

Mechanism of Additives in Electroplating of Sn-Zn Alloy

By M. An, Y. Zhang, J. Zhang, Z. Yang & Z. Tu

The mechanism of additives in electroplating Sn-Zn alloy has been researched by rotating disk electrode (RDE), cyclic voltammetric stripping (CVS), Hull Cell tests and polarograph methods. The experimental results show that the additives have the property of adsorption on the surface of electrodes, impeding the reaction of electric deposition. This leads to increase of electrochemical polarization, grain refinement, leveling and bright appearance. This paper offers a theoretical mechanism of adsorption, leveling and brightening capabilities of additives. Finally, the values of the optimum leveling capability corresponding to the concentration of the additives is reported.

Tin-zinc alloy plating (70 to 80% tin) has been promoted and used as a partial replacement for cadmium. The alloy offers the best protection for steel and its solderability is excellent. Its friction and wear characteristics are also good. This study resulted in a suitable system and bath composition, including additives and operating conditions. To prove the roles of leveling and brightening by the additive, Sn-Zn alloy (75.8% Sn, 24.2% Zn) electrodeposition has been studied by means of rotating disk electrode (RDE) and cyclic voltammetric stripping (CVS). The cathodic behavior of the additive was investigated by polarograph and Hull Cell tests.

Experimental Procedure

The constituents of the plating solution and operating conditions are as follows:

SnCl ₂ · 2H ₂ O	24 g/L
Na ₃ C ₆ H ₅ O ₇ · 2H ₂ O	80 g/L
ZnSO ₄ · 7H ₂ O	30 g/L
K ₂ C ₄ H ₄ O ₆ · 1/2H ₂ O	25 g/L
(NH ₄) ₂ SO ₄	60 g/L
Additive YJ-1	1.4 g/L
(mixture of peptone and piperonal)	
pH	6
Temp	20 °C

All the diffusion layers on the rotating electrodes had the same thickness, and the relation between their effective thickness δ_{eff} and the square root of rotation speed can be expressed as:

$$\delta_{\text{eff}} = 1.62 \gamma^{1/6} D^{1/3} \omega^{1/2}$$

where δ_{eff} is the effective thickness of the diffusion layer, γ is the coefficient of dynamic viscosity, D is the coefficient of diffusion and ω is the angular velocity.

When the disk rotates at high speed, δ_{eff} is small, expressing the peak; when the disk rotates at low speed, δ_{eff} is large, expressing the valley. If the relation between i and $n^{1/2}$ is linear, it can be judged that the polarization process is controlled by diffusion; also that the additives have leveling capability.

Rotation speeds: $n_1 = 1000$ rpm, $n_2 = 1680$ rpm, $n_3 = 3100$ rpm
Scanning speed: 10 mV/sec.

The CVS method makes the electrode potential of the rotating disk vary cyclically, and the alloy on the electrodes deposits and dissolves alternately. This method can be used to measure the leveling capability. When the electrodes are in a static state, the diffusion layers are comparatively thick, equivalent to a micro-valley, but when the electrodes are rotating, the diffusion layers are comparatively thin, equivalent to a micro-peak.

$$L = \frac{A_s - A_r}{A_s} \times 100\%$$

where L is the leveling capability, A_s is equivalent to the deposit capacity in a micro-valley and A_r is equivalent to the deposit capacity in a micro-peak.

Hull Cell Method

Specimens of low-carbon steel were polished with emery paper for metallography, then scratched with abrasive paper

RED & CVS Methods

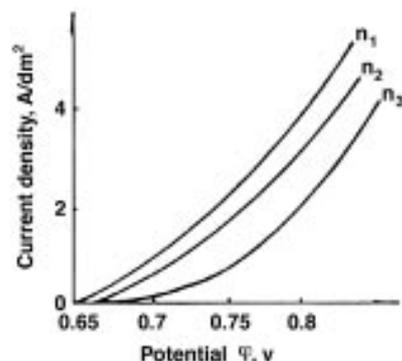


Fig. 1—Variation of current density with rotation speed.

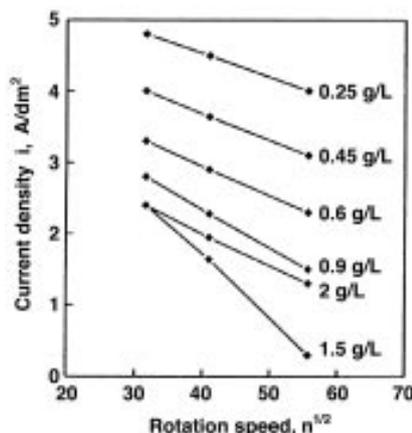


Fig. 2—Relation of i and $n_{1/2}$ for additive concentrations.

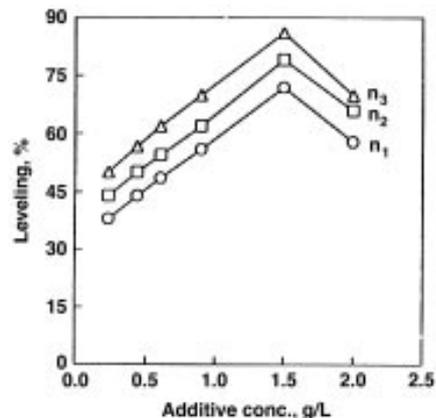


Fig. 3—Relation between leveling capability and additive concentration for different rotation speed.

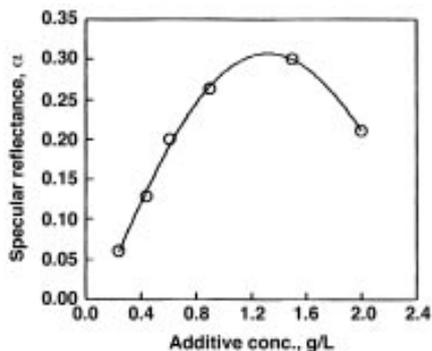


Fig. 4—Change of specular reflectance with concentration of additive.

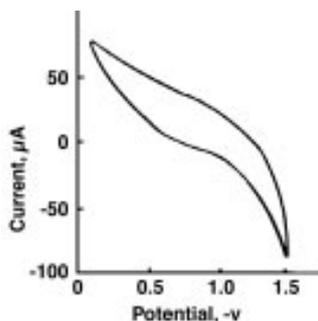


Fig. 5—Cyclic voltammogram of additive YJ-1.

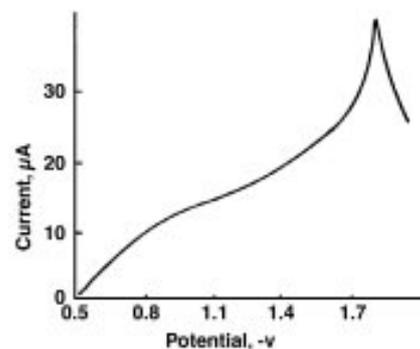


Fig. 6—Polarogram of additive YJ-1.

for water polishing. Next, activated by hydrochloric acid, they are electroplated for 10 min on condition that $i = 2$ A/dm². Finally, the specular reflectance of the electroplated coating was measured by a digital display profile meter. The wavelength of the light source was 565 nm. The specular reflectance of a standard sample is 52 percent. If the light source matches international standards, the specular reflectance will be the glossiness. The specular reflectance can be shown as:

$$\alpha = \frac{I_{il}}{I_r}$$

where α is the specular reflectance, I_{il} is the intensity of incident light and I_r is the intensity of reflected light.

Polarograph Method and CVS Method

The electrolyte solution was prepared with reagent grade chemicals and distilled water, with 1 mol/L KCl solution as a support electrolyte.

Scanning speed: 50 mV/sec, scanning range: $\phi = 0 \sim -1.5$ V.

Results & Discussion

Study of Leveling & Cathodic Behavior by the RDE Method

As shown in Fig. 1, when additive YJ-1 (1.5 g/L) is added to the base solution, polarization in the deposition process will increase with increase of the rotation speed of the electrodes. Under the condition of constant potential, current will decrease slowly with increase of the rotation speed of the electrodes. Figure 2 shows that the relation between i and $n^{1/2}$ is linear. This illustrates that the process of impedance is controlled by diffusion (*i.e.*, additive YJ-1 has the capability of leveling. In the figure, the slopes of the curves grow with the increase of additive concentration. When YJ-1 concentration is 1.5 g/L, the curves are steepest. This illustrates that at that point, the adsorbed quantity of the leveling agent diffused on the micro-convex and concave surfaces of the electrodes shows the most displacement and that leveling capability is also the greatest.

Study of Leveling Capability by the CVS Method

It can be seen from Fig. 3 that additive YJ-1 acts as a leveler. With increase of the additive, leveling action will increase. When the additive concentration reaches the limit of resistance, its leveling capability will be greatest. Also, when the rotation speed of the electrodes increases, its leveling capability will increase as well.

Study of Brightening by the Hull Cell Method

As shown in Fig. 4, when the additive concentration increases, the specular reflectance will increase. When the additive concentration reaches the maximum of leveling capability (corresponding value), the specular reflectance is the greatest and the coating is the brightest. The additive's brightening action is remarkable.

Study of the Electrode Behavior of the Additive by CVS & Polarograph Methods

Figure 5 is a cyclic voltammetric diagram. When $\phi = -0.7$ V, electrochemical reduction takes place and its half-peak potential is $\phi_{1/2} = 0.84$ V. Figure 6 expresses that the polarographic half-wave potential of additive YJ-1 reduced on electrodes, ($\phi_{1/2} = -1.42$ V relative to mercury-film electrode) is basically in agreement with the cyclic voltammetric half-peak potential ($\phi_{1/2} = -0.84$ V (vs. SCE)). This illustrates that while the Sn-Zn alloy deposits, electrochemical reduction really takes place in additive YJ-1.

Conclusions

1. The base solution for electroplating Sn-Zn alloy becomes much more efficient by the addition of additive YJ-1. The additive has the property of adsorption on the surface of electrodes, impeding the reaction of electrolytic deposition. This leads to increase of electrochemical polarization, grain refinement, level coating and bright appearance.
2. In the plating solution, additive YJ-1 promotes leveling. Its optimum leveling capability corresponds to a concentration of 1.5 g/L. The maximum values of leveling can be obtained.
3. Additive YJ-1 can be adsorbed on the surface of cathodes and will be reduced electrochemically at $\phi = -0.7$ V. Because its adsorbing quantity is different on micro-convex-concave surface of cathodes, its impedance is also different. Moreover, the additive joins in the electrochemical reaction. This makes current efficiency decline in micro-concave areas less than that in micro-convex areas. Both of the above-mentioned factors make the deposition capacity in convex areas less than that in concave areas. They make the surface of the coating level and facilitate a glossy appearance.

Editor's note: Manuscript received, March 1998.

References

1. E. Budman & M. McCoy, *Metal Fin.*, **93**, 10 (Sept. 1995).
2. V.S. Vasantha, M. Pushpavanam & V.S. Muralidharan, *Plat. and Surf. Fin.*, **82**, 81 (June 1995).

3. Y.J. Zhang, X.W. Yang & Z.M. Tu, *Chinese J. of Nonferrous Metals*, 7(4), 57 (1997).

About the Authors



Maozhong An is an associate professor in the Department of Applied Chemistry, Harbin Institute of Technology (HIT), 92 West Da Zhi St., Harbin 150001, P.R. China. His research interests include metal finishing and surface treatment. He has published one book and more than 40 papers. He holds an MS from HIT.*



Zhelong Yang is an associate professor in the Department of Applied Chemistry, Harbin Institute of Technology, P.R. China. His research interests include electrolytic and electroless plating. He has published one book and more than 45 papers on electroplating and related fields. He holds a BS from HIT.



Jingshuang Zhang is a professor at the Department of applied Chemistry, Harbin Institute of Technology, P.R. China. He is a laboratory director and accomplished inventor. He has published more than 50 papers on metal finishing and surface treatment. He received his BS degree from HIT.

Yingjie Zhang (no photo available) is an associate professor in the Department of Chemistry, Kunming Institute of Technology, P.R. China. Her research interests include metal finishing and surface treatment. She has published more than 20 papers. She holds an MS from HIT.



Zhenmi Tu is a professor in the Department of Applied Chemistry, Harbin Institute Of Technology, P.R. China. His research interests are electrolytic and electroless plating and metal finishing. He is an Adviser of the Electroplating Association of China, and Vice President of the Surface Treatment Association of Heilongjiang Province. He has published two books and more than 70 papers on metal finishing and related fields.

**To whom correspondence should be addressed.*

The electrodeposition mechanism of the Zn-Ni-Mn alloy was found to be an anomalous type. The high corrosion resistance of the Zn-Ni-Mn alloy, as well as its preferable surface appearance, has been ascertained compared with the electrodeposited Zn-Ni alloy under homogeneous conditions. It was found that Mn can be codeposited with Ni or with Ni and Zn under studied conditions where it does not deposit in its pure form. The incorporation of these additives in the electrolytes modified the composition, morphology, and crystallographic structure of the alloy deposits. Cyclic voltammetry indicated the formation of several alloy phases as cobalt was added to these zinc baths. 3NCP had the greatest impact on the process, limiting the Co content and changing the structure of the deposit.

PROPERTIES OF SOME ALLOY SYSTEMS

Some eutectic alloy systems, such as Bi-Sn, In-Sn, Sn-Ag, Sn-Cu, and Sn-Zn, have been studied very extensively in the past already. Some other systems such as Sn-Bi-Ag, Sn-In-Ag, Sn-Sb, or Sn-Zn-In systems or the eutectic alloys described above doped with other elements are investigated due to their promising mechanical strength and creep resistance. The results of those investigations are briefly summarized below. Hence, addition of 1% Cu dramatically slows coarsening of eutectic Sn-Bi, presumably via similar mechanism.

52In-48Sn

52In-48Sn is considered the lowest melting point practical solder. The mechanism of the four additives in the electroplating process was studied, and the results may provide theoretical guidance for selecting additives for the Cu-Zn-Sn electroplating process.

Graphical Abstract. [Open image in new window.](#) Keywords. Imitation gold plating Cu-Zn-Sn alloy Additives Electroplating. This is a preview of subscription content, log in to check access. Notes.