

ELECTRODEPOSITION OF ZINC-NICKEL ALLOY FROM FLUOBORATE BATHS — AS A SUBSTITUTE FOR ELECTROGALVANISING

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Use of fluoborate electrolytes have been investigated for depositing a suitable composition of zinc-nickel alloy on mild steel for better corrosion protection. In the present investigation, the plating and bath conditions have been optimised so that zinc-nickel alloy coating from fluoborate solutions find applications for plating wires as well as other articles advantageously in the place of zinc coatings.

Key words: Zn-Ni alloy, fluoborate baths, electrodeposition

INTRODUCTION

Many changes have taken place in the technology of production of galvanized coatings on steel and efforts were made from time to time to enhance the corrosion resistance of the zinc coatings [1]. In automotive industry the conventionally precoated steel has been used increasingly to enhance the corrosion resistance of body parts. But they do not fully meet the requirements of cosmetic corrosion resistance, formability, weldability and paintability.

In industrially advanced countries, in the last few years, the steel companies have started producing alloy plated steel sheets for automobile bodies and the high corrosion resistance performance of these coatings has drawn widespread attention. A major development in this area is the introduction of zinc-nickel (8 - 20%) alloy coatings. Presence of a few metallurgical phases in this composition range offers unusual corrosion resistance — six times more than pure zinc coatings [2]. Also, it is claimed as a viable substitute for cadmium coatings in marine exposures [3]. Although the characteristic property of zinc-nickel coating is its improved corrosion resistance as compared with zinc coating of comparable thickness, other properties such as good weldability, good paintability etc. have made it valuable in many fields like automobile industries [4]. Zinc-nickel alloy, being harder than zinc, can be buffed to a high lustre and being a less reactive surface, retains the high finish. The buffed alloy surface is of bluish colour and not unlike chrome plated. This attractive finish can be applied to small hand tools, toy parts and tags. When the surface of the alloy is treated with phosphate or chromate conversion coatings the paintability becomes good.

A number of electrolytes have been reported in the literature for depositing zinc-nickel alloy in various percentage compositions and most of the reports detail electrodepositing the alloy at lower current densities [5]. Earlier work by the authors on a chloride-sulphate bath confirmed the possibility of depositing the alloy at higher current densities [6]. In this paper, the authors have investigated the possibility of depositing the zinc-nickel (8-20%) alloy from a fluoborate bath at higher current densities so that the system can find applications for plating wires as well as other articles advantageously in the place of zinc coatings.

EXPERIMENTAL

The bath composition and its operating conditions chosen for the present study are shown in Table I. The chemicals used were of LR grade. The electrolyte was prepared and purified in the usual way. The pH was adjusted with additions of nickel carbonate slurry or fluoboric acid.

Table I: Typical bath composition and operating conditions

Nickel fluoborate (g/l)	60
Zinc fluoborate (g/l)	75
Boric acid (g/l)	40
pH	3.5
Temperature (°C)	50 ± 2°
Cathodic current density (A/dm ²)	8 - 10
Anode	Zinc and nickel strips in 9 : 1 area ratio

To judge the quality of the deposit over a range of current densities, pH and temperature, experiments were carried out in a standard 267 ml Hull cell at a suitable cell current for 5 minutes. The test results were used to optimise the bath composition and operating conditions.

To analyse the percentage of zinc and nickel in the deposit, plating was carried out on an accurately weighed stainless steel sheet of 5 cm x 5 cm size at various current densities, pH and temperature with and without agitation (employing magnetic stirrer), by following the standard sequence of plating operations. Subsequently, the plated panel was weighed, the deposit was stripped in 20% nitric acid and the solution is made up to 100 ml in a standard flask. Zinc in the solution was determined volumetrically by the EDTA method. The difference between the weight of the deposit and the estimated weight of zinc was taken as that of nickel.

A few of the zinc-nickel (8 - 14%) alloy deposited samples were subjected to accelerated corrosion test (CASS test) in a salt spray chamber and the results were compared with those of zinc deposited from an acid sulfate bath.

RESULTS AND DISCUSSION

Effect of current density

The relationship between the concentration of zinc in the bath and that in the deposit is shown in Fig. 1.

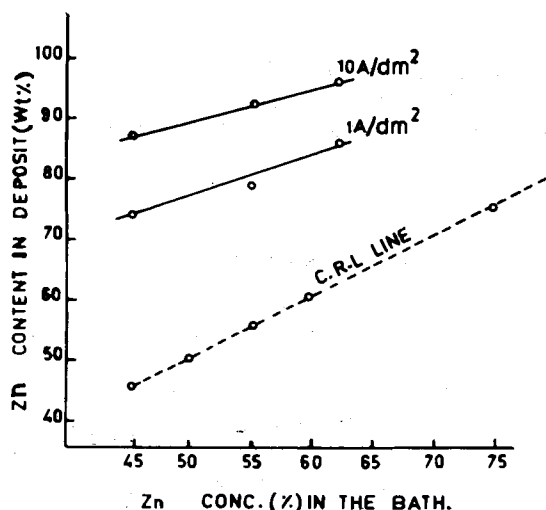


Fig. 1: Influence of zinc conc. in the bath vs Zn conc. in the deposit. Bath: Ni (as fluoborate) 60 g/l; Zn (as fluoborate) 50-100 g/l; pH 3.5; Temp. 50°C

The Composition Reference Line (CRL) refers to a solution and deposit of equal composition. Thus it is observed that the zinc deposits preferentially although it is less noble than nickel. The process is, therefore, classified as anomalous codeposition.

The effects of current density and concentration of zinc in the electrolyte on the content of the alloy deposit are shown in Fig. 2.

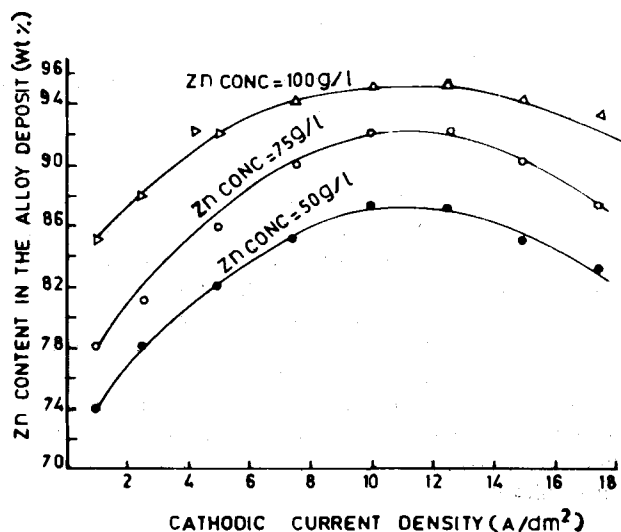


Fig. 2: Effect of current density on the Zn content of alloy deposits as a function of Zn conc. in the bath. Bath: Ni (as fluoborate) 60 g/l; Zn (as fluoborate) 50-100 g/l; Temp. 50°C; pH 3.5

The zinc content increased with current density and was maximum at 10 A/dm². In Hull cell tests coarse and rough deposits with dull appearance were observed for low current densities whereas smooth, fine grained and adherent deposits, could be obtained at optimum current densities. With further increase of current density, a drop in percentage of zinc was noted. During this high current density deposition the diffusion process occurring in the solution may not supply the cathode with enough of zinc ions to maintain the higher percentage of zinc and hence the drop in weight percentage of zinc is observed.

Effect of pH

The solution pH is found to have a key role as its control gives rise to constant alloy composition in this system. The effect of current density on the zinc content was studied as a function of pH (Fig. 3), the pH being varied between 2.2 and 4.7

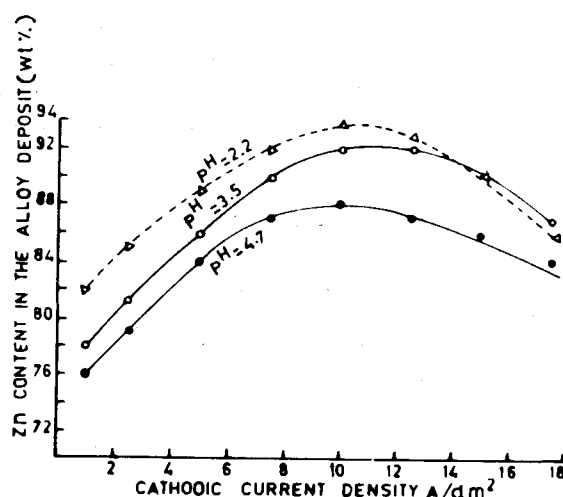


Fig. 3: Effect of current density on the Zn content of alloy deposits as function of bath pH. Bath: Zn (as fluoborate) 75 g/l; Ni (as fluoborate) 60 g/l; Temp 50°C

At low pH values due to the evolution of hydrogen, a coarse and rough deposit was observed. When the pH of the zinc-nickel bath was increased from 2.2 to 4.7, the zinc content of the deposit gradually decreased at all current densities. The desired composition range was obtained by operating the bath at pH of 3.5.

Effect of temperature

The effect of temperature of the bath on the zinc content of the alloy deposits obtained at pH 3.5 is shown in Fig. 4. Hull cell studies clearly showed that by operating the bath at 50°C a bright deposit could be obtained over a wide range of current densities. In general, in all the current densities studied, the content of zinc in the alloy increased with decrease in temperature. However, this is more pronounced at 8 - 12 A/dm². For example, the zinc content of the alloy deposits increased from 85 to 93 % by weight with a decrease

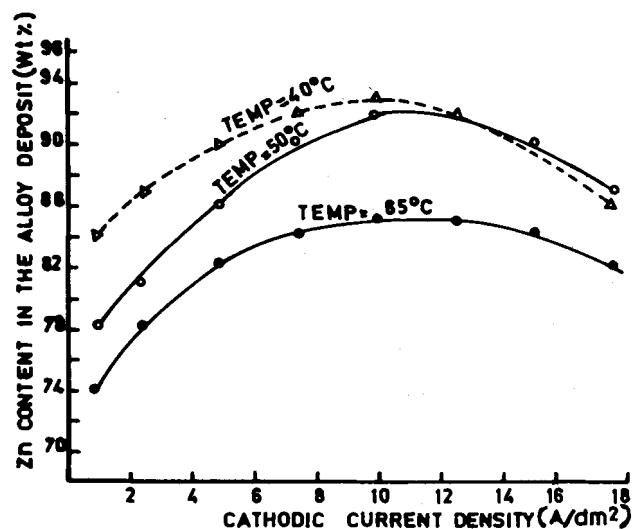


Fig. 4: Effect of current density on the Zn content of alloy deposits as function of bath temperature. Bath: Ni (as fluoborate) 60 g/l; Zn (as fluoborate) 75 g/l; pH 3.5

in bath temperature from 65° to 40°C at a current density of 10 A/dm². When the bath temperature is decreased, the diffusion rate of nickel ions may slow down by comparison with that of zinc ions and this may explain the nature of the curve obtained as reported elsewhere [7].

EFFECT OF AGITATION

The effect of agitation on the zinc content of the alloy deposit obtained at pH 3.5 is shown in Fig. 5.

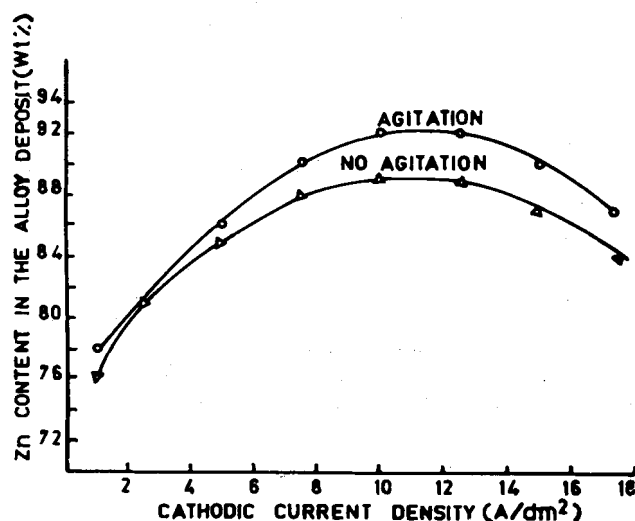


Fig. 5: Effect of agitation on the Zn content of the alloy deposit. Bath: Ni (as fluoborate) 75 g/l; Zn (as fluoborate) 60 g/l; Temp 50°C; pH 3.5

Agitation effects are comparatively small but it does slightly increase the zinc content of the alloy. As seen from the graph there is not much appreciable change in composition of the deposit with agitation.

Studies on corrosion resistance

The static electrode potential of the zinc-nickel (8-14%) alloy was measured in a 3.5% sodium chloride solution against saturated calomel electrode (SCE). The static potential of the alloy (-985 mV) is considerably more positive to zinc (-1026 mV) and more negative to steel (-550 mV) under identical experimental conditions. This shows that the zinc-nickel (8-14%) can electrochemically protect the substrate steel.

In another test, zinc-nickel (8-14%) and zinc plated samples of 2 μ m thick coatings of each were immersed in 3.5% sodium chloride solution. In zinc plated samples rust spots appeared after 60 hours of immersion whereas in the alloy samples no change was noted till 350 hours under similar conditions.

A few alloy plated samples of 25 μ m thick were subjected to CASS test in a salt spray chamber following ASTM-B 117 specification and compared with pure zinc coatings similarly tested. In zinc plated samples a white corrosion product of zinc was initially observed, followed by red rust. None of these coatings was found to withstand more than 40 hours. In zinc-nickel alloy specimens corrosion products were noted only after 220 hours indicating its corrosion resistance to be more than five times the electro-galvanised coatings.

CONCLUSION

The present investigations show that the zinc-nickel (8-14%) alloy can be deposited from fluoborate baths at higher current densities than usual. Corrosion studies show that compared to electrogalvanised coatings, the alloy has five times more protection against corrosion of steel.

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