Study on improving nickel recovery efficiency of electroless nickel coating process

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Abstract

The chemical deposition of metal from an aqueous solution of a salt of said metal has an electrochemical mechanism, both oxidation and reduction (redox), reactions involving the transfer of electrons. The oxidation of a substance is characterized by loss of electron, while reduction is distinguished by a gain of electrons. The major drawback of Electroless Nickel coating is its high cost of production. The main reason for its high cost is poor nickel recovery efficiency. It is seem to be in the order of only 25%. Hence in my study an attempt was made to improve the nickel recovery efficiency.

Keywords: Electroless nickel process; Surfactant; Reducing agent; Stabilizers; Accelerator.

1. Introduction

Electroless nickel (EN) coating process was first discovered by Brenner and Riddel, 1946 in the middle of the 20th century (Mallory and Hajdu, 1991) which was widely accepted by other electrochemists. Various research works were done in this topic. EN coating process is the deposition of a metallic coating on a substrate without the use of any external voltage or current. It is chemical metal deposition because the electrons required to bring about the discharge of metal ions are produced by a chemical reaction in solution. EN deposition of metal is made from solutions containing reducing agents, the electrons needed to reduce the metal ions are provided by the reducing agents. Sodium hypophosphite is the widely used reducing agent. EN deposition form only on certain catalytically active surfaces (autocatalytic deposition). A variety of metals can be electrolessly plated even non-conductive surfaces can be coated. Major advantages over the electroplating process are uniform direct deposition on surface activated non – conductors, deposition on irregular surfaces, and the formation of less porous, more corrosion resistant deposits (Wolf Riedel, 1991). ENi-P coating is widely accepted because of its unique coating properties such as high hardness and excellent resistance to corrosion, abrasion and wears (Mallory and Hajdu, 1991; Wolf Riedel, 1991; Baudrand, 1994). In electroless process, metal deposition is driven by the catalytic oxidation of the reductant on the substrate surface [1]. Inspite of all its distinct advantages, the main drawback of EN coating is its high cost of production. The main reasons being high cost of chemicals used, nickel wastage in the form of metal bearing sludge, poor nickel recovery from the bath etc. The EN recovery efficiency is read to be poor in the order of only 25% (Elansezhian, Ramamoorthy and Kesavan Nair, 2010). Some of the nickel particles formed during coating deposits on the substrate surface and the rest of them escape from the substrate, which is not useful and hence it is a waste (Mallory and Hajdu, 1996; Cheong, Luan, and Shoesmith, 2004). Hence an attempt is made to improve the nickel recovery efficiency. The concept of adding passive additives to improve the nickel recovery efficiency is employed here. Nickel recovery efficiency was not significantly influenced by the addition of surfactants such as SDS and CTAB however the coating efficiency improved to 95% (Elansezhian, Ramamoorthy and Kesavan Nair, 2010). Possible methods to increase the nickel recovery efficiency are by adding

passive additives such as surfactants, stabilizers, accelerator and excess reducing agent. The effect of adding passive additives such as stabilizers, accelerators and use of excess reducing agent (RA) to the electroless bath are the areas which were not explored adequately by the previous researchers. In this investigation the above mentioned methods are adopted and their effects on the nickel recovery efficiency are studied.

2. PROBLEM DEFINITION

One of the basic characteristics of electroless deposition process is the fact that it is essentially an autocatalytic process (Elansezhian, Ramamoorthy and Kesavan Nair, 2010). Substrate surface must be activated for the commencement of this autocatalytic reaction. Other parameters such as temperature, chemical composition of the bath etc. must also be made favorable for starting the reaction. The reaction starts spontaneously and deposition happens in a controlled manner only for some time over the substrate surface.

 The entire process could be divided in to two phases:

Phase (1) – Steady state reaction

The autocatalytic reaction phase confined to the surface of the substrate starts slowly and gradually accelerates to a steady state in about a few minutes and continued upto 30 minutes as shown in Fig.1 (a).

Fig.1 (a)   Fig. 1 (b)

Phase (2) – Unsteady state reaction

When the reaction is continued beyond 30 minutes, nickel particles get deposited on the region other than substrate surface as shown in Fig.1 (b). The reaction proceeds vigorously in the entire bulk of the solution leaving fine metallic nickel particles in sludge form at the bottom of the container and is presented in Fig. 2.

Fig.2.Nickel wastage

 The time mentioned is specific to the experimental conditions used in the present study. The possibility to improve the overall efficiency of the electroless coating process is to prevent the nickel particles from a) leaving the substrate or b) reaching

locations other than the substrate surface in case they do get detached from it (Elansezhian, Ramamoorthy and Kesavan Nair, 2010).

3. PROPOSED STUDY AND EXPERIMENT

3.1 Addition of surfactant: Surfactant is surface active agents that lower the surface tension of a liquid, allowing easier spreading, and lower the interfacial tension between electrolyte and the substrate. In our study surfactant namely Sodium Lauryl Sulphate (SLS) is introduced into the electrolyte bath and their effect on surface tension and contact angle are investigated.

3.2 Addition of excess amount of reducing agent:

The excess reducing agent (RA) by mass is added periodically. It reduces more Nickel ions in the electrolyte bath thereby increasing nickel recovery efficiency.

3.2 Addition of stabilizers: Stabilizers prevent the decomposition of electroless nickel plating solutions. It also increases the effect of reducing agents which increases the recovery efficiency. In our study stabilizers namely thiourea (S1), glycine (S2) and malic acid (S3) were introduced into the electrolyte bath.

3.3 Addition of accelerator: Accelerators increase the plating rate without causing bath instability. In our study accelerator namely succinic acid (A) is introduced into the electrolyte bath.

3.4 Preparation of the substrates: Substrate material chosen for coating is mild steel. Mild steel stock rod was turned to about 24 mm diameter and cut to 7 mm thickness to be used as substrates. Specimens were then annealed at $800\,^0$C for 2 hrs to relieve from work stress and furnace cooled to refine the grain structure. Finally the samples were surface finished by grinding followed by disc polishing.

3.5 Pretreatment of the substrates: Prior to the coating it must be ensured that the substrate is free from any impurities. So pretreatment is very important to achieve efficient coating. The pretreatment procedure consists of cleaning the substrate with acetone, rinsing with distilled water, dipping in methanol for 2 min, acid pickling for 1 min. [10% $H_2 SO_4$ by volume], rinsing in distilled water followed by a methanol wash.

3.6 EN Plating bath and operating conditions:

The composition of the plating bath and plating conditions are presented in Table 1.

Table1: Compositions of plating bath for electroless Ni – P used in the experiments

PARTICULARS	QUANTITY (G/L) OF THE BATH
Nickel chloride	30
Sodiumhypo phosphite	40
Tri sodium citrate	25
Ammonium chloride	50
Temperature	85ºC (±1ºC)
pH	9 – 10

The surfactant SLS with concentration 0.18g/l was added to solution before electroless nickel deposition. Then stabilizers S1, S2, S3 with concentration 1 ppm were added to the bath and an accelerator A with concentration 1 ppm is added to the bath. Temperature was maintained at $85\,^0$C ($\pm1\,^0$C). The electrolyte bath was

heated indirectly through an electrically heated oil bath. The temperature of the oil bath was controlled by an ON/OFF relay and Proportional Integral Derivative (PID) controller. Temperature of the electrolyte bath was monitored using a thermometer. The pH of the electrolyte bath was maintained between 9 and 10 by adding sodium hydroxide solution. The total initial volume of the plating bath restricted to 150 ml (unless otherwise mentioned). The coating duration is 2 hours after which the bath decomposes as shown in Fig.3.

3.7 Estimation of efficiencies: For the purpose of comparing the relative merits of ENi-P deposited with and without presence of surfactants, two types of efficiencies are considered in the present investigation.

1. Nickel recovery efficiency (Ni_r) (Shipley,1984)

Ni_r is defined as the total metallic nickel (Ni_m) recovered from the bath in a fixed time expressed as a percentage of theoretical nickel content (Ni_T) of the bath solution

$$(Ni_r)\% = ((Ni_m)/ (Ni_T)) * 100 \qquad (1)$$

2. Nickel coating efficiency (Ni_c) (Shipley,1984)

Ni_c is defined as the adherent nickel deposited on the specimen ((Ni_s) in fixed time expressed as a percentage of the total metallic nickel (Ni_m) recovered from the bath solution:

$$(Ni_c)\% = ((Ni_s)/ (Ni_m)) * 100 \qquad (2)$$

Nickel coating efficiency is commercially more significant since a high value of nickel recovery efficiency (Winowlin Jappes, Ramamoorthy and Kesavan Nair, 2005) as defined above does not necessarily imply better and adherent deposition on the specimen.

4. RESULTS AND DISCUSSION

4.1 Effect of surfactant on surface tension and contact angle of EN bath: Surfactant plays a vital role in decreasing the surface tension of the EN bath thereby improves the spreading the electrolyte over the substrate surface. Surface tension is observed to be decreased with increasing surfactant concentration (Alsari, Khulbe and Matsuura, 2001). The surface tension is found to be about 42.4 mN/m without the addition of surfactant. SLS surfactant of 0.18g/l concentration is added to the bath and the surface tension reduces to about 25.6 mN/m. Contact angle values is found to have similar results as surface tension values. It decreased with addition of surfactant. In the absence of surfactant, contact angle is found to be 81.3°. In presence of SLS surfactant it found to about 32°. The digital wetting images of electrolyte without surfactant tend with surfactant are shown in Fig.4.

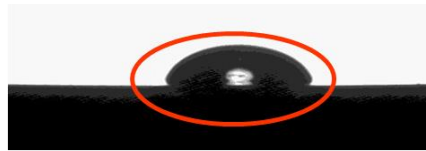Fig.4.a. Without surfactant

Fig.4.b.With surfactant (0.18g/l concentration)

4.2 Effect of excess reducing agent on nickel recovery efficiency: The reducing agent plays an important role on recovery of nickel from the bath. The variation of nickel recovery efficiency as a function of excess reducing agent is presented in Fig.5.
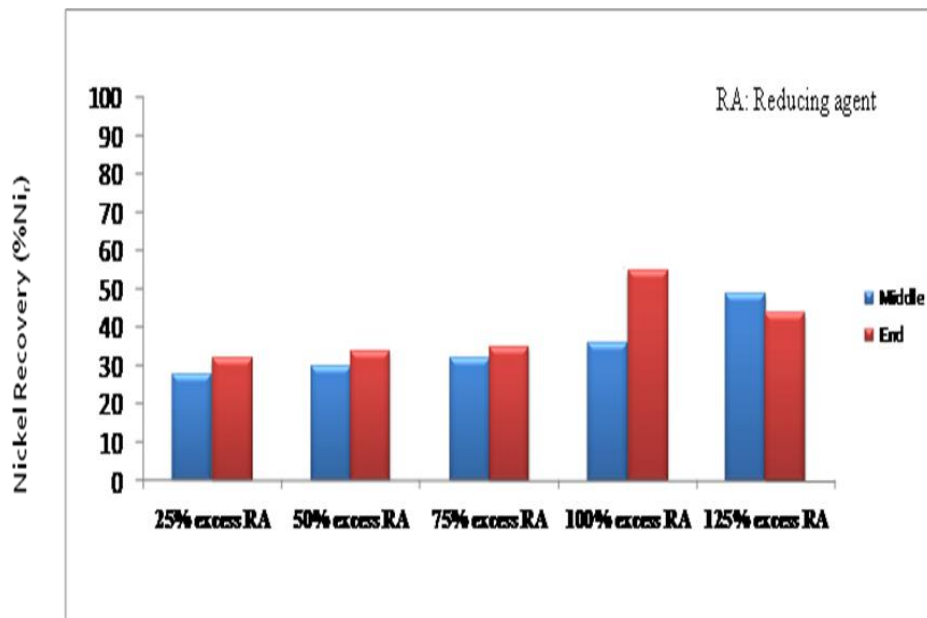

Fig.5 Nickel recovery efficiencies for various excess RA

Without the addition of excess reducing agent the recovery efficiency was very low about 25% only. The recovery efficiency increased with increase in the concentration reducing agent, it was 29% at the middle and 31% at the end for the 25% excess reducing agent and it increased to 32% at the middle and 55% at the end for 100% excess reducing agent and with further increase in the concentration reducing agent, nickel recovery efficiency decreased to 49% at the middle and 44% at the end. The decrease in recovery efficiency is the due to the saturation of reducing agent which decomposed the bath. The nickel coating efficiency decreased as nickel recovery efficiency kept increasing, it was 84% at the middle and 82% at the end for the 25% excess reducing agent and it decreased to 80% at the middle and 76% at the end for 100% excess reducing agent as shown in the Fig.6.
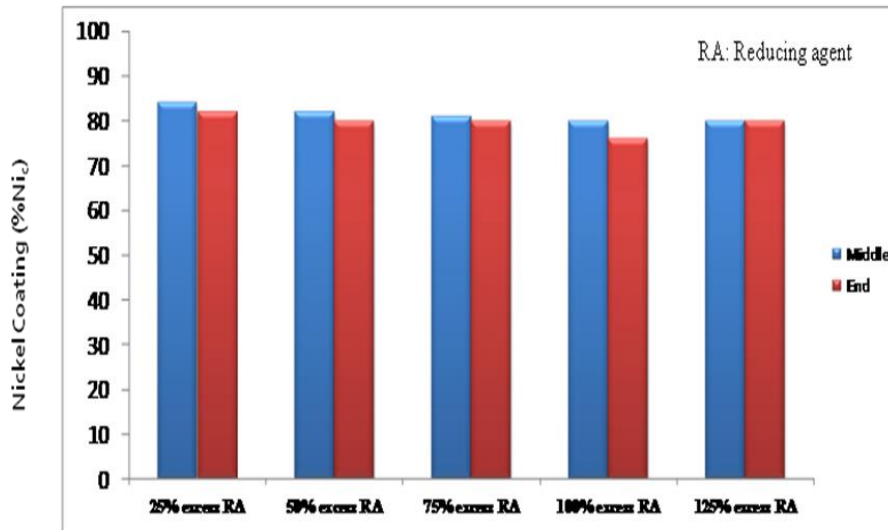
Fig.6 Nickel coating efficiencies for various excess RA

4.3 Effect of stabilizers and accelerator along with 100% excess reducing agent on nickel   recovery efficiency:
With the addition of excess reducing agent the recovery efficiency increased upto 55% whereas the coating efficiency was poor in the order of 82% as shown in Fig. 6, this difficulty must be overcome to make our EN coating technique industrially viable. For this purpose various passive additives such as stabilizers and accelerator were tried. Addition of stabilizers aided in improving the coating efficiency as shown in Fig. 8 but the coating duration was 3 hours. And when accelerator was added the coating duration was 1½ hours. Nickel recovery efficiency was almost the same but coating efficiency was less as shown in Figs 7, 8
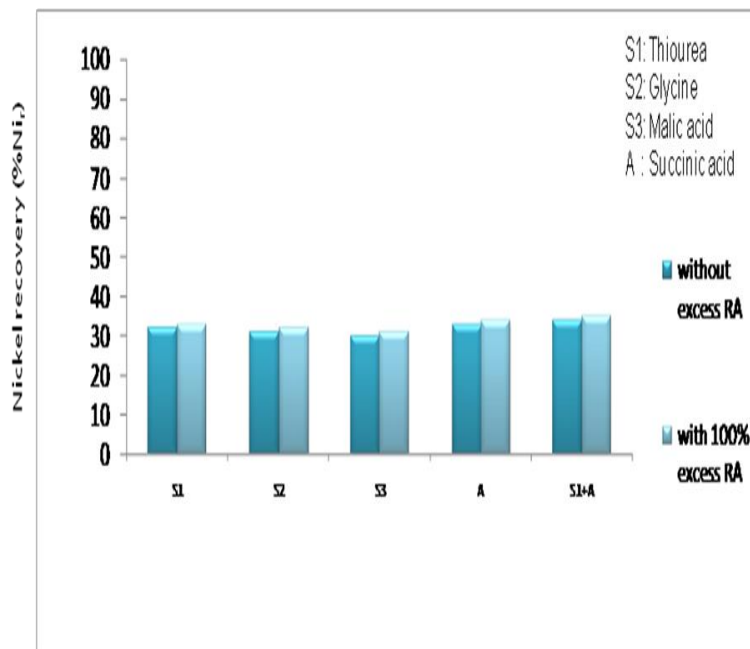

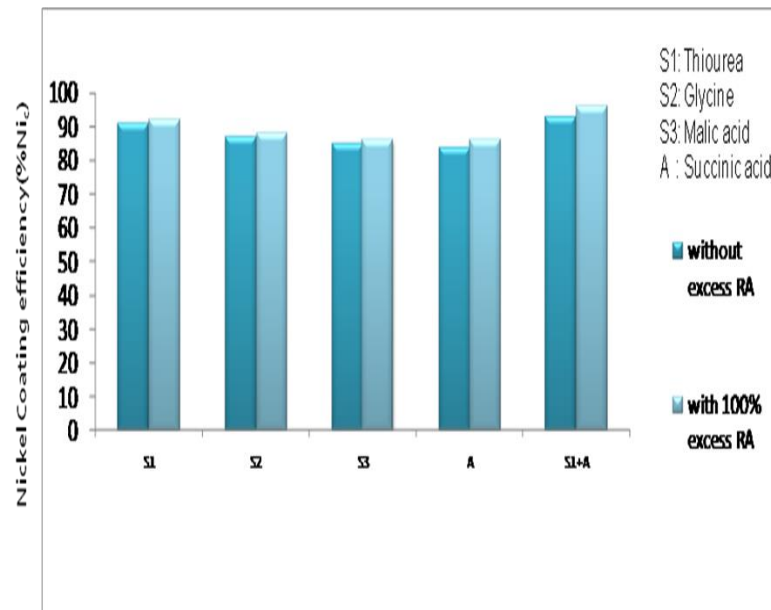Fig.7 Nickel recovery efficiencies for passive additives

Fig.8 Nickel coating efficiencies for passive additives

but the coating duration being 1½ hours. So in order to compromise between these two coating duration and to obtain optimal results both stabilizer and accelerator were added together to the bath with 100% excess reducing agent it was seen that nickel coating efficiency has improved significantly to 96% but the recovery efficiency being 30% as shown in Fig. 8.

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