one expects no impact of sulfate on the tin thickness at a given current density.



Effects of SO₄⁻² on Tin (IV) Oxidation:

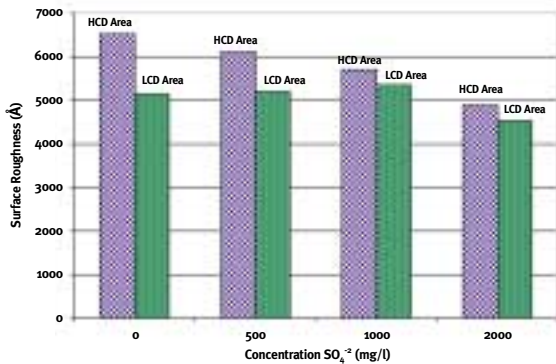
Intentional additions of SO₄⁻² from 500 mg/l to 2000 mg/l in Sn-MSA plating solutions (2,500 mg/l to 10,000 mg/l in 70% MSA – levels never encountered in modern manufacturing processes) produced no additional Sn(IV) over a thirty-day period compared to a SO₄⁻²-free Sn solution. In fact, it appears that small amounts of sulfate may actually be beneficial in controlling stannic formation in these solutions. Thermodynamic calculations show the free energy for the reaction between Sn⁺² and sulfate is favorable (-33.00 kcal/mol) indicating a possible complex of stannous ion with sulfate thus minimizing the propensity for sludge generation.

$$\Delta G_{rxn} = (\Delta G^0_f(\text{SnSO}_4) - [(\Delta G^0_f(\text{Sn}^{+2}) + (\Delta G^0_f(\text{SO}_4^{-2}))])$$



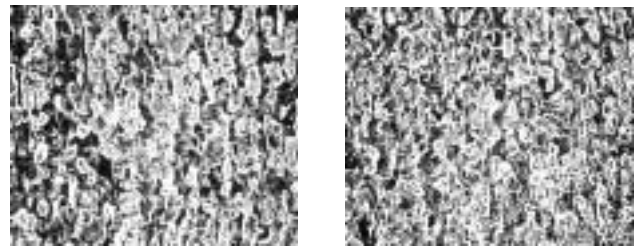
Effects of SO₄⁻² on Surface Roughness:

Increasing the concentration of free sulfate in the matte tin electrolytes from 500 mg/l to 2000 mg/l resulted in little change in the surface roughness of the matte tin coatings:

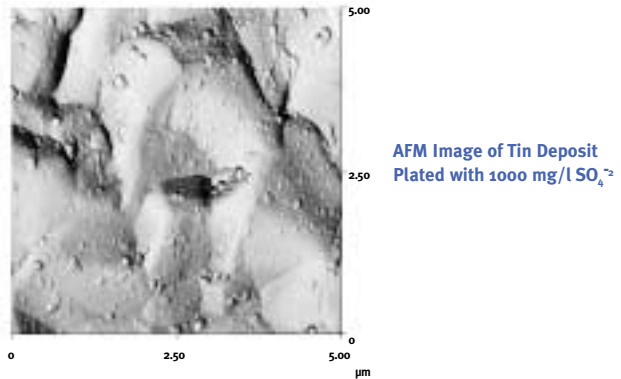


The sulfate remains soluble in the acid tin solution and helps to control the concentration of stannic in the plating electrolytes. Some sulfate may actually be beneficial in the Pb-free solutions in precipitating undesirable cations such as lead and antimony.

Effects of SO₄⁻² on the Surface Morphologies of Tin Coatings: Surface analysis techniques such as optical microscopy, scanning electron (SEM) and atomic force (AFM) microscopies were used to study changes in the tin deposit morphology with increasing amounts of sulfate in the plating electrolyte. It was found that sulfate has very little impact on the surface features or grain sizes.



Dark-Field Images of Tin Deposits (Left – No SO₄⁻²; Right – 2,500 mg/l SO₄⁻²)



AFM Image of Tin Deposit Plated with 1000 mg/l SO₄⁻²

Conclusions: Sulfate in acid tin solutions does not pose any significant problems at concentrations < 2000 mg/l (~10,000 mg/l in 70% MSA). The SO₄⁻² remains soluble in the tin electrolytes and is not co-deposited, nor does it adhere to the matte tin coatings. It has little influence, if any, on the electrochemical reduction of Sn⁺², the roughness, deposit thickness, composition, or morphology of the matte tin deposits.

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