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Physico-Chemical Properties of Zn-Fe Alloy Deposits from an Acid Sulphate Bath Containing Triethanolamine

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ABSTRACT

The composition, properties, structure and morphology of electrodeposited Zn-Fe alloy deposits obtained from an acid sulphate bath containing triethanolamine have been investigated. A bath containing less zinc (20%) produced an alloy deposit with higher zinc content (80%), i.e. anomalous co-deposition process. The composition of alloy remained constant with pH of the plating bath and thickness of the alloy deposit. The cathodic current efficiency depends on plating variables. The shift in deposition potentials of Zn-Fe alloy is a chief cause in the co-deposition process to produce alloy of varying composition. Phase structure determination by X-ray diffraction studies showed a wide variety of inter metallic phases such as η , Γ , Γ_1 and α . Zn-Fe alloy showed a superior corrosion resistance than zinc coatings. An alloy containing greater than 40% Fe showed a good paintability. Hardness of the alloy deposits increased with increase in iron content in the alloy. Smooth, uniform and fine grained deposits were obtained for the Zn-Fe alloy containing 20% Fe.

1. Introduction

In the past couple of decades many attempts have been made on developing a high corrosion resistance steel especially for an automotive body panels. Recently electrodeposited Zn-Fe alloy has been found to be suitable for this purpose. Electrodeposited Zn-Fe alloy can act as sacrificial anode for corrosion protection of steel. An alloy containing 15-25% Fe shows an excellent corrosion resistance, formability, weldability, workability, adaptability to phosphating and chromating and an alloy deposit containing 40% Fe or more shows an excellent paintability. The electroplating of Zn-Fe alloys has been reported to be an alternative substitute for cadmium coating [1, 2]. The Zn-Ni alloys have been deposited from various types of baths like sulphate-chloride [3, 4], chloride [5], sulphate [6-14], acetate [15] and alkaline sulphate baths [16-22].

The literature findings reveal the absence of comprehensive work on the electrodeposition of Zn-Fe alloy from acid sulphate bath containing triethanolamine. The aim of the present investigation is to develop the optimum plating bath with suitable composition and plating conditions for obtaining good quality Zn-Fe alloy deposit with 15 -25% Ni and to study properties, structure and morphology of Zn-Ni alloy deposit.

2. Experimental Methods

The plating bath solution was prepared using distilled water and laboratory grade chemicals. The bath solution was purified as described earlier [23]. The optimum bath composition and plating conditions used in the present study are given in Table 1.

Electrodeposition was carried out galvanostatically from 250 mL bath solution by using 1 cm² stainless steel as cathode and 2 cm² zinc as anode at 323 K under stirred conditions. The panel so plated was weighted and stripped in 20% HNO₃, made up to 100 mL in a standard flask, the zinc and iron contents in the test solution was analyzed by atomic adsorption spectrometry (Varian spectra model AA 30). The cathodic current efficiencies and deposition rates were calculated in a conventional manner. The thickness of the alloy deposit was measured by Elcometer (Model 250 FN, England). The ductility alloy deposit and adhesion of the

alloy deposit to the base metal (steel) was tested by a bending test. The porosity of the alloy deposit was determined by Ferroxy test. Static potentials of zinc and Zn-Fe alloy deposits dipped in 3.5% NaCl were measured with respect to saturated calomel electrode. Tensile strength of the alloy deposit (10 μ m thick) was determined by a tensile strength testing machine (Tensiometer). Hardness of alloy deposits was determined on Vickers scale (load 50 g). Adhesion of the paint of Zn-Fe alloy deposit was evaluated by cross hatching method. Corrosion testing of zinc and zinc-iron alloy plated steel panels by accelerated neutral salt spray method was examined for 96 hours as per ASTM B117 specification in 5% NaCl at 35 \pm 2 $^{\circ}$ C.

The phase structure of Zn-Fe alloy deposits obtained from acid sulphate bath containing TEA have been determined by X-ray powder diffraction (Filter CuK α , 30kV, 20 mA, 4000 counts). The surface morphology of the alloy deposits was examined under Scanning electron microscope (Model JEOL-JSM-840A).

Table 1 Optimum bath composition and operating conditions to electroplate zinc-iron alloy having the composition 15-25%

Bath component	Concentration
ZnSO ₄ ·7H ₂ O	156 g/L
(NH ₄) ₂ SO ₄ ·FeSO ₄ ·6H ₂ O	178 g/L
Triethanolamine	14 mL/L
Na ₂ SO ₄	20 g/L
Ascorbic acid	3.52 g/L
Boric acid	30 g/L
Sodium lauryl sulphate	0.05 g/L
pH	4.0
Temperature	50 $^{\circ}$ C
Agitation	Normal
Current density	15 Adm ⁻²

3. Results and Discussion

3.1 Composition

Fig. 1 shows the variation of the alloy composition with the bath composition for three different TEA concentrations. In the graph, the line AB is the composition reference line (CRL) represents the metal contents in the bath solution and in alloy deposit are of the same composition. A bath solution with less zinc content containing a definite concentration of

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TEA was found to produce zinc rich alloy, i.e. the curve lies clearly well above the CRL line. Thus, the electrodeposition of Zn-Fe alloy from acid sulphate bath containing TEA is the characteristics of anomalous co-deposition.

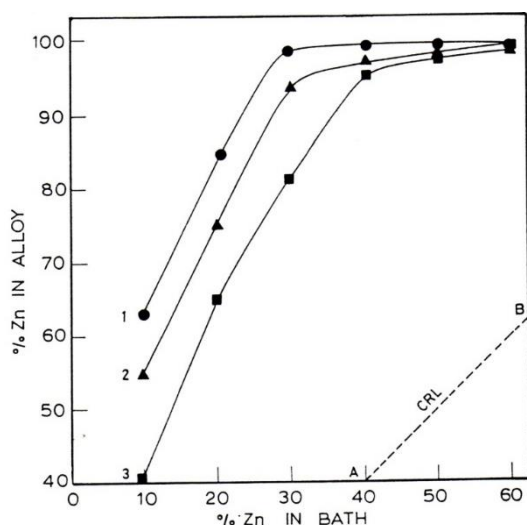


Fig. 1 Effect of metal ion ratio (zinc to iron) in the bath on the composition of Zn-Fe alloy. Bath composition: total metal content 0.5 M, $[Zn^{2+}]$ 0.05–0.3 M, $[Fe^{2+}]$ 0.2–0.45 M, TEA 0.025–0.6 M, Na_2SO_4 20 g/L, H_3BO_3 30 g/L, ascorbic acid 3.52 g/L, sodium lauryl sulphate 0.05 g/L, temperature 50 °C, current density 15 Adm^{-2} , pH 4.0, thickness ~ 8 μm , stirred condition. Curve 1: 0.1 M TEA, Curve 2: 0.6 M TEA, Curve 3: 0.025 M TEA

Experiments were carried out at 15 Adm^{-2} with 0.1 M TEA concentration at 50 °C to study the effect of pH on the alloy composition. The percentage of zinc in the alloy deposit remained constant with increase in pH (1–6) of the plating bath for different ratios of zinc to iron. This is because of the deposition potential of the metal complex in the bath solution is not affected by the pH. Increase in temperature of the operating bath increases the percentage of zinc in the Zn-Fe alloy deposit (Fig. 2), which is obvious in the anomalous co-deposition. An increase in temperature during anomalous co-deposition process increases the concentration of the less noble metal (zinc) in the cathode diffusion layer which in turn enhances the deposition of less noble metal which is already depositing preferentially.

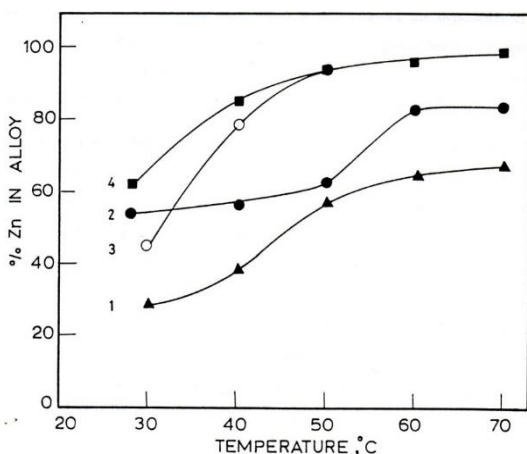


Fig. 2 Effect of temperature on the composition of Zn-Fe alloy. Bath composition: total metal content 0.5 M, $[Zn^{2+}]$ 0.05–0.1 M, $[Fe^{2+}]$ 0.4–0.45 M, TEA 0.025–0.6 M, ascorbic acid 3.52 g/L, TEA 0.025–0.6 M, Na_2SO_4 20 g/L, H_3BO_3 30 g/L, sodium lauryl sulphate 0.05 g/L, current density 10–20 Adm^{-2} , temperature 30–70 °C, pH 4.0, thickness ~ 8 μm , stirred condition. Curve 1: 80/20 Zn/Fe, cd 20 Adm^{-2} , Curve 2: 90/10 Zn/Fe, cd 20 Adm^{-2} , Curve 3: 80/20 Zn/Fe, cd 10 Adm^{-2} , Curve 4: 90/10 Zn/Fe, cd 10 Adm^{-2}

To study the effect of complexing agent (TEA) in the bath on the composition of alloy deposit, the electrodeposition of Zn-Fe alloy was carried out from the bath containing various concentrations of TEA (0.025–0.6 M) at a current density of 15 Adm^{-2} at 50 °C and pH 4.0. As the concentration of TEA was increased in the bath, the percentage of zinc in the alloy increased to a maximum and then decreased slightly with increase in concentration of TEA (Fig. 3). For all the three ratios of zinc to iron, the percentage of zinc in the alloy was maximum when TEA

concentration was 0.1 M. At lower concentration of TEA (< 0.1 M), the zinc might form a loose complex which facilitates in the smooth discharge of the zinc metal at the cathode. At higher concentration of TEA (> 0.1 M). The zinc might form a strong complex with TEA, which might hinder the rapid deposition of zinc.

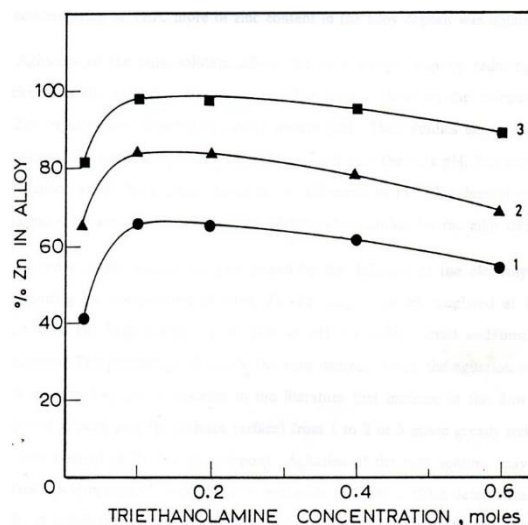


Fig. 3 Effect of TEA on the composition of Zn-Fe alloy. Bath composition: total metal content 0.5 M, $[Zn^{2+}]$ 0.05–0.15 M, $[Fe^{2+}]$ 0.35–0.45 M, ascorbic acid 3.52 g/L, TEA 0.025–0.6 M, Na_2SO_4 20 g/L, H_3BO_3 30 g/L, sodium lauryl sulphate 0.05 g/L, temperature 50 °C, current density 15 Adm^{-2} , pH 4.0, thickness ~ 8 μm , stirred condition. Curve 1: 70/30 Zn/Fe, Curve 2: 80/20 Zn/Fe, Curve 3: 90/10 Zn/Fe

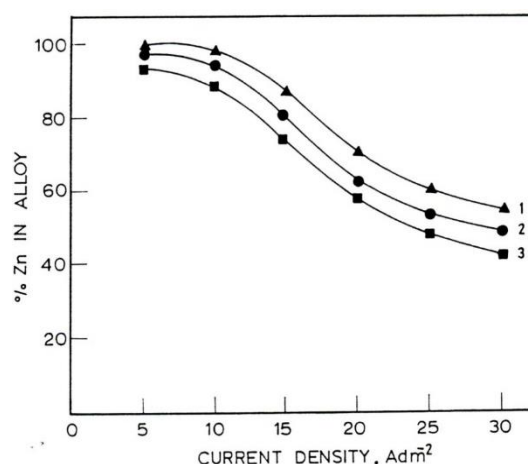


Fig. 4 Effect of current density on the composition of Zn-Fe alloy. Bath composition: total metal content 0.5 M, $[Zn^{2+}]$ 0.05 M, $[Fe^{2+}]$ 0.45M, TEA 0.025–0.6 M, Na_2SO_4 20 g/L, H_3BO_3 30 g/L, ascorbic acid 3.52 g/L, sodium lauryl sulphate 0.05 g/L, temperature 50 °C, thickness ~ 8 μm , pH 4.0, stirred condition, current density 5–30 Adm^{-2} , Curve 1: 0.1 M TEA, Curve 2: 0.6 M TEA, Curve 3: 0.025 M TEA.

In order to study the effect of current density on the composition of Zn-Fe alloy deposit, experiments were carried out at various current densities (5–30 Adm^{-2}) for three different concentrations of TEA (0.025 M, 0.1 M and 0.6 M) in the bath. The percentage of zinc in the alloy decreased with increase in current density at all the three concentrations of TEA. The dependence of the composition of the alloy on the current density is shown in Fig. 4.

The effect of stirring on the alloy composition was studied by carrying out experiments under stirred as well as unstirred conditions. The percentage of zinc in the alloy obtained from the bath containing different concentrations of TEA (0.025 M, 0.1 M and 0.6 M) was almost constant thickness. The constancy of the alloy composition across thickness of the alloy during the Zn-Fe alloy plating from acid sulphate containing TEA shows a uniform rate of deposition.

In order to find out whether there is co-deposition of zinc with iron or not, the relation between cathode current density and the cathode potential has been studied by measuring the deposition potentials with respect to saturated calomel electrode.

Fig. 5 shows the characteristics of the cathode current density and cathode potential (typical cathode potential curves for the electroplating of Zn-Fe alloy and of the parent metals). Curve 1 is the cathode potential curves for the deposition of iron alone from the acid sulphate both

containing TEA (0.1 M). The iron deposition seems to occur at about -0.96 V. Curve 2 is that of zinc deposition. The deposition potential for the zinc deposition was near -1.02 V and Curve 3 is that of Zn-Fe alloy deposition from the same bath solution. The deposition potential for Zn-Fe alloy deposition was around -1.12 V, the position of Zn-Fe alloy deposition curve is shown to lie right of the less noble parent metal (zinc). From this, it is clear that why zinc deposits preferentially than iron, i.e. anomalous co-deposition.

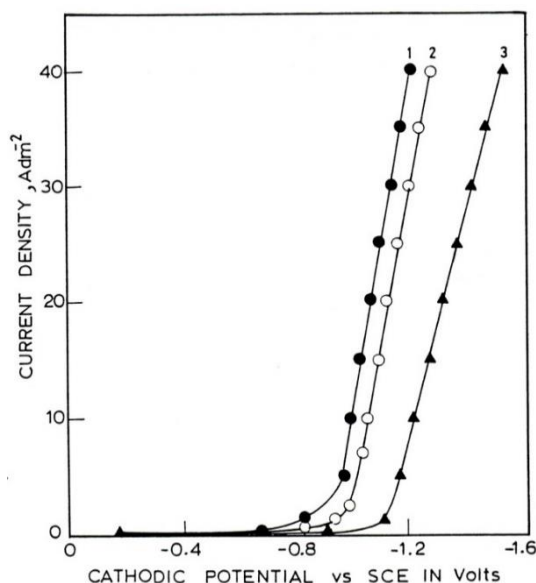


Fig. 5 Cathodic polarization curves for the deposition of Zn, Fe and Zn-Fe alloy from an acid sulphate bath. All solutions contained TEA 0.1 M, Na_2SO_4 20 g/L, H_3BO_3 30 g/L, ascorbic acid 3.52 g/L, pH 4.0, temperature 50 °C, solutions were stirred. Curve 1: Deposition of iron alone, Curve 2: Deposition of Zinc alone, Curve 3: Deposition of Zn-Fe alloy from the same bath solution, the concentration of iron and zinc in the bath was same as those in the individual baths.

Deposition rate of the Zn-Fe alloy were calculated for each experiment with TEA concentration. The rate of deposition initially increased sharply with TEA concentration and reached a maximum at a TEA concentration of 0.1 M. Beyond this maximum the rate falls with further rise in TEA concentration. The cathodic current efficiency (CCE) was calculated for each experiment to study the dependence of the CCE on current density. With increase in current density, CCE also increased. At any given current density and in the presence of known concentration of TEA, the CCE decreased with rise in temperature of the operating bath (Table 2). Agitation of the bath solution caused CCE to increase.

3.2 Properties

The adhesion Zn-Fe alloy deposit to the base metal (steel) was tested by a standard bending test. Zn-Fe alloys were electroplated for different thickness (2–12 μm) on mild steel panels (1×4 sq. inch). Each sample was subjected to bending test, the alloy coating did not show visually any cracks even after 180° bending. This indicates a good adhesion of the alloy to the base metal.

Table 2 Effect of temperature of the bath on cathodic current efficiency (CCE) and composition of Zn-Fe alloy

Temperature (°C)	% Zn in Zn-Fe alloy deposit	CCE (%)
30	62.54	99
40	85.92	84
50	94.16	78
60	96.93	75
70	99.13	63

The Zn-Fe alloy coated on steel panels (3×3 sq. inch) to a thickness of 2–12 μm were used to measure the porosity of the alloy deposit. A filter paper soaked in potassium ferricyanide (1%) solution was placed over the alloy plated steel panels and the number of blue spots developed on the filter paper with time was taken as the measure of the porosity of the deposit. The alloy deposits were pore free at sufficiently higher thickness ($>8 \mu\text{m}$).

The ductility of the Zn-Fe alloy was measured by a simple bending test. The alloy deposits coated on mild steel panels (1×4 sq. inch) to a thickness of 12 μm were subjected to a bend test up to 180°. The alloy deposits did

not show any visual cracks at the point of bending. The microhardness of 25 μm thick alloy deposits was measured on Vickers hardness tester (50 g load). As expected, increase in the percentage of iron in the alloy deposit enhanced the hardness (Table 3). The static potentials of Zn-Fe alloy and zinc were measured in 5% NaCl solution. Table 3 also shows that the static potentials of alloys which were significantly more positive to pure zinc and more negative to mild steel under identical experimental conditions.

Corrosion testing of zinc and zinc-iron alloy plated steel panels by accelerated neutral salt spray method was examined for 96 hours as per ASTM B117 specification in 5% NaCl at 35 ± 2 °C, pH 7.0. The Zn-Fe alloy sample were compared with pure zinc plated on steel panels. A white corrosion product (rust) was observed after 35 hours. It was followed by red corrosion product (red rust) of steel after 45 hours. Moreover, none of these panels with stood corrosion for more than 50 hours of the test. In the Zn-Fe alloy plated steel panels, blisters of white and red rust appeared only after 90 hours indicating that Zn-Fe alloy can protect steel from corrosion more efficiently than pure zinc.

Table 3 Effect of percentage of iron in Zn-Fe alloy on the microhardness and static potentials

% Fe in alloy deposit	Microhardness in VHN (load -50 g)	Static potential in mV vs. SCE in 3.5% NaCl
Zn	80	-1078
Zn-5% Fe	122	-1041
Zn-10% Fe	135.9	-1001
Zn-15% Fe	139	-954
Zn-20% Fe	145.2	-914
Zn-25% Fe	152.4	-882
Zn-30% Fe	157.5	-845
Zn-35% Fe	164.1	-807
Zn-40% Fe	172.0	-754
Mild steel	-	-700

3.3 Structure and Morphology

The phase structure of electrodeposited Zn-Fe alloy deposit was determined by X-ray powder diffraction. Fig. 6(A) shows the constitution diagram of electrodeposited Zn-Fe alloy versus the percentage of zinc in the Zn-Fe alloy deposit. Fig. 6(B) shows the phase composition of electrodeposited Zn-Fe alloy versus the percentage of zinc in the Zn-Fe alloy deposit. The electrodeposited Zn-Fe alloy deposit has metastable structures and individual phases co-exist over a wide range of composition. These are: η (100–93% Zn), Γ (79–90% Zn), Γ_1 (93–74% Zn), and α (60–0% Zn). The phase diagram of as-plated Zn-Fe alloy has been compared with annealed alloy at 360 °C. The feature in this diagram is that the solid solubility of zinc in iron (α - phase) is limited to 20 wt.% zinc in the pure form and extends up to 62 wt.% zinc along with Γ - phase. The range of co-existence of α - phase was much longer in the as-plated alloy samples than in the equilibrium alloy (annealed). The Γ - phase exists in a range up to 79 wt.% zinc, an alloy containing more than 93 wt.% zinc showed a pure η - phase. The η and Γ_1 phases co-exist between 79–93 wt.% zinc. The Γ_1 phase does not appear in as-plated alloy.

The surface morphology of Zn-Fe alloy deposits was examined under scanning electron microscope. Fig. 7 shows the change in the surface morphology of the deposit with increase in the percentage of iron in alloy deposit. Morphology of the alloy deposit containing 20% Fe was found to be granular.

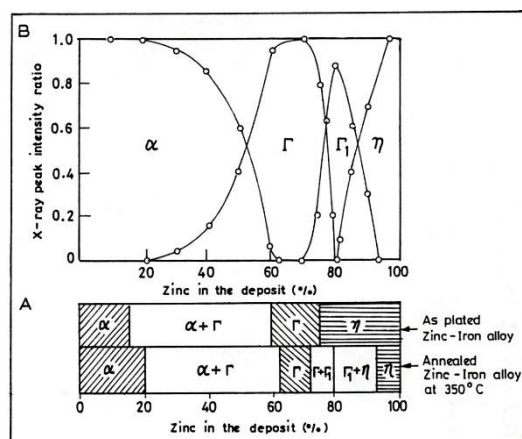


Fig. 6 (A) Constitution diagram of electrodeposited Zn-Fe alloy versus the percentage of zinc in the Zn-Fe alloy deposit and (B) phase composition of electrodeposited Zn-Fe alloy versus the percentage of zinc in the Zn-Fe alloy deposit

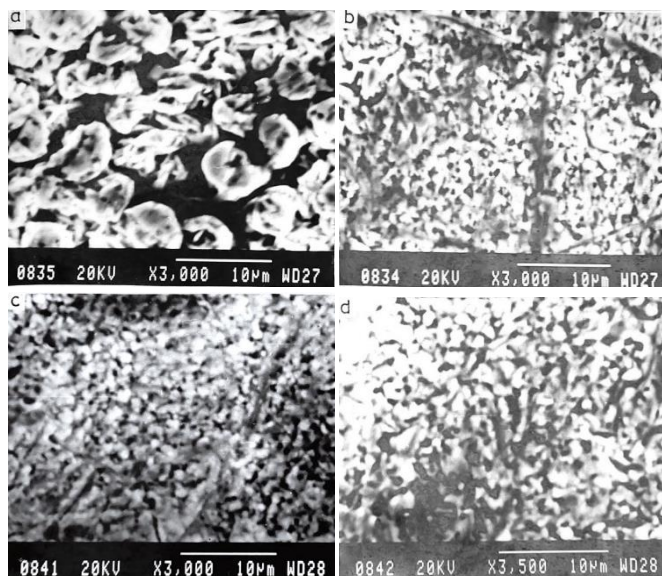


Fig. 7 Scanning electron micrographs of Zn-Fe alloy containing different percentage of iron from an acid sulphate bath containing TEA a) 0% Fe, b) 10% Fe, c) 15% Fe and d) 20% Fe

4. Conclusion

Electrodeposition of Zn-Fe alloy having 15-25% Fe from an acid sulphate bath containing triethanolamine follows anomalous co-deposition. A bath containing less zinc (20%) produced an alloy deposit with higher zinc content (80%). The percentage of zinc in the alloy varied with bath composition (Zn/Fe ratio), current density, temperature, stirring and concentration of TEA in the bath. The composition of alloy remained constant with pH of the plating bath and thickness of the alloy deposit. The cathodic current efficiency depends on plating variables. Bath composition and operating conditions were optimized to electrodeposit Zn-Fe alloy containing 15-25% Fe. The shift in deposition potentials of Zn-Fe alloy is a chief cause in the co-deposition process to produce alloy of varying composition. Phase structure determination by X-ray diffraction studies on Zn-Fe alloy deposit shows a variety of inter metallic phases such as: η , Γ , Γ_1 and α . Zn-Fe alloy shows a superior corrosion resistance than zinc coatings. An alloy containing greater than 40% Fe shows a good paintability. Hardness of the alloy deposits increased with increase in iron content in the alloy. Smooth, uniform and fine grained deposits were obtained for the Zn-Fe alloy containing 20% Fe.

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