Analytical Techniques for Problem Solving



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The Effect of Chromium Contamination In a Tin Plating Bath

A major wire manufacturer in the United States plates tin (Sn) on copper wire for telecommunication and military applications. The wire is plated from a methanesulfonic acid (MSA) electrolyte at current densities in the range of 100 to 200 mA/cm², at line speeds of ~400 meters/minute. The plating process must be carefully controlled to produce the highest quality wire at the lowest cost. Key parameters to control in the plating process are the concentration of the following: tin, acid, wetting agent, grain refiner, antioxidant and contaminants.

Problem

Excessive stannous concentration decrease was experienced in the plating baths during normal operating conditions, accompanied by significant Sn containing sludge at the bottom of the plating tank. As discussed previously, the Sn concentration must be controlled to produce the desired product quality; furthermore, Sn usage is one of the main costs associated with this process. The loss of Sn as sludge, therefore, affects both quality and cost. Routine chemical and materials diagnostics found that—with the exception of stannous concentration—all other chemical constituents (acid, wetting agent, grain refiner and antioxidant) were within working range.

Analysis

Impurities were suspected of having a detrimental effect and of being responsible for the problem. Iron and chrome had been reported to accelerate stannous oxidation because of the rich redox chemistries they inherit. Inductively Coupled Plasma (ICP) performed on the production solution samples exhibited very high levels of iron and chrome; 0.7 g/L and 0.2 g/L, respectively. In a separate study, the presence of iron, up to 15 g/L, did not cause substantial stannous oxidation in an MSA medium, which was the electrolyte used by the wire manufacture. Therefore, chrome was suspected as the primary source of the problem.

In order to confirm the above assessment, the following experiments were carried out in the laboratory. 0.2 g/L of chrome (in the form of Cr^{3+}) was added to a newly prepared tin plating solution, and air was bubbled through the test vessel to introduce the oxidation source, oxygen. Solution flow or agitation was provided with a rotating shaft to mimic the solution agitation in production. As a reference, a tin plating bath was prepared without chrome and tested in an identical manner. After two and a half days, a 20-percent reduction of stannous ion concentration from the solution containing Cr^{3+} was observed. Fine solids were also observed at the bottom of the vessel. The reference solution showed no reduction of the stannous ion concentration, and no solids were present.

Solution

Having confirmed that Cr^{3+} was the source of tin concentration drop, a solution to the problem was required. Short term, it was important to recover the existing plating baths (450 gal), because this represented a significant cost to the customer; long term, it was important to determine the source of the Cr^{3+} .



Two methods, standard carbon treatment and "clarification," were utilized to reduce the presence of Cr^{3+} in the plating solution. In the latter case, "clarification" entails the use of a polymeric flocculent to precipitate the unwarranted contaminant. Results are summarized in the table.

The following recommendations were submitted to production:

- For the "troubled" plating bath, a clarification treatment is required.
- For future process control, periodic analysis of chrome should be implemented.
- Sources of chrome contamination should be identified for preventive maintenance.

Conclusion

The production site ultimately identified the source of the chrome contamination: stainless steel washers, wrenches, bolts and nuts at the bottom of the plating cell. Now that these items have been removed, this problem has not reoccurred. *Pass*

Removal of Cr³⁺ & Fe²⁺ After Carbon Treatment & Clarification

Treatment of Sample	Cr, PPM Fe, PPM	
As received	190	713
Carbon treatment	119	560
Clarification	not detectable	not detectable