Brush Plating of Tin-Zinc Alloy as an Alternative of Cadmium

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Introduction

Sacrificial coatings are applied to surfaces both by bath and by selective brush plating to protect the underlying substrate from corrosion. The sacrificial coating corrodes in preference to the substrate, a property which is especially important when the substrate is scratched or damaged. Cadmium has long been used to provide this protection for structures, equipment and fasteners. It is easy to plate and it has desirable properties that include corrosion protection, lubricity, anti-galling, electrical conductivity, and low hydrogen embrittlement.

Government mandates and environmental concerns are driving manufacturers to find alternatives for cadmium. Developing a suitable replacement for cadmium plating is essential for the protection of high strength steel components of aircraft. The success of the tin-zinc alloy in the automotive industry should help provide the impetus to advance its application as an alternative for the cadmium plating in aircraft industry.

Although cadmium plating has been replaced by tin-zinc and other zinc alloys in the automotive industry, it is still being used in the aircraft industry on high strength steel components such as landing gear for corrosion protection. Cadmium plating remains the choice for aircraft components as the plating does not cause hydrogen embrittlement (HE), which degrades the mechanical properties of high strength steels. But because of its toxic nature, there is a tremendous amount of pressure both in Europe and in the US to stop its use. Therefore, identifying a suitable, non-embrittling cadmium replacement is of great interest.

SIFCO Applied Surface Concepts has developed a new, non-embrittling, Tin-Zinc brush plating solution.

Tin-Zinc Alloys

Tin-zinc alloys offer excellent sacrificial corrosion protection for steel by combining the barrier protection of tin and the galvanic protection of zinc, without the bulky corrosion product associated with a simple zinc coating. In addition to corrosion protection, the tin-zinc alloy provides good lubricity, wear resistance, and excellent solderability.

Figure 1

Chromate treatment is being applied to a main landing gear bushing brush plated with a sacrificial coating

A Review of Tin-Zinc Electroplating Solutions

As a precursor to the development of its new Tin-Zinc brush plating solution, SIFCO reviewed and evaluated the performance of both alkaline and neutral Tin-Zinc baths.

Although the hardness and corrosion resistance of the alkaline bath were acceptable, the elevated solution temperature required for the deposition of the Tin-Zinc was highly detrimental to the anode cover material that is a requirement for brush plating. But most importantly, the plated deposit did not pass hydrogen embrittlement testing.

The neutral Tin-Zinc baths performed similarly. Although more easily applied at room temperature and with acceptable corrosion protection, the deposits failed to pass hydrogen embrittlement tests – even after a relief bake.

SIFCO Electrolyte for Brush Plating

SIFCO Applied Surface Concepts has developed a neutral, sulfate-glucinate Tin-Zinc solution, SIFCO Process® Tin-Zinc LHE Code 4019 that provides a deposit of 80% tin and 20% zinc, and contains no toxic chemicals. The various electrolytes and plating conditions investigated in this study are shown in Table 1.

Tests with type 2a HE rings and type 1a.1 HE notch bars have shown that when deposited at > 50 °C, the deposit meets the ASTM 519 requirement without a post plating relief bake. Plating at a lower temperature does, however, require a post plating relief bake.

Further, our research identified a neutral nickel deposit that can be applied prior to the tin-zinc deposit plated at room temperature, eliminating the need for a post plating HE relief bake for high strength steel. Tests with both of type 2a HE rings and type 1a.1 HE notched bars demonstrate that the tin-zinc brush plating process at room temperature passes the HE test if the neutral nickel pre-plate is applied.

Table 1 Comparison of tin-zinc electrolytes for brush plating

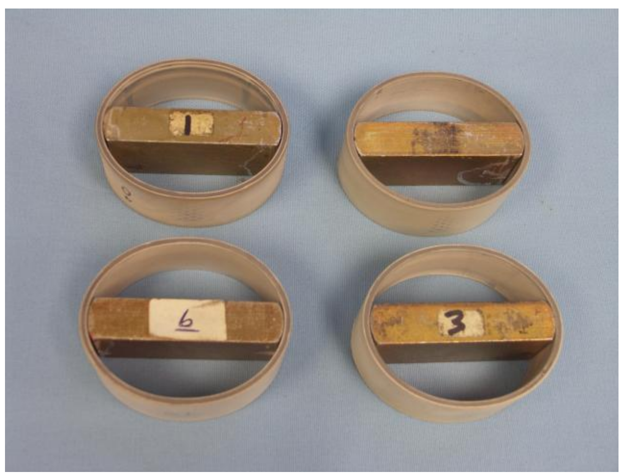
	Alkaline	Neutral based	SIFCO 4019 Neutral
Solution pH	> 13.0	6.0 ~ 7.0	6.0 ~ 7.0
Metals (g/l)	88 ~ 100	~ 35	32 ~ 36
Active metal ingredients	Sn^{4+}, Zn^{2+}	Sn^{2+}, Zn^{2+}	Sn^{2+}, Zn^{2+}
Cathode current density, ASI	0.5 ~ 2.0	0.5 ~ 1.5	0.5 ~ 1.5
Plating temperature, °C	60 ~ 70	18 ~ 22	20 ~ 60
Cathode efficiency, %	~ 80	~ 40	~ 40 at 20 °C ~ 80 at 50 °C
Plating rate, mil/min	~ 0.13 at 1 ASI	~ 0.11 at 1 ASI	~ 0.11 at 20 °C, 1 ASI ~ 0.22 at 50 °C, 1 ASI

As a replacement for cadmium, brush plated Tin-Zinc would be applied onto localized areas of new parts, or for localized touch-up on repair parts. SIFCO's Tin-Zinc provides two options for the application of a non-embrittling Tin-Zinc.

It is generally accepted that it is the absorption of the hydrogen atom that causes hydrogen embrittlement. At high temperature, hydrogen atoms form stable hydrogen molecules at a high rate that alleviates the problem of hydrogen absorption. High temperature also improves plating efficiency that generates less hydrogen. Therefore, plating at an elevated temperature reduces the problem of hydrogen embrittlement.

The absorption of the hydrogen atom by the steel substrate can also be impeded by a nickel barrier layer. When hydrogen atoms are generated during a plating process, they can be absorbed by the steel substrate to cause hydrogen embrittlement. As the diffusion coefficient of hydrogen in nickel is low, the amount of hydrogen that can be absorbed is reduced due to the nickel barrier layer. Both plating at the elevated temperature and pre-plating with a nickel barrier layer are effective ways to prevent hydrogen embrittlement. Figure 1 is a photograph of 2a rings plated with the SIFCO's Tin-Zinc Code 4019 that have passed the HE test. Figure 2 is a photograph of 1a.1 notched bars also plated with Tin-Zinc Code 4019 after 200 hours of hydrogen embrittlement testing.

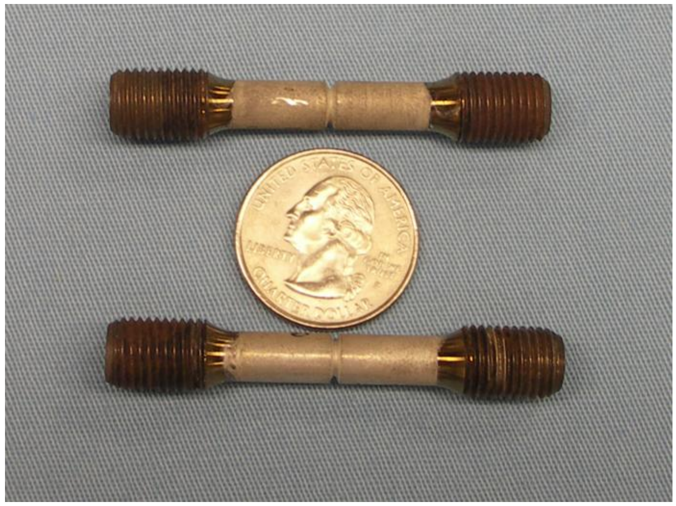
Figure 1
Tin-zinc alloy plated 2a rings with stress bars inserted



The plating efficiency is about 80% at a current density of 0.5 ~ 1.5 A/in^2 if plated at > 50 °C. The plating efficiency is reduced to about 45% if plated at ambient temperature. Temperature does not significantly influence the composition or the hardness of the deposit.

Several samples have been plated on panels and tubes to the thickness of > 3 mil (75 µm). The samples are cross sectioned, mounted, and polished for micro hardness measurement. The load of Vickers hardness test is 10 grams. The measured hardness is between 14 and 20 Vickers with average close to 17 Vickers. There is no significant difference in hardness between the brush plated tin-zinc alloy and the tin-zinc alloy plated by commercially available processes of alkaline or neutral baths.

Figure 2
Tin-zinc alloy plated 1a.1 notched bars after 200 hours of HE test



The tank plated tin-zinc alloy is soft, as is the brush plated tin-zinc alloy. The hardness is comparable to cadmium. It is anticipated that the coating has good lubricity and solderability. Figure 3 is an optical micrograph of the coating on a steel substrate. The polished surface was nital etched to reveal the microstructure of the tin-zinc alloy.

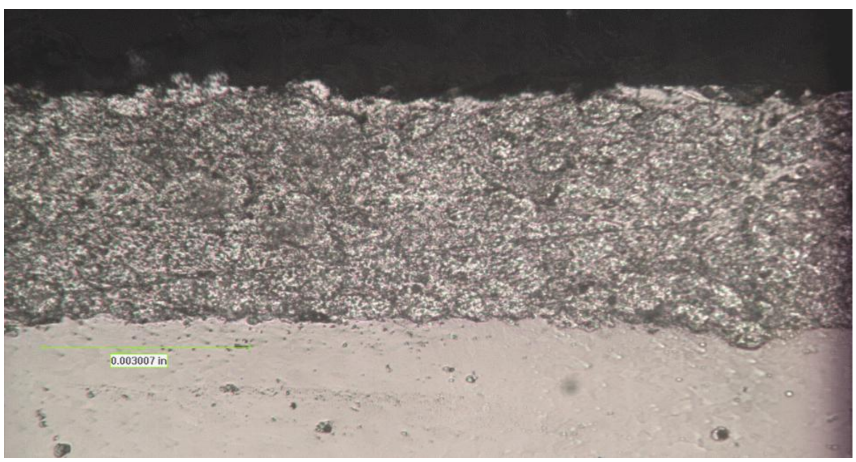


Figure 3
Cross section of tin-zinc alloy coating on steel substrate

The corrosion resistance of chromated (hexavalent) tin-zinc has been extensively examined in the past and the excellent performance is well known. As with cadmium, the poisonous nature of hexavalent chromium has led to its severe restriction (even more than that of cadmium).

In this investigation, the conversion coatings applied to the tin-zinc are limited to trivalent chromium and chromium free coatings.

Without a conversion coating, the white corrosion starts to appear after 24 hour of salt spray. The white corrosion becomes extensive after 96 hour of salt spray. For 0.5 mil of deposit, red corrosion starts around 500 hours of salt spray. A commercially available trivalent chromium conversion coating has been tested on the brush plated tin-zinc. The tin-zinc alloy coating with this conversion treatment endured 96 hours of salt spray with minimum white corrosion. Figure 4 is a photograph of a panel after 96 hours of salt spray. For 0.5 mil of the Tin-Zinc Code 4019 deposit, red corrosion appears between 600 ~ 800 hours of salt spray.

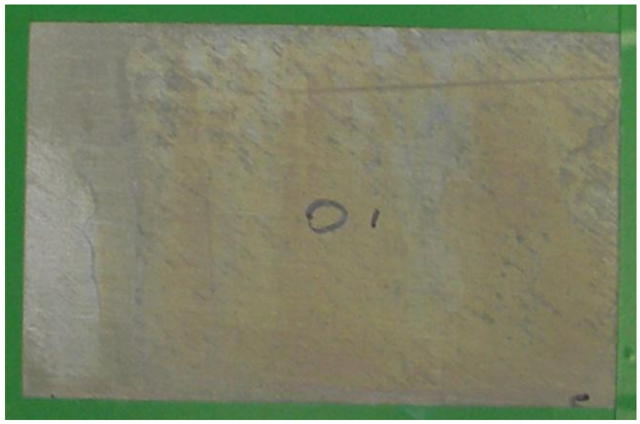


Figure 4
Steel panel with tin-zinc alloy coating and a trivalent chromium conversion coating after 96 hours of salt spray test

Chromium free conversion coating (18, 19) is also tested on the tin-zinc deposit. The active ingredients for the conversion coating are zinc phosphate, fluotitanic acid, ammonium molybdate, and organic polymer. Therefore, it is free of chromium and cobalt salt (another hazardous chemical in some trivalent conversion coatings). The more environmentally friendly chromium free conversion coating has been reported to have performance comparable to a trivalent conversion coating on a zinc deposit (18). There is no report on its corrosion test on a tin-zinc deposit. The brush plated tin-zinc with the chromium free conversion coating performed well in a salt spray test. There was little white corrosion after 96 hours of salt spray carried out following ASTM B 117. Figure 5 is a photograph of the test result. It is comparable or better than the panel with the trivalent chromium conversion treatment. For 0.5 mil of deposit with the conversion coating, red corrosion also appears between 600 ~ 800 hours of salt spray.

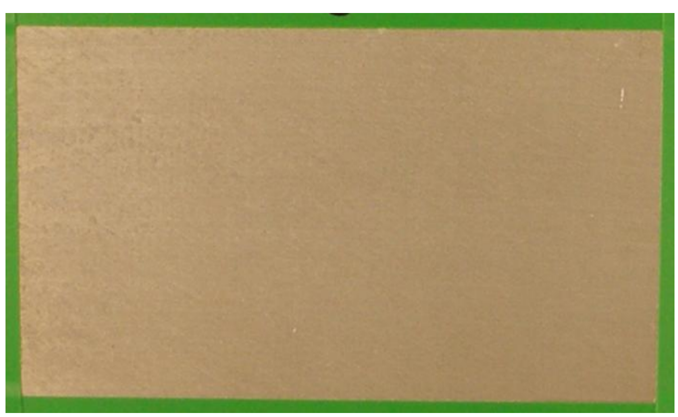


Figure 5
Steel panel with tin-zinc alloy coating and the chromium free conversion coating after 96 hours of salt spray test

Summary
SIFCO Applied Surface Concepts has developed a brush plated deposit, Tin-Zinc, Code 4019, that provides sacrificial corrosion protection without the use of toxic chemicals.

The deposit is 80% tin, 20% zinc by weight. Neutral salt spray tests on the brush plated deposit have shown basis metal protection up to 500 hours with a 0.5 mil coating. When combined with the appropriate conversion coatings (trivalent chromium, or chromium free), the formation white zincate corrosion products is prevented for 96 hours of salt spray.

SIFCO's Tin-Zinc, Code 4019 will meet the ASTM 519 requirement without a post-plating HE relief bake

- When the deposition is carried out at > 50 °C or,
- At room temperature when a neutral nickel preplate is used

SIFCO's Tin-Zinc is a viable cadmium replacement candidate

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