

ZINC - MANGANESE ALLOY PLATING - A CRITICAL REVIEW

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Hundreds of alloy baths of the commonly plated metals have been reported in the literature and continue to be investigated by plating researchers. The field of zinc alloy plating has undergone enormous development in comparison to any other plating during the last few decades. It is also the fact that in total literage and number of installations, zinc is the leading metal deposited in the electroplating world. Plating electrolytes are subjected to constant change from a multitude of variables such as bath temperature, pH, CD, bath composition, addition agents, impurities, anode polarization, degree of agitation and nature of current. With the increased sophistication of the industry and the introduction of automated bath analysis, control of alloy plating bath may be much less of a factor. The basic reason for plating from an alloy bath is to produce some desired change in the deposit unobtainable from the pure metal bath. The toxicity of cadmium has led to the development of several zinc alloy systems. Such alloys also possesses excellent corrosion resistance in comparison to cadmium. Amongst the four commercially available zinc alloy systems such as zinc - nickel, zinc - cobalt, zinc - iron and zinc - manganese the last one is least investigated though it possesses excellent corrosion resistance. This paper gives a critical review of zinc - manganese alloy deposition system.

Keywords: Alloy deposition, manganese alloys electrodeposition, zinc alloy plating, Zn-Mn alloy plating

INTRODUCTION

In recent years considerable research work has been carried out in the field of zinc and its alloys plating mainly for the automotive field. In this context continuous electro-galvanizing assumes greater importance due to the formation of rust. It is a common practice consumers are dissatisfied with the formation of rust in a newly purchased automobile within one year. As the automobile market is assuming greater importance in the competitive international market, automotive manufacturers throughout the world instituted research and development programs to prevent or at least delay, automotive body rust. In recent years, automobile manufacturers are now offering warranties against body panel rusting through for as long as ten years. Even less expensive cars have non rusting warranties of 5 years. The main combatant in the fight against automotive body rust has been electrogalvanised zinc and zinc alloys. The major culprit in automotive rust is the expensive use of salt in winter to prevent ice formation on highways in cold countries of the world. In presence of moisture this salt creeps into

the crevices inside a car's body and attacks the body steel from the inside out. This type of corrosion is not seen until it has eaten through to the painted outer surface of the car body.

The protective coatings for automotive applications must meet the following requirements [1-3].

- (a) It must offer maximum corrosion protection.
- (b) It should not adversely affect the mechanical properties of steel during mechanical forming operations such as stamping and deep drawing without cracking or flaking.
- (c) During welding, it should produce consistent quality welds without peeling off of the coating, flooding, brittleness or welding seam irregularity.
- (d) It should be compatible with the commonly used automotive painting systems. It should produce an acceptable factory paint finish with a good appearance and good paint adhesion. Satisfactory adhesion and protection of the painted finish after corrosion has been initiated should also be maintained.

Alloy composition

Zn-Mn alloy coatings can be electrodeposited from several baths. Some of the promising compositions are given in the Table I. Zn-Mn alloy plating bath based on fluoborate has also been investigated by Sugimoto *et al.* [23]

Factors affecting stability of the bath

The major problem faced in the operation of the citrate based baths is the precipitation of Mn(III) citrate complex and hence the solution is unstable. Urakawa *et al.* [9,24,25] alleviated the precipitation problem by keeping the pH between 5.4 and 6.0 at a bath temperature of 323 K and secondly by adding pieces of metallic zinc or manganese to the bath which reduced the Mn(III) back to Mn(II). During the plating process, oxidation of manganese species took place on the anode, but addition of zinc powder in the bath allowed Mn(III) citrate to be reduced to Mn(II) citrate [26]. Potassium bromide as additive was recommended by Bozzini *et al.* in improving the bath stability [10]. The problem of bath precipitation was also studied by Sulcius *et al.* [27]. Triethanolamine is found to improve the bath stability [20].

Mechanism of zinc-manganese alloy plating

Mn is the most electronegative metal which can be electrodeposited from aqueous solutions. The Mn discharge reaction is inevitably accompanied by hydrogen evolution. C.E. varies with C.D. and temperature; as the temperature is raised the C.D. at which the highest C.E. is obtained increases, although the highest C.E. is obtained at 298 K. An increase in Rotating disk electrode (RDE) velocity results in a systematic decrease in C.E. [15].

To understand the nature of these effects, the dependence of the partial rate of Mn deposition reaction on potential was analyzed. There are three characteristic zones on the curves. At low overvoltages the log of reaction rate varies linearly with potential. The slope of the Tafel line varies slightly with a change in Mn(II) concentration and is equal to 28-21 mV. The electrochemical reaction order with respect to Mn(II) ions is close to 1.4. Thus the kinetics of the Mn deposition process from the standard sulphate-ammonium bath can be described by the equation:

$$I = k_c (C_{Mn(II)})^{1.4} \cdot \exp\left(\frac{-RT}{zf}\right) \quad (1)$$

with an increase in C.D. the cathodic curves deviate from Tafel lines. Two zones of limiting C.D. separated by a zone where deposition rate increases again with a decrease in electrode potential, are distinguished. Contrary to the behaviour in the Tafel and the first limiting current region the deposition rate at the second limiting current region is insensitive to the concentration of Mn(II) ions. Moreover, the deposition rate is independent of the rotation speed of the RDE over the whole potential range, indicating that rate limitations are not caused by mass transport phenomena but are of kinetic nature. On the other hand the limiting C D increases with an increase in temperature and in the presence of selenic salt additives.

Further investigations have been carried out combining the effects of high speed electro deposition and a pulsed current waveform [5]. Investigations concluded that with pulse on/off durations of 1-5 ms this form of current controlled electrodeposition tended to reduce the manganese contents of the electrodeposited alloys. Pulse electrodeposition was found to be very beneficial in equalizing alloy composition over the surface of the RCE. With DC electrodeposition edge (ie. close to the RCE carrier) to center alloy variation were quite large. Choice of appropriate pulse conditions brought these differences down to more acceptable values.

Influence of addition agents

It was reported that small concentrations of some additives in the bath influence the alloy electrodeposition process [10]. Small amount of selenium in the form of selenous acid (0.05-0.20 gl^{-1}) and ammonium selenate (0.5- 2.0 gl^{-1}) to the sulphate-citrate bath considerably changes the electro deposition process of Zn-Mn alloy. Both additives enhance the current efficiency at intermediate and high current densities. These additives also enables the deposition of high manganese alloys at low current densities [11,15,16]. The presence of selenium also leads to the appearance of the β phase which is stabilised at higher current densities. It also influences the morphology of Zn-Mn alloy coatings. Typical plate like and globular crystallites are observed. Gelatin, agar-agar and selenic acid as additives were

reported for the citrate-based bath for improving the characteristics of the deposit [7,12,20]. The major problem of the citrate based bath is the very low cathode current efficiency values of 40% have been quoted, with improvements to 60% occurring with the addition of small amounts of sodium thiosulphate [9].

Influence of operating parameters

Variations of bath composition, temperature, pH, and current density affect manganese content in terms of the alloy, current efficiency, quality and appearance of the coatings [5-10].

Alloy composition

Sagiyama *et al.* [9] carried out detailed investigation with respect to the alloy composition. Their study revealed the effect of current density and flow rate on the composition of Zn-Mn alloys deposited from the sulphate - citrate bath. Only zinc which is electro chemically more noble than manganese, was deposited in the low current density range ($< 10 \text{ A.dm}^{-2}$). The two metals were co-deposited at a higher current density. The content of manganese, which is less noble than zinc, increased with increasing current density. Manganese peaked at 30 or 40 A.dm^{-2} and decreased with further increases in current density. In this current density range, the deposit was burned. An increase in flow rate extended the current density range to a point at which only

zinc was deposited, and decreased the Mn content when current density was fixed. Furthermore, an increase in flow rate shifted the current density at which the Mn content peaked.

The effect of temperature on the composition of alloys electrodeposited from the sulphate - citrate bath is as follows: Raising the temperature had about the same effect as increasing the flow rate. The effect of pH on the Mn content of the coating is that the Mn content declined with a decrease. The relationship between the Mn content of the deposit and the metal percentage of Mn in the bath ($\text{Mn}^{2+} / \text{Zn}^{2+} + \text{Mn}^{2+}$) is as follows: The total metal ion concentration was kept constant at 0.42 M. The percentage of Mn in the deposit increased directly with the metal percentage of Mn in the bath, but the increase depended on current density. The effect of the sodium citrate concentration is as follows: A decrease in sodium citrate reduced the Mn content of the deposit. The composition of electrodeposited Zn-Mn alloys varied considerably with a change in plating variables. The effects of these variables on partial cathodic polarization curves were also investigated.

Cathode current efficiency

The cathode current efficiency decreased as the manganese content of the deposit increased. Cathode current efficiency is expressed as follows:

TABLE I: Promising compositions of Zn-Mn alloy

Salt	Concentration in Molar						
Zinc sulphate	0.75	0.75	0.18	0.24	0.03-0.06	0.18	0.18
Manganese sulphate	1.25	1.25	0.65	0.18	0.25	0.65	0.30
Magnesium sulphate	0.63	0.63	—	—	—	—	—
Sodium citrate	—	0.10	0.72	0.60	—	0.72	1.00
Ammonium sulphate	—	—	—	—	0.4	—	—
Ammonium selenate	—	—	—	—	0.003	0.01	—
EDTA	—	—	—	—	0.03-0.06	—	—
pH	2.30	2.30	5.30	5.60	1.9-2.5	5.30	5.3
Temperature (K)	298-308	298-308	30	45	298-308	303	30
C.d. A.dm^{-2}	1-10	1-10	1-10	1-10	10-15	5-20	11
Reference	(4)	(4)	(10,11)	(19,11)	(12-14)	(11.16)	(17-19)

$$\eta = \frac{(i_{zn} + i_{Mn})}{(i_{zn} + i_{Mn} + i_{H_2})} \quad (2)$$

$$= \frac{\left(1 + \frac{i_{Mn}}{i_{zn}}\right)}{\left(1 + \frac{i_{Mn}}{i_{zn}} + \frac{i_{H_2}}{i_{zn}}\right)} \quad (3)$$

$$= \frac{\left(1 + \frac{i_{zn}}{i_{Mn}}\right)}{\left(1 + \frac{i_{zn}}{i_{Mn}} + \frac{i_{H_2}}{i_{Mn}}\right)} \quad (5)$$

Where i_{zn} , i_{Mn} and i_{H_2} represent the partial current density of zinc, manganese and hydrogen respectively. The equation demonstrates that the cathode current efficiency is determined only by the Mn content if i_{H_2}/i_{zn} or i_{H_2}/i_{Mn} constant; i_{H_2}/i_{zn} is constant in the potential range in which zinc and manganese are co-deposited. In contrast, i_{H_2}/i_{Mn} is nearly constant where data for deposits containing more than 10 percentage wt Mn are plotted. Because i_{H_2} and i_{Mn} are nearly dependent of flow rate and temperature in the range of deposition it is understood that i_{H_2}/i_{Mn} is not affected by flow rate and temperature.

The effect of pH on cathode current efficiency for the sulphate - citrate bath is as follows: The cathode current efficiency was not affected by pH 5.0 to 5.6. However, the cathode current efficiency decreased at pH values lower than 4.5.

Although the standard bath has a high cathode efficiency, this value is reduced as the manganese concentration is increased. Therefore, additives for increasing efficiency were investigated. Adding small amounts of sulfur compounds such as sodium thiosulfate, telluric acid, and selenic acid markedly increased efficiency. Sodium thiosulfate proved to be the best because it has not adversely affect corrosion resistance or paint adhesion as did the other additives. Addition of sodium thiosulfate improved cathode efficiency from about 40 to 50 percent for alloys containing approximately 40 percent Mn.

Crystal structure

Studies on phase structure of electrodeposited Zn-Mn system showed the formation of mixtures of stable zinc, γ and meta stable Σ and β phases [10].

Morphology

Morphology of Zn-Mn alloy showed that it evolves generally from a plate like crystals with elongated plate lets to globular form as current density increases. The typical morphology of pure Σ phase deposits is strictly globular [10].

Typical SEM surface morphologies of the deposits from the sulphate - citrate bath at low current densities showed the hexagonal lamellar morphologies typical for Zn layers. Zn-Mn layers obtained at higher c.d.s. show the formation of less defined groups of platelets.

The evolution of the morphological grain size, as measured by a standard image analysis procedure, is reported by Bozzini *et al.* [4] as a function of deposition c.d. and is coherent with the formation of large morphological crystals in normal metals. Secondary inhibition effects cannot be observed. [4], because of the variation of morphological type with the variation of deposition c.d. as commented above. Differences in the residence time of surface additions can be addressed in order to explain larger grain sizes of Zn-Mn with respect to Zn samples.

X-ray diffraction patterns and analysis of the relative peak intensities, texture coefficients and deformability indices (sum running over pyramidal planes) were made by Bozzini *et al.* [4].

Mechanical properties of Zn-Mn alloy electrodeposits

Bozzini *et al.* [4] carried out detailed analysis of mechanical properties. The relevant mechanical properties are related to cold plastic forming, namely: hardness H, plasticity δ , wear resistance R; the latter property can be related to other independently measurable mechanical properties through relations of the kind [29]: $R = a.K^\alpha.H^\beta.E^\gamma$ where E is Young's Modulus, K is the fracture toughness and a , α , β , γ are positive constants. In the present case K is very high and cannot be measured with indentation techniques for supported films. It can, therefore, be assumed to be independent of the deposit and once H, δ and E are known, it is possible to forecast the plastic formability of the coatings, which is positively correlated with δ and negatively correlated with H and E. δ can be estimated either with Milman's plasticity parameter δ_H or via knowledge of the plastic flow curve. In addition it should be recalled that the plastic

properties of the coatings being dealt with are also a function of their crystal structure.

Electrochemical corrosion behaviour in acidic chloride environment

The immersion potentials of Zn-Mn with various Mn contents from deposited sulphate bath are compared to the immersion potential of pure Zn deposits [4]. It was found that the Zn-Mn alloys are more noble than Zn layers and the degree of nobility is positively correlated with Mn content. Such a behavior cannot be explained on thermodynamic grounds for two reasons: (1). Presence of mixed potentials; and (2) Mn is less thermodynamically noble than Zn; the formation of passivating layers can be hypothesized and XPS evidence proves the presence of Mn_2O_3 and ZnO on the surface of electrochemically attacked low manganese Zn-Mn films.

Anodic polarization curves of low manganese Zn-Mn alloys do not display the passivating behavior observed for high manganese coatings. Estimation of anodic kinetic parameters (corrosion c.d. and polarization resistance) showed a better anodic resistance for the Zn-Mn (1.5%) alloy, which is, in any case, much poorer than that of high manganese layers [4].

Corrosion resistance

The area where Zinc-Manganese shows the greatest promise is in its excellent corrosion resistance when compared to zinc and zinc alloy coatings. Faust and co-workers [17,18] found that deposits of the alloy containing less than 50% manganese gave poor protection against corrosion. The reason for this was thought to be the presence of micropores in the coating.

Sagiyama and co-workers [24,28], Govindarajan and co-workers [6] and Gabe and co-workers [7,20] have examined the corrosion resistance of the alloy as a sacrificial coating on ferrous substrates. Sagiyama used salt spray testing to gain a relationship between manganese content and time to red rusting of the substrate steel.

It was found that the time to red rust for a deposit containing 50% Mn of a thickness of approximately 3 μm , is 800-2000 hours in the unpassivated state. Furthermore an increase in Mn content over 50% only improves the corrosion resistance slightly. Govindarajan has also evaluated the corrosion resistance but in an acetic

acid salt spray test. The results cannot be easily compared but do illustrate a 100% increase in corrosion resistance of Zn-Mn compared to electrodeposited zinc. Gabe also carried out conventional neutral salt spray testing but used zinc alloy coated steel which had been subsequently phosphated and cathodically electro-painted to 25 μm . It was concluded that the Zn-Mn coated systems (50% Mn content) convey the greatest degree of protection.

To understand how zinc-manganese actually protects ferrous surfaces some investigators have undertaken corrosion potential measurements [6,28]. This work has illustrated that initially, in chloride environments, the Zn-Mn corrosion potential shifts to slightly more noble values (typically to ~ -920 to -960 mV vs Ag/AgCl). It remains at this potential until dissolution of the substrate steel raises the potential more significantly and marks the end of the sacrificial protection offered by the alloy. Polarization of zinc and zinc-manganese electrodeposits has also been carried out during salt spray testing [28]. These showed that the alloy had a lower corrosion current than for zinc, suggesting a sustained lower corrosion rate.

Analysis of corrosion products on zinc-manganese coating has also been carried out. X-ray diffraction measurements suggest that these contained $\gamma\text{-Mn}_2\text{O}_3$ and $\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2$ with an increase in this ratio with increase in manganese content in the alloy. The $\gamma\text{-Mn}_2\text{O}_3$ is considered to suppress the reduction of oxygen at the surface of the coating and hence reduce cathodic activity.

Corrosion resistance after painting has also been evaluated [28]. The blistering resistance for a 3 μm thick alloy coating was found to be equivalent to a 5 μm zinc coating and increasingly better with greater manganese contents. The growth of blisters is caused by the dissolution of the deposit under alkaline attack from cathodic sites. The nature of the deposit which dissolved was found to be entirely zinc, suggesting that manganese was resistant to alkaline attack and hence less likely to blister.

Perforation corrosion was evaluated by cyclic corrosion testing [20]. The relationship between depth of corrosion and manganese content in the alloy deposit showed a minimum depth in the range 30-50% manganese for a 3 μm thick deposit. This result was significantly better than

for 5 μm of zinc. The phosphatability of the alloy coating was also very good. A very fine film of phosphate crystals was formed which were found to be hopeite $[(\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O})]$ and manganese, the latter dissolves into the phosphate film and substitutes some of the zinc in the hopeite lattice. Manganese content in the film increases with increase in the alloy electrodeposit and the film may be represented as $[\text{Zn}_{3-x}\text{Mn}_x(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}]$. Phosphating increases both paintability and corrosion resistance after painting [20].

Pcst treatment

Chromate conversion coatings avoids staining, discolouration, tarnishing and improves corrosion resistance for both indoor and outdoor environments. The better protective ability of the iridescent chromate film on Zn-Mn coatings related to the uniform corrosion of this microcracked conversion layers. The elemental and chemical compositions of chromate passive film on Zn coating was determined on the surface and in the depth by XPS. The film thickness was to increase from the colourless through iridescent yellow to uniformly coloured dark yellow chromate film. It was found that besides chromium compound, Zn and Mn corrosion products were present in the films [20,30].

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