Recycle of Contaminated Zinc-Nickel Plating Bath by Selective Recovery of Iron

Gök, Özge*+; Turan, Fatih
Mining Engineering Department, University of Dokuz Eylul, Buca, TÜRKIYE

ABSTRACT: *Electroplating is a preferred method of coating the surface of metallic materials such as steel for wear and appearance reasons. Recently, zinc, nickel, or zinc-nickel coatings have been widely used to prevent corrosion of vehicle parts such as brake pads and connecting equipment. However, in the plating bath used in the plating processes, iron contamination might occur due to the partial dissolution of the metal parts over time, causing dark-colored defects on the plating material during electroplating. In this study, the recycling of the plating bath electrolyte by precipitation of iron ions from the solution was investigated. The addition of 7 g/L zinc dust at 30°C minimized the iron concentration in a short time (20 minutes) without affecting the quality and content of the coating bath. The chemical and physical analyses of the precipitate and electrolytes were performed by AAS, XRD, and EDX. The galvanic quality of the decontaminated electrolyte was tested at a current density of 250 A/m² and 298 K.*

KEYWORDS: *Electroplating; Precipitation; Iron; Zinc; Nickel; Contamination.*

INTRODUCTION

Zinc-nickel coatings are used to coat the surfaces of many materials that require high abrasion resistance to climatic and/or chemical conditions, such as automotive parts, fuel and hydraulic system components, precision sealing elements, aerospace industry, agriculture, construction, and electrical transmission equipment. The application of such alloy coatings began in the 1980s [1] and has slowly but steadily increased since then. The service life of parts such as connectors is longer than conventional coatings using zinc-nickel electroplating [2]. The alloy coatings are advantageous because of their optimal cathodic corrosion protection and high resistance to thermal stress (up to 120 °C). Zinc-nickel surface coatings are usually used on steel, cast iron and powdered metals. Zinc-nickel can be co-deposited from both acidic and alkaline non-cyanide solutions. Although acidic baths

have higher nickel content and current efficiency, alkaline baths are chosen for their uniform plating properties and non-corrosive behavior [3].

In general, zinc-nickel alloy coatings produced by electrolysis on steel parts consist of 85-90% zinc and 10-15% nickel. The standard concentration of the electrolyte used usually includes 7.5-12.14 g/L zinc oxide, 0.8-1.6 g/L nickel sulfate hexahydrate, 75-135 g/L sodium hydroxide solution and 10% variable organic reagents (polyethyleneimine, triethylenetriamine, N,N'-bis (3-amino-propyl) ethylenediamine, tetraethylenepentamine, triethanolamine, tartrate, ammonia etc. [3]) for zinc-nickel electroplating at bath temperatures from 10°C to 38°C [1].

Current density, concentration, stirring speed, temperature and pH are the main parameters affecting the quality of electrolytic plating. In case of low nickel and

---

* To whom correspondence should be addressed.
+E-mail address: ozge.solak@deu.edu.tr, faith.turan@deu.edu.tr
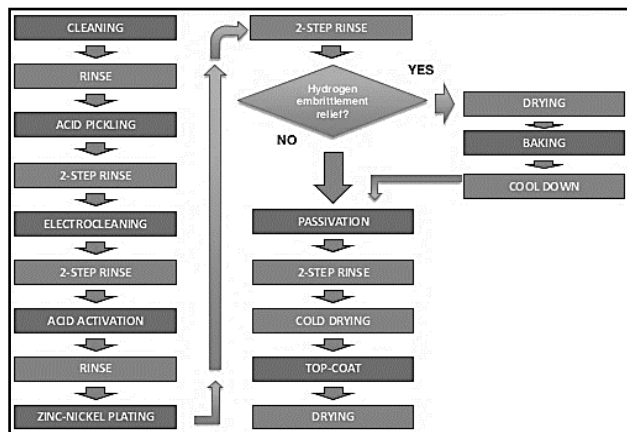
Fig. 1: Typical flowsheet of Zn-Ni electroplating process [5]

Table 1: Alkaline bath components and operating conditions for plating zinc-nickel alloy

Components/Parameters	Concentrations/Values
Zinc (added as ZnO)	6.0-7.0 g/L
Nickel (added as NiSO$_4$)	0.83-1.3 g/L
NaOH	110-130 g/L
Replenisher	10 mL/L
Wetter	0.5 mL/L
Sodium carbonate	<10 g/L
Operating Temperature	20-28 °C
Cathode current density	1.5-2.5 A/dm^2

boric acid content, low temperature, high iron content or aluminium contamination, dark spots (partial burn) may appear on the electroplated parts [4].

The flowsheet of the plating process is shown in Fig. 1. Electroplating can be performed in the rack electroplating and barrel electroplating processes.

In zinc-nickel electroplating electrolytes, iron contamination increases with time, and high iron concentrations lead to the formation of dark-colored parts called "burnt". Since the renewal of bath solutions increases the cost of electroplating, the iron content is often reduced by various methods (dilution, clarification of the solution, etc.) [6]. However, as the concentration of complexing reagents in the solution decreases, leaving metals such as iron, zinc and nickel in the form of ions at alkaline pH, regeneration of the reagents is required over time. The main purpose of this study was to recycle the electroplating electrolyte by minimizing the iron content without affecting the organic components (such as brighteners, complexing agents, surfactants etc.)

Thermodynamics predicts the removal of metals (Ni, Co, Fe, Cd, etc.) by precipitation with the addition of zinc dust, since zinc is more electronegative than these metals. There are applications to cementation with zinc dust to purify various solutions [7, 8, 9]. Cammi et al [7] published a patent on two-step cementation of Cu, Cd, T, Ni, Co, Ge, As, and Sb contained in an electrolyte from zinc ore leaching with zinc dust. The electrolyte with a pH of 5.4 had been used for the electrolysis of zinc. The inverters stated that the co-deposition of these metals contaminated the cathodic deposition by reducing the hydrogen overvoltage and its evolution at the cathode instead of zinc. It was reported that cementation of the Cu, Cd, and Tl impurities in the first phase at 50° C was relatively easy and did not require any activator additions. In contrast, cementation of Ni and Co was difficult, requiring an excessive amount of zinc dust and higher temperatures (70° C). In this process, the concentration of Cu, Cd, Co and Ni was reduced 1000-fold. Van der Pas and Dreisinger [8] studied the mechanism of cobalt removal from zinc electrolytes by cementation of zinc dust in the presence of copper and antimony. The authors reported that the cementation of cobalt by zinc dust from a zinc electrolyte is difficult because of the inhibition of cobalt reduction by zinc ions. Cobalt was deposited in the form of a cobalt-zinc alloy consisting primarily of under-deposited zinc. In the study [9] on the leaching and cementation of heavy metals from electric arc furnace dust in an alkaline medium, zinc dust was used to precipitate Pb, Cu, Cd, Fe, and Cr. The precipitation efficiency was over 50% for metallic impurities under (Pb: 96%, Cu: 76%, Cd: 89%, Fe: 61%, Cr: 75%) cementation conditions such as a Zn/Pb ratio of 1.2 and 10 M NaOH at 50° C in 2 hours.

In this study, the zinc powder is used to remove the iron content from the plating bath, which contains organic components.

EXPERIMENTAL SECTION

The zinc-nickel electroplating electrolyte sample was supplied by an electroplating company that manufactures zinc-nickel-plated automotive parts. The components of the original electroplating electrolyte and the operating conditions applied in the plant are listed in Table 1 [10]. The metal content of the electrolyte was determined by chemical analysis of the liquid samples after centrifugation of the electrolyte at 1000 rpm.

The experiments were conducted in a temperature-controlled 0.50 L four-neck glass reactor with a capacity of

Table 2: Sample of Electroplating Electrolyte

Concentration (mg/L)	Fe	Ni	Zn	Cr	Mn	Co	Cu	Al
	275	1375	6414	112	5,2	3	0,8	<0,1

0.50 L and a condenser (Fig. 2). The reactor was charged with the sample electrolyte and various amounts of analytical grade zinc dust (Zn/electrolyte (g/L): 5, 7, 9) with a particle size of 35 μm. The solution was mixed well with a magnetically driven twin impeller at a stirring speed of 10 s^{-1}.

The temperature of the solution was kept constant at 30°C to improve precipitation kinetics. The initial pH was 14. At fixed time intervals (10 min), 5 ml of the solution was withdrawn, filtered, and the filtrate was analyzed for Fe, Zn, and Ni content using a Perkin Elmer PinAAcle 500 atomic absorption spectrophotometer (AAS); the chemical analysis of the initial solution is shown in Table 2. The major elements in the solution are Fe, Zn, and Ni.

Chemical and X-Ray Diffraction (XRD) analyses were performed on the magnetic solid samples obtained from the precipitation. A Rigaku Miniflex II X-ray diffractometer with Cu Kα radiation was used for XRD analysis. Mitutoyo Digi-Derm 1100 coating thickness gauge was used to measure the coating thickness.

An electroplating experiment was performed to investigate whether the obtained solution (containing 9 g/L Zn, pH 14) was successfully recycled and did not affect the plating efficiency. In the experiment, a Zn-Ni coating was applied to a representative car part using a sample solution with high iron concentration and an iron-removed solution. Electroplating was conducted in iron and iron-removed alkaline solutions (7-15 g/L Zn^{2+}, 130 g/L NaOH, 1,2 g/L Ni^{2+}) at a galvanostatic current density of 250 A/m^2 and 298 K. The thermodynamic data available in the literature were used to construct a Pourbaix diagram using HSC Chemistry 5.0 software [11].

RESULTS AND DISCUSSION

In the investigation method for the removal of iron from electroplating solutions, an attempt was made to precipitate iron ions with zinc metal considering their reduction-oxidation potentials (REDOX). The standard reduction potentials of Fe, Zn, and Ni ions, which play the main role in the solution at 25 ° C, are given in Eq. (1-3) [12]. It should be noted that the standard reduction potentials of Fe, Zn, and Ni ions given are not the potentials involved in the process because the conditions in the experiment are not standardized. Although solution ionic strength and

Fig. 2: Experimental set-up for precipitation tests

temperature are important parameters, the standard potential values suggested (due to the higher oxidation potential of zinc compared to other metals) that iron might precipitate with zinc. The main concern was precipitation of other metal components when iron was precipitated.

$$Ni^{2+} + 2e^- \rightarrow Ni_{(k)} \qquad E^° = -0,26 \text{ V} \qquad (1)$$

$$Fe^{2+} + 2e^- \rightarrow Fe_{(k)} \qquad E^° = -0,44 \text{ V} \qquad (2)$$

$$Zn^{2+} + 2e^- \rightarrow Zn_{(k)} \qquad E^° = -0,76 \text{ V} \qquad (3)$$

Also, thermodynamic analysis of the species in solution using HSC Chemistry 5.0 software (Fig. 3) under similar conditions shows that $ZnFeO_4$ and Fe_3O_4 compounds occur in more alkaline and oxidative environments.

The analytical results presented in Fig. 4 indicate that the experiments performed with 9 g / L Zn gave the highest iron removal ratio. Moreover, a Fe removal efficiency of 75% was achieved in the first 20 minutes with the addition of 7 g/L zinc. The decrease in the values obtained with 5 g/L zinc after 20 minutes could be interpreted as a deficiency of free zinc cations due to either complex formation or precipitation as a metal complex. Also, it could be due to the new equilibrium between nickel-iron-zinc. Since this affects the operating cost, the optimum zinc yield could be chosen depending on the concentration of nickel remaining in the solution and the quality of the plating. Fig. 5 shows the co-precipitation amounts of nickel and zinc from the electrolyte.

It was found that the optimum Ni removal ratio is 5% with the addition of 7 g/L zinc powder in the first 20 min. The amount of zinc remaining in the solution was found to be 65%. The results confirmed the expected behavior of the active metals in the solution (Fig. 5). The Zn/Ni ratios in the electroplating bath were found to be consistent
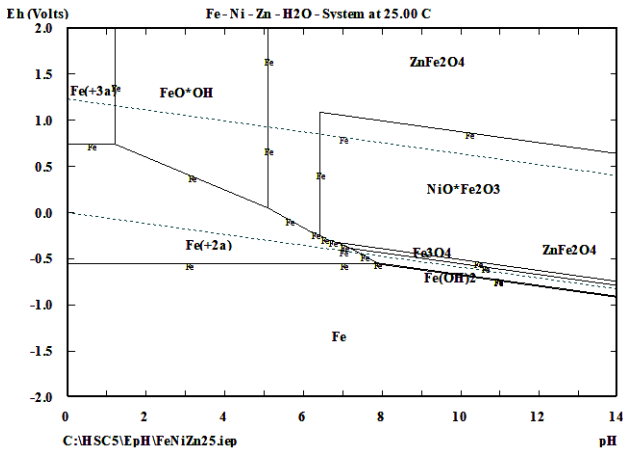
Fig. 3: Pourbaix diagram of Fe-Ni-Zn-H2O species at 298 K[C_{Fe}: 4,91x10^{-3} molal, C_{Ni}: 2,33x10^{-2} molal, C_{Zn}: 2,05x10^{-1} molal]
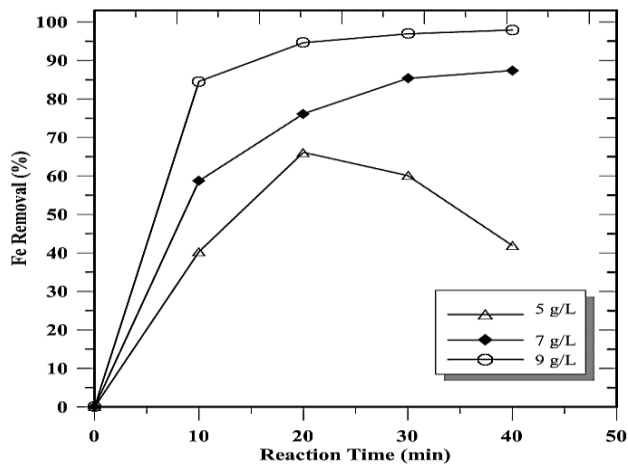
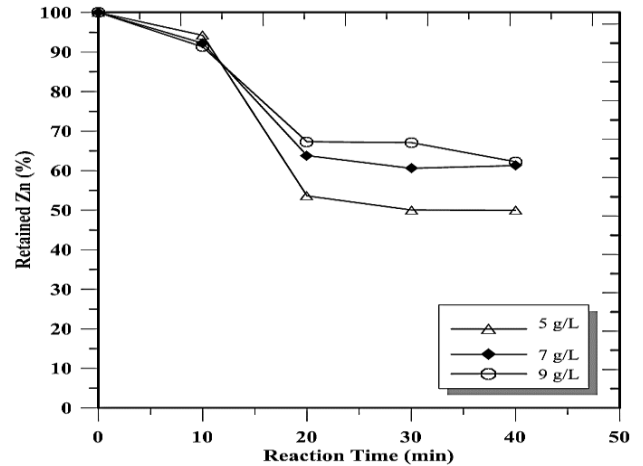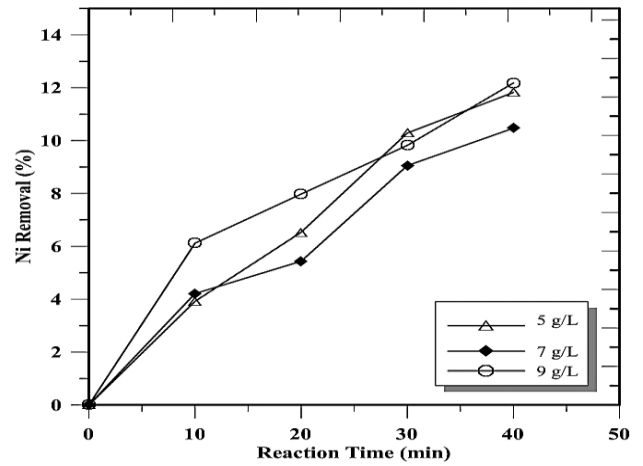*Fig. 4: Fe Removal Efficiency at different Zn concentrations*

Fig. 5: Nickel removal ratio (up) and retained Zinc (down) at different zinc concentrations
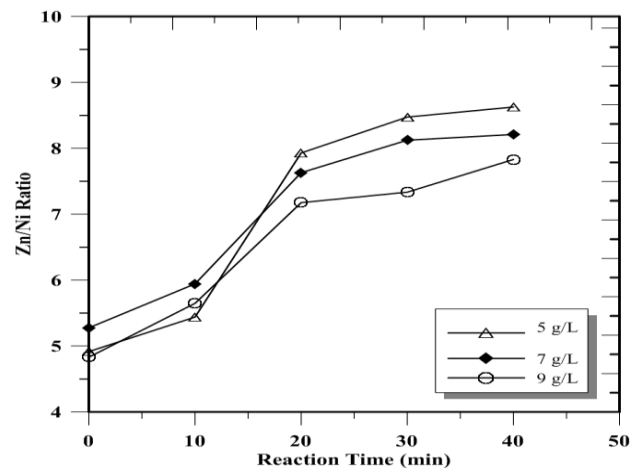
*Fig. 6: Zn / Ni ratios in the solution obtained with different zinc concentrations*

with the precipitation tests. Fig. 6 reveals that the target ratio remained close to the operating conditions in the experiment where 7 g/L Zn was added. At the end of 20 min, 5% of the nickel was lost due to the addition of 7 g/L zinc dust. This is due to the fact that zinc is more electronegative than nickel; therefore, the latter should precipitate as nickel metal when zinc is dissolved. Although the reduction of nickel concentration is not desirable and may lead to deterioration of corrosion resistance; the addition of the required amount of nickel, which gives a Zn//Ni ratio of 7/1, can be made for the next reuse.

The chemical analysis of the precipitate obtained during the tests is given in Table 2. XRD analysis of the solid sample showed that the precipitated material contains oxidized iron [$Fe_{3,6}Fe_{0,9}(O,OH,SO_4)_9$], NiO and ZnO.

Also the magnetic test for the precipitate indicated that the precipitation process could be easily conducted in-situ

by removing the precipitate with a magnet. Grain size analysis indicated that d_{50} of the precipitated material was 50 µm (Fig. 7).

Table 2: Compositions of electrolyte after iron precipitation with 9 g/L zinc dust addition

Concentration (mg/L)	Fe	Ni	Zn	Cr	Mn	Co	Cu	Al
	5.9	1181	9248	33,6	3,5	1,2	<0,1	<0,1

Table 3: Chemical composition of the precipitate

Grade (%)	Fe	Ni	Zn
	34.3	15.2	50.5
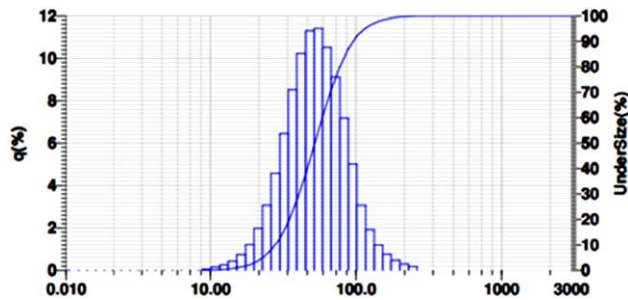
*Fig. 7: Particle size distribution of the magnetic precipitate*

Electroplating experiments were conducted in both iron-contaminated (280 mg/L) and decontaminated electrolytes (7-15 g/L Zn^{2+}, 130 g/L NaOH, 1.2 g/L Ni^{2+}) at a galvanostatic current density of 250 A/m², and 298 K. The precipitated material was removed from the electrolyte solution. The solution with the higher Fe^{2+} concentration was electroplated as shown in Fig. 8 (left), and the coating after removal of the iron species is shown in Fig. 8 (right). The coating thickness was determined using Mitutoyo Digi-Derm 1100 coating thickness gauge in the range of 15-25 µm.

XRD analyses of the coated and uncoated parts are presented in Fig. 9. The analyses show that the electroplated parts are coated with iron oxide compounds at higher iron input concentrations. The zinc-nickel coating on the stainless steel is also confirmed by the XRD analysis.

CONCLUSIONS

The present work investigates the removal of iron components causing dark spots on the electroplated Zn-Ni parts by adding zinc powder and its effects on the quality of electroplating. Optimum Fe removal ratios were found to be 7 g/L for Zn.

The electroplating experiments indicated that with the removal of iron from the electrolyte, dark spots were no longer observed. The results of the experiments were promising for the electroplating companies due to the recycling potential of the bath solution. In a brief cost
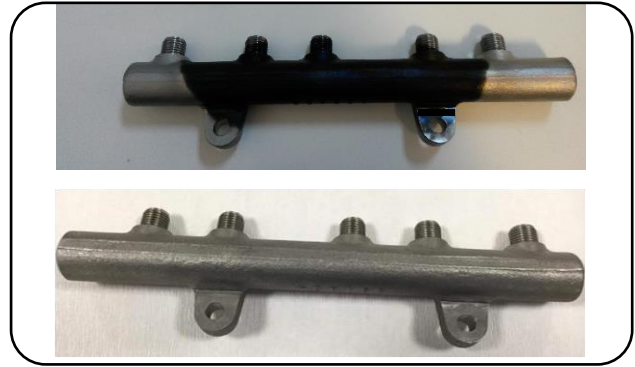
Fig. 8: Electroplated parts (up: at high Fe concentration, down: after removal of Fe ions)
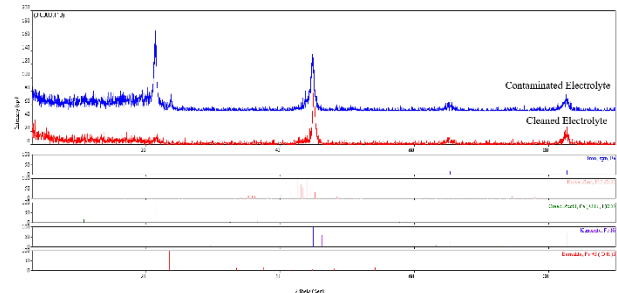
Fig. 9: XRD analyses of electroplated parts with contaminated and cleaned electrolyte

analysis, it could be said that over 95% of the replacement cost could be saved. In addition, the precipitate can be marketed with its ferromagnetic properties. Moreover, these magnetic properties facilitate the handling of the precipitate. The magnetic iron-containing product can also be precipitated in a conical settling tank, which can be integrated with the coating bath and circulated with the required additives.

REFERENCES

[1] Schario M., "Better Alloy Control of Alkaline Zinc Nickel Baths", Product Finishing Magazine, Columbia, (2017).

[2] Gatto G, Nahlawi Jr.T, Kramer R., Flesch J., What Engineers Should Know about Zinc-Nickel Coatings?, Machine Design, Sourceesb, 26-32 (2017).

[3] Muresan L.M., Eymard J., Blejan D., Indrea E., Zn-Ni Alloy Coatings from Alkaline Bath Containing Triethanolamine Influence of Additives, *Studia Universitatis Babeş-Bolyai. Chemia*, **55(1):** 37-44 (2010).

[4] Chatterjee B., Electrodeposition of Zinc Alloys, *Jahrbuch Oberflachen Technik*, **62:** 76-105 (2006).

[5] Altuncu E., "Which is the Best Plating Practice for Zn-Ni Deposition? Barrel or Rack Plating", Turkchem News Portal, (2019).

[6] Qu Z., Su T., Zhu S., Chen Y., Yu Y., Xie X., Yang J., Huo M., Bian D., Stepwise Extraction of Fe, Al, Ca, and Zn: A Green Route to Recycle Raw Electroplating Sludge, *Journal of Environmental Management*, **300:** 1-13 (2021).

[7] Lian J., Chen Q., Hu H., Wang W., Deep Purification of Zinc Ammoniacal Leaching Solution by Cementation with Zinc Dust, *The Chinese Journal of Process Engineering*, **10:** 879-885, (2010).

[8] Van der Pas V., Dreisinger D.B., A Fundamental Study of Cobalt Cementation by Zinc Dust in the Presence of Copper and Antimony Additives, *Hydrometallurgy*, **43:** 187−205 (1996).

[9] Yuea T., Niub Z., Hua Y., Hana H., Lyua D., Suna W., Cr(III) and Fe(II) Recovery from the Polymetallic Leach Solution of Electroplating Sludge by Cr(III)-Fe(III) Coprecipitation on Maghemite, *Hydrometallurgy*, **184:** 132-139 (2019).

[10] MacDermid, https://agilligan.co.uk/docs/Enviralloy _Ni_12-15.pdf (2021).

[11] Roine A., HSC Chemistry©5.0. Outokumpu Research, Finland, (2002).

[12] Brett C., Brett A.M., Electrochemistry Principles, Methods and Applications, Oxford Science Publications, NY. 326 (1993).