

Electroless deposition of Fe–Ni alloys from acidic and alkaline solutions using hypophosphite as a reducing agent

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Abstract: The deposition of Fe–Ni alloys from acidic and alkaline solutions, using hypophosphite as a reducing agent, is studied in this work. The experimental results confirm the autocatalytic nature of this process. The composition of alloys is practically independent of the temperature deposition. Fe–Ni alloys produced from acidic solutions contained less than 1% Fe. The amount of Fe in Fe–Ni alloys produced from alkaline solutions was estimated to be about 15 %. The deposition of Fe–Ni alloys was significantly faster in the alkaline than in the acidic solutions, due to more pronounced hydrolysis of Fe(II) and Ni(II) ions under the alkaline conditions. The Fe–Ni alloys produced from both acidic and alkaline solutions contain phosphorus and as such have amorphous structure.

Keywords: hydrolysis; chemical deposition; mechanism.

INTRODUCTION

The electroless deposition of iron group metals or related alloys is important, due to their applications in the electronics, automotive and aerospace industries. These coatings exhibit attractive magnetic, corrosion and wear resistant properties. In microelectronics packaging, electroless deposited nickel alloys are used as a barrier diffusion layer.

The electroless deposition of nickel is well established in industry since Brenner reported the composition of the electrolyte and the appropriate conditions under which this process can successfully proceed.¹ The reducing agents of Ni(II) ions used in the autocatalytic deposition of nickel include sodium hypophosphite, sodium borohydride dimethyl amine borane (DAMB) and hydrazine.²

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An application of hydrazine leads to the deposition of pure metals, *e.g.*, nickel or cobalt.³ On an industrial scale, most commonly used reducing agents are hypophosphite or boron-containing compounds which lead to the production of Ni–P or Ni–B alloys, respectively.⁴ These alloys are nanocrystalline or amorphous. Although the electroless deposition of nickel, or any other iron group metal, is well established in the industry worldwide, the mechanisms of these sophisticated processes are not yet completely understood. The different mechanisms explaining the autocatalytic deposition were proposed thus far. For a review of these concepts, *i.e.*, metal–hydride, mixed potential, metal–hydroxide and universal mechanisms, the reader is directed to the publications^{2,4} and references therein.

Similarly as in the electrodeposition, in the electroless deposition of nickel and its alloys, the simultaneous hydrogen evolution unavoidably takes place. The simultaneous hydrogen evolution may lead to an increase in pH at the surface at which the electroless deposition proceeds and thus to the hydrolysis phenomena. Contrarily to its electrodeposition counterpart, the electroless deposition of Fe–Ni alloys was far less investigated. The aim of this work was an attempt to compare the electroless deposition of Fe–Ni alloys from acidic and alkaline solutions.

EXPERIMENTAL

The copper substrates were used in the present work in order to deposit Fe–Ni alloys. As received, the copper substrates were very carefully washed, degreased and stored under ethanol. After the cleaning procedure, the copper substrates were immersed into an acidic solution containing 0.01 g/L Pd(II). After the activation step in Pd(II)-containing solution, the copper substrates were carefully washed with distilled water and immediately immersed into the electroless plating solutions under proper conditions, which are explained in the subsequent text.

The deposition of Fe–Ni alloys was carried out from acidic or alkaline solutions using sodium hypophosphite as a reducing agents of Ni(II) and Fe(II) ions. The main solution had the following composition: NiSO₄·6H₂O 9.13 g/L, FeSO₄·6H₂O 4.79 g/L, NaKC₄H₄O₆·4H₂O 33 g/L and NaH₂PO₂·2H₂O 22 g/L. The composition of the electrolyte was based on the reference⁵ where the amount of DMAB was changed with NaH₂PO₂·2H₂O. For the acidic solutions the pH was adjusted to about 4.5, using 0.1 M solution HCl dropwise. Similarly, for the alkaline solutions, the pH was adjusted to about 11.5 using 10 % solution NH₄OH dropwise. Unless otherwise specified in other sections, the deposition was carried out for 30 min. After the deposition was completed, the samples were very carefully washed with distilled water and stored in ethanol for future analyses.

X-ray diffraction (XRD) measurements were performed using Rigaku Ultimate IV system (CuK_α radiation of 1.5405 Å; operated at 40 kV and 44 mA). Diffraction data were recorded with a step size of 0.05° at 2°/min scan speed. Scanning electron microscopy (SEM) images were obtained using JEOL JAMP-9500F. Magnifications are shown in the respective figures.

For the chemical analysis, the deposited Fe–Ni alloy films were dissolved in 1:4 HNO₃ aqueous solution and then the composition was determined by atomic absorption spectroscopy (AAS) method. The surface morphology and the structure of the electroless deposited Fe–Ni alloys were analyzed using SEM and XRD methods.

RESULTS AND DISCUSSION

Deposition of Fe–Ni alloys from acidic solutions using hypophosphite as a reducing agent

A dependence of mass of the Fe–Ni alloy deposited from an acidic solution on temperature is presented in Fig. 1. Similarly to other electroless processes, this figure clearly shows that there is an increase in mass of the deposited Fe–Ni alloy with rising temperature.

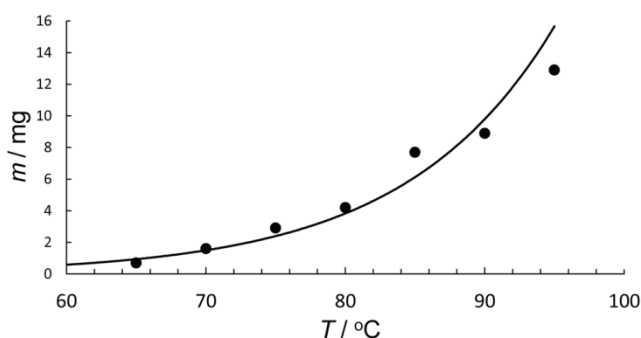


Fig. 1. Mass of Fe–Ni alloy as function of temperature. Deposition was carried out from an acidic solution with hypophosphite as a reducing agent, for 30 min.

The autocatalytic nature of this electroless process is confirmed by the results presented in Fig. 2, where the mass of Fe–Ni alloy deposited at 80 °C is shown as a function of time. Fig. 2 illustrates that a prolonged time of deposition leads to an increase in mass of the deposited alloy. The solution was very stable during the deposition even after several hours. No precipitation of metallic powders was observed in the bulk solution.

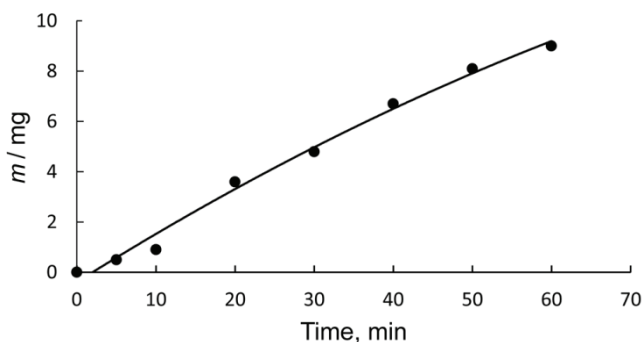


Fig. 2. Mass of Fe–Ni alloy as function of time of deposition, acidic conditions (80 °C).

The composition of the electroless deposited Fe–Ni alloy as a function of temperature is presented in Fig. 3. The results show that the composition of the alloy is practically independent of temperature. The deposits predominantly con-

sist of about 86 mass % Ni and about 14 mass % P. The amount of Fe in the deposit was practically negligible and was estimated at less than 1 mass %.

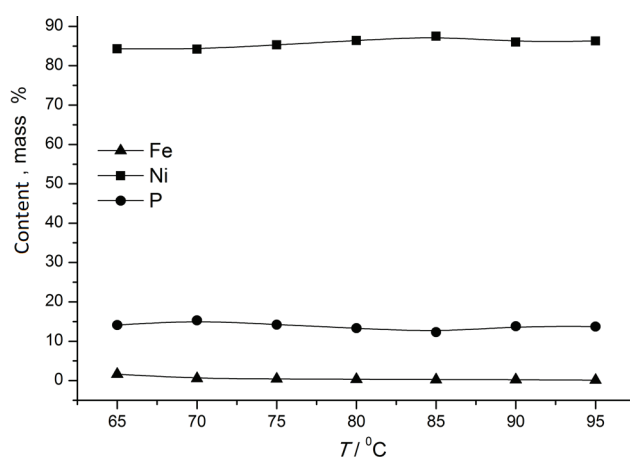


Fig.3. Composition of Fe-Ni alloy as function of temperature.

The deposited Fe-Ni alloys appeared smooth and shiny. The SEM analysis found that the surface roughening is more pronounced at higher temperatures. The SEM images of the deposited Fe-Ni alloys are shown in Fig. 4. As can be seen from Fig. 4a at 80 °C, the surface morphology of deposited alloys is practically featureless. At 95 °C the formation of bulbous or cauliflower surface morphology is observed. This observation is expected, since an increase in temperature leads to an increase in the rate of deposition. An increase in the rate of deposition causes an increase in the surface roughening, as described in the literature.⁶

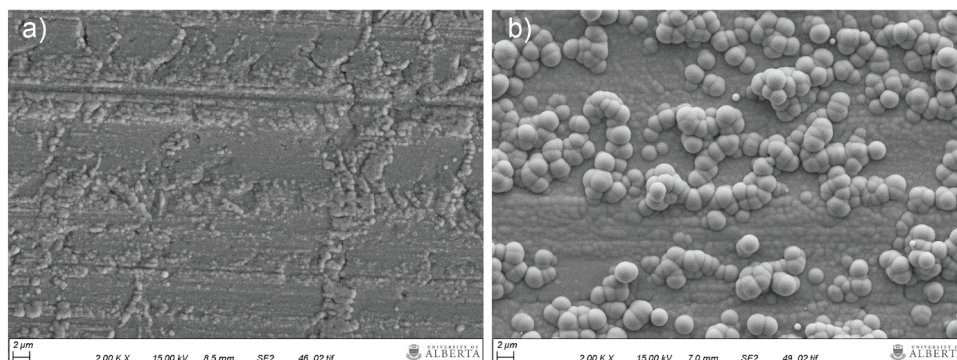


Fig. 4. SEM images of deposited Fe-Ni-P alloys at: a) 80 and b) 95 °C.

According to the XRD analysis, the deposited Fe-Ni-P alloys are amorphous. A typical XRD pattern of these deposits is shown in Fig. 5. A broad

diffraction peak can be seen in Fig. 5, suggesting the amorphous structure of the deposited Fe–Ni–P alloys.

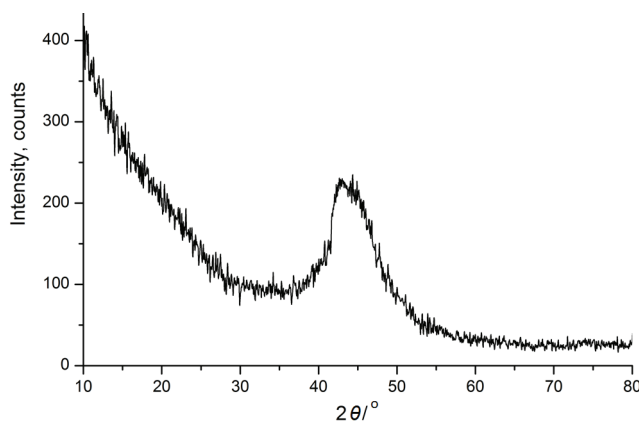


Fig. 5. XRD pattern of Fe–Ni–P deposit from an acidic solution with hypophosphite as a reducing agent, deposition time 30 min (85 °C).

Deposition of Fe–Ni alloys from alkaline solutions using hypophosphite as a reducing agent

In Fig. 6 the dependence of mass of Fe–Ni alloy deposited from an alkaline solution as a function of temperature is illustrated.

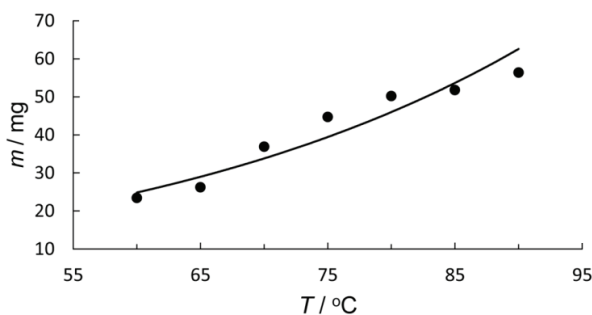


Fig. 6. Mass of Fe–Ni alloy as function of temperature. Deposition was carried out from an alkaline solution with hypophosphite as a reducing agent for 30 min.

As in the acidic solutions, an increase in temperature leads to an increase in the mass of Fe–Ni deposited, as shown in Fig. 6, when this process is carried out under alkaline conditions. By a comparison of the results presented in Figs. 1 and 6 it can be concluded that the electroless deposition of Fe–Ni alloys is significantly faster in alkaline than in acidic conditions.

Similarly to the acidic solutions, the electroless deposition under the alkaline conditions proceeds in the autocatalytic mode as presented by the results in Fig.

7. An important difference in the dependences of mass of the deposited Fe–Ni alloy on time for the acidic and the alkaline conditions is obvious by comparing the Figs. 2 and 7. As the results presented in Fig. 7 clearly show, the dependence of mass on time passes through a maximum for the alkaline conditions, while that for the acidic conditions continuously increases (Fig. 2). An appearance of the maximum in the dependence of the mass on time in Fig. 7 can be attributed to the so called “bath instability”.⁷ It is well established that during the electroless deposition in the autocatalytic mode, an increase in temperature or time leads to an increase in the rate of deposition and consequently of the mass of the deposit. However, the significant increases in either temperature or time may reach the bath instability (Fig. 7) and under such conditions, the deposition takes place not only at the surface of a substrate, but as well in the bulk solution as powders.⁸

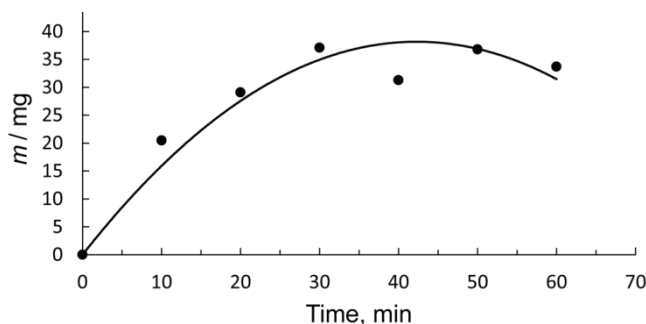


Fig. 7. Mass of Fe–Ni alloy as function of time of deposition, alkaline conditions (80 °C).

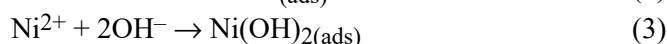
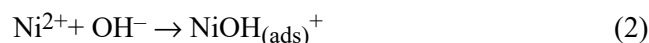
This is the reason why after about 30 min in the particular solution investigated, the mass of the deposited Fe–Ni alloy at the surface of the substrate decreased. Although the phenomenon of “bath instability” is far more complicated, and depends not only on temperature and time, but as well on the concentrations of the reducing agent, metal ions being reduced, complexing agents etc., these aspects were not analyzed in the present work. The intention of this work was to investigate the effects of time and temperature only, using the solutions from which an electroless deposition of Fe–Ni alloy in the autocatalytic mode is possible. In generic terms, an increase in the concentration of the reducing agent would lead to an increase in the rate of deposition.^{2,3,8,9} However, too high concentration of the reducing agent may trigger the bath instability and the deposition of metal powders in the bulk solution.^{8,9} Similarly, lower concentrations of the complexing agent, while the concentrations of the metal ions being deposited and that of the reducing agent are constant, would provoke the bath instability.

Taking into consideration the “metal–hydroxide mechanism” which explains the electroless deposition of metals due to the hydrolysis phenomena and the formation of intermediate hydrolyzed species, that are further reduced to a metal

using an appropriate reducing agent, the electroless deposition of Fe–Ni alloys can be explained as follows. At the Pd activated catalytic surface, the ionization of water takes place according to the reaction:



Due to the adsorption of OH^- at the metal surface, the hydrolysis of Ni^{2+} and formation of hydroxo-complexes takes place as follows:



The hypophosphite ions interact directly with the hydrolyzed species as presented with the reactions:



A combination of the Eqs. (4) and (5) leads to:



The similar reactions are attributable to the deposition of iron from iron-hydrolyzed species, *i.e.*, FeOH^+ and $\text{Fe}(\text{OH})_2$:



Deposition of phosphorus can be described with the following equation:



The composition of the electroless deposited Fe–Ni alloy from an alkaline solutions as a function of temperature is presented in Fig. 8. The composition of the alloy is practically independent of temperature. The deposits predominantly consist of about 70 mass% Ni, about 16 mass% Fe and approximately 14 mass% P. It is considerably important that the amount of Fe in the deposit, obtained from the alkaline conditions is significantly larger than that in the Fe–Ni alloys produced under the acidic conditions (see Fig. 3). An increased amount of Fe in Fe–Ni deposits is attributed to more obvious hydrolysis at higher pH.¹⁰ The results of the present work strongly suggest that an increase in pH leads to an increase in Fe content. Tartrate ions ($\text{C}_4\text{H}_4\text{O}_6^{2-}$) are well known complexing agents of Fe(II) and as such prevent the hydrolysis and formation of Fe(II) hydroxides. At lower pH, as observed in the present work during the deposition from acidic solutions, the amount of the deposited Fe is less than 1 mass %, suggesting that the hydrolysis of Fe(II) is negligible. Under the alkaline conditions, the Fe(II) ions produce FeOH^+ and $\text{Fe}(\text{OH})_2$ species progressively. The hydrolyzed Fe(II)-species are further reduced with hypophosphite to Fe at the catalytic surface. Consequently,

the amount of Fe in the deposited Fe–Ni alloys from alkaline solutions is significantly larger.

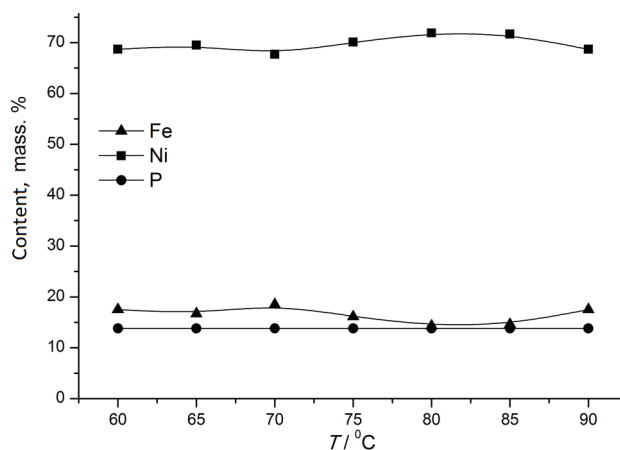


Fig. 8. Composition of Fe–Ni alloy as function of temperature.

The deposited Fe–Ni alloys from the alkaline solutions were smooth and shiny in appearance, similar to those produced under the acidic conditions. SEM images of Fe–Ni alloys deposited from alkaline solutions are shown in Fig. 9. Some pores were observed in the SEM images (left), which are attributed to the simultaneous hydrogen evolution during the deposition process. Also, some globular surface morphology is visible.

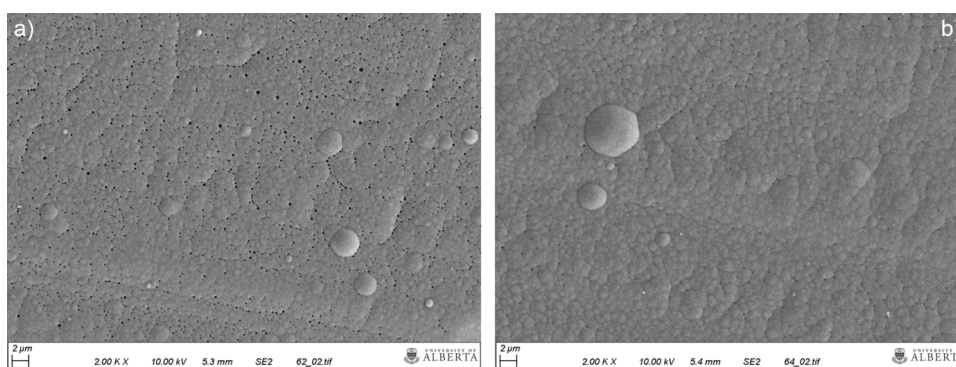


Fig. 9. SEM images of deposited Fe–Ni–P alloys from alkaline solutions at: a) 75 and b) 85 °C.

According to the XRD analysis, the deposited Fe–Ni–P alloys from alkaline solutions and similarly to those produced under the acidic conditions are amorphous. A typical XRD pattern of these deposits with a broad diffraction peak is shown in Fig. 10. The appearance of this broad peak in the XRD pattern suggests the amorphous structure of the deposited Fe–Ni–P alloys. As reported earlier,^{2,4}

the amorphous structure of the electroless deposited iron group metals and alloys is always observed when the hypophosphite is used as a reducing agent. It is believed that an incorporation of phosphorus during the deposition of metals and alloys of the iron group unavoidably leads to the production of amorphous structures.

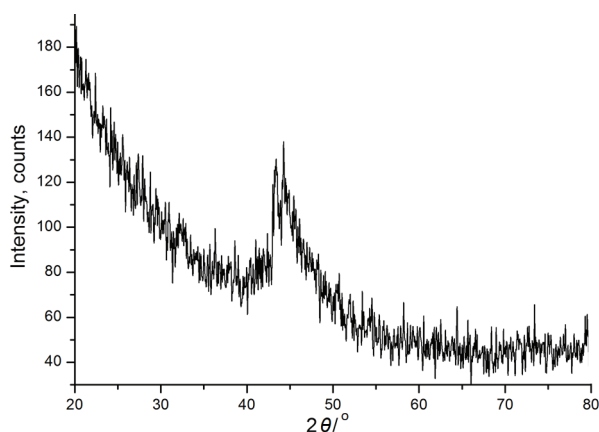


Fig. 10. Typical XRD pattern of Fe–Ni–P deposit from alkaline solutions (80 °C).

CONCLUSION

The electroless deposition of Fe–Ni alloys can be quite successful from both acidic and alkaline solutions. Under the acidic conditions, the amount of Fe in the deposited films is negligible (less than 1 %). The amount of Fe in Fe–Ni alloys produced under the alkaline conditions is estimated at about 15 %. Due to a more pronounced hydrolysis at higher pH, the rate of deposition of Fe–Ni alloys is faster than that in the acidic conditions. The electroless deposited Fe–Ni alloys, from both acidic and alkaline conditions, contain about 14 % P and as such display an amorphous structure.

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ИЗВОД

ХЕМИЈСКО ТАЛОЖЕЊЕ ЛЕГУРА ГВОЖЂА И НИКЛА ИЗ КИСЕЛИХ И БАЗНИХ РАСТВОРА СА ХИПОФОСФИТОМ КАО РЕДУКЦИОНИМ СРЕДСТВОМ

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У овом раду је проучавано хемијско таложење легура гвожђа и никла из киселих и базних раствора, користећи хипофосфит као редукционо средство. Експерименталним

результатима potvrđena je аутокаталитичка природа овог процеса. Показано је да је састав добијених легура независан од температуре таложења. Легуре гвожђа и никла добијене из киселих раствора садрже мање од 1 % гвожђа. Удео гвожђа у легурама добијеним из алкалних раствора износи око 15 %. Таложење легура гвожђа и никла знатно је брже у базним растворима захваљујући израженијој хидролизи Fe(II) и Ni(II) јона. Легуре које се добијају из ове две врсте раствора садрже фосфор и услед тога су аморфне структуре.

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