

# Electroless Nickel Plating

Fundamentals to Applications

edited by  
Fabienne Delaunois  
Véronique Vitry  
Luiza Bonin



CRC Press  
Taylor & Francis Group

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# Foreword

I am delighted to write a foreword for this book entitled *Electroless Nickel Plating: Fundamentals to Applications*, edited by Prof. Véronique Vitry, Prof. Fabienne Delaunois, and Dr. Luiza Bonin, with contributions from many eminent researchers in this field. Electroless plating has emerged significantly since its accidental discovery in 1946 by Brenner and Riddell. During the past three decades, there has been intense research activity in this field. Bringing out a book on electroless plating now is timely and essential, as the earlier books on this topic date back to 1991. This book consists of nine chapters, with a good blend of fundamental aspects of electroless plating and its recent developments. The coverage of topics is comprehensive and it ranges from the chemistry of electroless plating, the green chemistry approaches in developing suitable formulations and the characteristics of electroless Ni-P and Ni-B coatings with special emphasis on corrosion resistance and tribological behavior. All the chapters are integrated well. The inclusion chapters on modified electroless nickel coatings, which consists of electroless Ni-P and Ni-B composite coatings, poly-alloy, multilayer, and graded coatings, is one of the highlights of this book. Presentation of a chapter on the emerging applications of electroless plating is unique and interesting. The contributors of this book have done a wonderful job in bringing out this book. I congratulate Prof. Véronique Vitry and other eminent contributors for their valiant effort in compiling a useful reference material. I foresee that this book shall be a valuable addition in university libraries worldwide and as a reference book for researchers in surface engineering.

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# Acknowledgments

This book was born as one of those crazy ideas that are usually put to the side, but this one did not accept to be forgotten and when we finally decided to go for it, none of us expected to enter in such an adventure and to bring it to fruition only a handful of months after Dr. Bonin's graduation.

There are many people who have made this possible and who we'd like to thank.

- The metallurgy lab at UMONS that has dealt with three very busy ladies during last 2 years.
- UMONS and the FNRS for the travel grant that allowed Prof. Vitry time to finalize this book.
- The University of Coventry, and mostly its Functional Materials Research Group, that has not only hosted Prof. Vitry but also provided help and moral support through the last rush. Shakiela, Andrew, and the others, thanks for all.
- The University of Gent, where Dr. Bonin continues her career, for allowing her to continue writing this book.
- All our friends who have helped us to alleviate stress during the last months of the writing process.
- Last, but not least, our families who have had to live with this book for the last year, and mostly Leonardo, who is not only Dr. Bonin's husband but also her chief copy-editor, as well as Jonas and Sonia, who have accepted to see their mother go away for weeks without complaint.



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# Editors



**Fabienne Delaunois** received her engineering degree in metallurgy and her PhD from the Engineering Faculty of Mons (FPMs) in 1993 and 2002, respectively. She's been working on electroless nickel-boron for more than 20 years and has authored approximately 20 publications in that field.

She's very active as an expert for industries in various fields such as failure analysis and corrosion. She is currently a Professor and the Department Head in the Metallurgy Laboratory at the Engineering Faculty of the University of Mons, Belgium, where she teaches principally Physical Metallurgy and Recycling.

She chaired the Chemistry and Materials Science department of the Engineering Faculty of UMONS from 2010 to 2017 and is a member of the board of two research centers in the field of materials: Materia Nova and BCRC-INISMa.

**Véronique Vitry** received her engineering degree in materials science from the Engineering Faculty of Mons in 2003 and first worked on optical PVD coatings for a research center. She then pursued her PhD in engineering from the University of Mons and graduated in 2010.

Her main research interest is electroless nickel plating, which she has been studying for more than 10 years, leading to more than 30 publications in international journals. She's also involved in the research on powder metallurgy, corrosion, recycling, and physical metallurgy.

She's currently a part-time associate professor and senior research and teaching associate at the Engineering Faculty of the University of Mons (UMONS), where she teaches process metallurgy and process modeling, thin films, nanotechnologies and spectroscopic methods in chemical and materials analysis.

She's the Vice president and Regional Chair for the North of France and Belgium of A3TS (the French Heat and Surface Treatment Association). She also chairs the International Relations Committee of the Failure Analysis Society (FAS), an affiliate of ASM.

She's currently an advisor to the Rector of UMONS on Internationalization at Home.

**Luiza Bonin** started graduate studies in materials engineering at the Federal University of Santa Catarina, in 2009. Since then, Luiza has been quite attracted to the principles of sustainable development and had the opportunity to work with new and greener synthesis processes. In 2013, she was granted with an academic mobility program and had the opportunity to perform a Master thesis at CIRIMAT (Toulouse, France) related to greener chemistry routes for the production of zirconia coatings. Immediately after her graduation in 2014, she moved to Belgium to start her PhD at the Metallurgy lab of the University of Mons, where she worked on the replacement of lead stabilizer in electroless nickel-boron deposits and the electrochemical/mechanical characterization of coatings that originated from greener baths. She has been working with new compositions of electroless nickel-boron since 2014, and she has authored 11 papers in the field of electroless nickel. Luiza received her PhD degree in 2018 and is currently working at the Ghent University.

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# List of Acronyms

<b>AA</b>	Aluminium Alloy
<b>AFM</b>	Atomic Force Microscope
<b>AISI</b>	American Iron and Steel Institute
<b>AMS</b>	Aerospace Materials Standard
<b>ASTM</b>	American Society for Testing and Materials
<b>BF</b>	Bamboo Fabric
<b>CEM</b>	Cation Exchange Membrane
<b>CFX</b>	Fluorinated Carbon
<b>CMC</b>	Critical Micelle Concentration
<b>CMMC</b>	Compositionally Modulated Multilayer Coatings
<b>CNT</b>	Carbon Nanotubes
<b>COF</b>	Coefficient of Friction
<b>CSP</b>	Crab Shell Particles
<b>CTAB</b>	Cetyl Trimethyl Ammonium Bromide
<b>DMAB</b>	Dimethyl Amine Borane
<b>DSC</b>	Differential Scanning Calorimetry
<b>DTAB</b>	Trimethyl Ammonium Bromide
<b>E</b>	Elastic Modulus
<b>ED</b>	Electrodeposition
<b>EDX</b>	Energy Dispersive X-ray (Spectroscopy)
<b>EIS</b>	Electrochemical Impedance Spectroscopy
<b>ELV</b>	End of Life Vehicle
<b>EMF</b>	Electromotive Force Series
<b>EMI</b>	Electro-Magnetic Interference
<b>EN</b>	Electroless Nickel
<b>EN</b>	European Normalization
<b>EP</b>	Electroless Plating
<b>ESP</b>	Electric Submersible Pump
<b>FCC</b>	Face Centered Cubic
<b>FGM</b>	Functionally Graded Material
<b>GDOES</b>	Glow Discharge Optical Emission Spectroscopy
<b>GFRP</b>	Glass Fiber Reinforced Plastic
<b>H</b>	Hardness
<b>HEED</b>	Hybrid Electro-Electroless Deposited Coatings
<b>HK</b>	Knoop Hardness Unit (Macro Hardness)
<b>hk</b>	Knoop Hardness Unit (Micro Hardness)
<b>HRC</b>	Rockwell Hardness Unit
<b>HRTEM</b>	High Resolution Transmission Electron Microscope
<b>HV</b>	Vickers Hardness Unit (Macro Hardness)
<b>hv</b>	Vickers Hardness Unit (Micro Hardness)
<b>LM</b>	UK/India Standard for Aluminium Alloys
<b>MEMS</b>	Micro Electro Mechanical System

<b>MIL</b>	USA Military Standard
<b>MMC</b>	Metal Matrix Composite
<b>MTO</b>	Metal Turnover
<b>NACE</b>	National Association of Corrosion Engineers
<b>NCZ</b>	Electroless Nickel Coated ZrO <sub>2</sub>
<b>NDP</b>	Diamond Nanoparticles
<b>NiB</b>	Nickel-Boron
<b>NiP</b>	Nickel-Phosphorus
<b>PC</b>	Polycarbonate
<b>PM</b>	Powder Metallurgy
<b>PP</b>	Polypropylene
<b>PS</b>	Polystyrene
<b>PTFE</b>	Polytetrafluoroethylene
<b>PVP</b>	Polyvinylpyrrolidone
<b>R&amp;D</b>	Research and Development
<b>RA</b>	Activated Rosin
<b>R<sub>a</sub></b>	Average Roughness
<b>RH</b>	Reductant ( <a href="#">Chapter 1</a> )
<b>RH</b>	Relative Humidity ( <a href="#">Chapter 4</a> )
<b>RMA</b>	Rosin Mildly Activated
<b>RoHS</b>	Restriction of Hazardous Substances (UK Directive)
<b>R<sub>p</sub></b>	Peak Roughness
<b>R<sub>q</sub></b>	Quadratic Roughness
<b>R<sub>t</sub></b>	Maximal Peak/Valley Distance
<b>R<sub>v</sub></b>	Depth of Valleys
<b>R<sub>z</sub></b>	Total Roughness
<b>SAE</b>	Society of Automotive Engineers
<b>SCE</b>	Standard Calomel Electrode
<b>SDS</b>	Sodium Dodecyl Sulfate
<b>SEM</b>	Scanning Electron Microscope
<b>SHE</b>	Standard Hydrogen Electrode
<b>SLS</b>	Sodium Lauryl Sulfate
<b>SMC</b>	Step-Wise Multilayer Coatings
<b>STM</b>	Scanning Tunneling Microscope
<b>TEM</b>	Transmission Electron Microscope
<b>TWI</b>	Taber Wear Index
<b>UI</b>	Ultrasonic Impulsion
<b>WEEE</b>	Waste Electrical and Electronic Equipment
<b>XRD</b>	X-ray Diffraction
<b>YSZ</b>	Yttria Stabilized Zirconia

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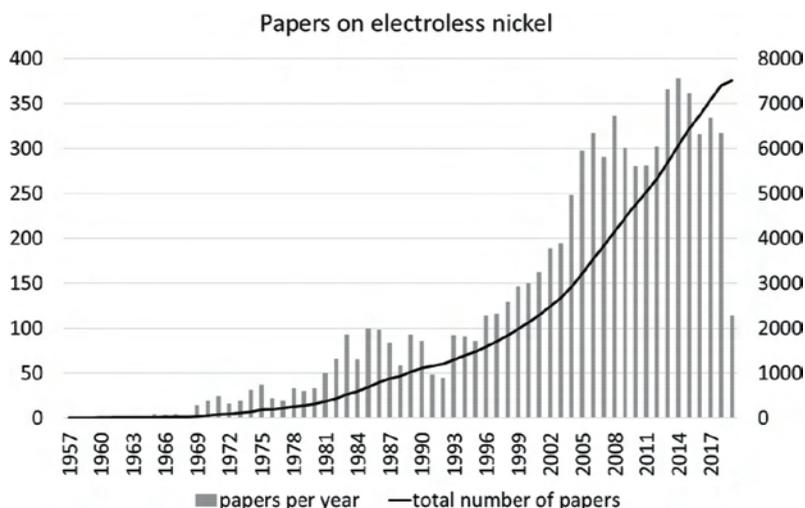
# Introduction

Electroless plating is a process that is at the same time very simple in its principles and very complex in its execution. It involves reduction of metallic salts (nickel for the coatings described in this book) to the metallic state by a chemical agent in an aqueous solution. The process thus does not use any external current sources, which brings it some really interesting advantages over electroplating such as the possibility to plate nonconductive materials and the absence of edge effects that allows to plate very complex-shaped parts with perfect throwing power and dimensional compliance as long as the solution can reach the surfaces to be plated. Other differences with electroplating include the absence of a metallic anode—metallic ions that are reduced are provided directly in the aqueous solution form—and the catalytic nature of the process, which is not only one of its most distinctive features but also one of its most complex ones. However, similar to electroplating, the reaction leading to the formation of the metallic deposit is electrochemical and includes charge transfer in the solution.

The versatility of electroless nickel plating, illustrated by a variety of coatings obtained with this method, from the electroless nickel-phosphorus to the more exotic nickel-boron, multi-alloyed coatings, multilayers and composites, and the specific characteristics of the process make electroless nickel coatings increasingly popular in large areas of industry. They are among the best candidates to replace hard chrome plating in most of its applications.

There are not many books on electroless nickel plating, and the field has not been the object of much scientific interest before the late 1990s, as shown in [Figure I.1](#). Out of the 25,700 papers on the subject retrieved by Google Scholar, 75 are from the 1950s, 500 from the 1960s, 700 from the 1970s, 1000 from the 1980s, 3000 from the 1990s, more than 8000 from the 2000s, and 13,000 from the last 10 years. The amount of knowledge that has been accumulated since the 2000s is astonishing. This period coincides, according to B. Zhang, with electroless nickel's entrance in its fourth stage of development: in-depth development including deep investigation into the mechanism and theory of electroless plating and the nanoelectroless plating stage.<sup>1</sup> Furthermore, as said by Weill as early as the 1980s, “the understanding that has been gained is to a great extent responsible for changing plating from an art to a science.”<sup>2</sup> The increase in knowledge about the field more than justified the publication of a new book that would include not only the theory and concepts of electroless nickel plating but also the new developments of the field and the deeper knowledge gained in recent years.

This book is our attempt to summarize the thriving and complex field of electroless nickel and to present in a concise form the present state of knowledge of both theoretical and applied aspects of electroless nickel. The theoretical part of this book includes not only a discussion of electrochemical thermodynamics of the process but also information about kinetics, nucleation, growth, and morphology of the coatings that are formed by electroless plating of nickel. In the more practical part,



**FIGURE I.1** Publications on electroless nickel as listed in Scopus on April 16, 2019.

information about the properties and applications of electroless nickel-based coatings are included, and information about recent developments in electroless plating such as the use of composites, ultrasound, multi-alloyed deposits, and multilayers, as well as when possible, meta-analysis of available data and quantitative discussion, are also included.

The [first chapter](#) addresses the thermodynamical conditions of electroless plating as well as the kinetics aspects of the process. It also discusses the catalytic nature of electroless plating and the role of various components in the electroless plating baths.

The [second chapter](#) is dedicated to the growth of electroless nickel coatings. In this chapter, some practical aspects such as substrate cleaning and activation are discussed and catalytic activity of substrate and growth modes of coatings are also discussed in depth.

[Chapter 3](#) examines all aspects of electroless nickel-phosphorus, which is the most popular avatar of the technology and is currently used in a large array of industrial applications. These coatings are described from plating bath chemistry and operation to properties, effect of heat treatment, and applications. Recent trends in the electroless nickel-phosphorus field, including the search for more environmentally friendly plating solutions, are also discussed.

The [fourth chapter](#), divided into two parts, is dedicated to electroless nickel-boron. The first part focuses on plating bath chemistry and properties of the coatings while the second part contains information about posttreatments and the way they affect electroless nickel-boron coatings.

The next four chapters are dedicated to modifications of the classic electroless plating process by various means. First, ultrasound assistance is described in [Chapter 5](#). The use of ultrasound during plating is an increasingly popular method for improving coating properties and increasing plating rate. It is also very useful

for the synthesis of composite coatings. Next, [Chapter 6](#) describes polyalloyed electroless nickel, which are coatings in which at least one other element is added to the electroless nickel-phosphorus or nickel-boron coating by co-reduction of metallic salts. These polyalloyed coatings present several very interesting properties and open various new areas of application to electroless nickel coatings. The next modification, discussed in [Chapter 7](#), is multilayer electroless nickel coatings. Multilayer coatings can be formed with a single material or by mixing materials, and they bring increased corrosion and wear resistance to electroless nickel coatings. Finally, composite electroless nickel coatings are discussed in [Chapter 8](#). The aim of using composite coatings is usually to decrease wear of the material by carrying out one of the following methods: addition of hard particles or addition of solid lubricant particles.

The last chapter of this book is dedicated to more practical aspects of electroless nickel coatings. The first part focuses on applications and both standard applications, such as increase in wear and/or corrosion resistance of the substrate materials, and more specific applications—catalytic materials, magnetic shielding, and so on—are discussed. The last section of the book presents advice for people who wish to begin using or making electroless nickel coatings.

This book is intended as a companion for professional electrochemists, advanced undergraduate and postgraduate students, and also for electroless plating specialists with a physical, technical, or chemical education, engineers, and specialists engaged in research on new coating technologies related to metallic layers and amorphous alloys.

The methods of metal and alloy deposition without the use of external current sources are very important in modern technology, especially in the production of new materials for applications in electronics, wear and corrosion resistant materials, medical devices, battery technologies, and so on. We hope this book will be useful for the readers and will help them develop a better understanding of those specific processes.

**Prof. Véronique Vitry**  
*Coventry, April 16, 2019*

## REFERENCES

1. Zhang, B. *Amorphous and Nano Alloys Electroless Depositions: Technology, Composition, Structure and Theory*, n.d.
2. Weill, R. 1982. "Plat." *Surf. Finish.* 69 (46): 18.



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# 1 Chemistry of Electroless Plating

*Mustafa Urgan*

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## 1.1 INTRODUCTION

Electroless metal deposition, also known as chemical deposition, is conducted in an electrolyte similar to metal plating, in which a chemical reducing agent is added. Thus, the metal ions are reduced not by polarizing the cathodic reaction by an external source but by the oxidation of the chemical reductant on the metal surface. In electroless deposition, a homogeneous coating thickness is achieved, independent of the shape of the metal parts to be deposited.

In this chapter, the basic principles of electroless plating will be outlined for providing the readers a scientific and technological perspective on the interdisciplinary and complex nature of electroless plating. This chapter starts with the comparison of electroless plating with other methods of deposition that use metal ions dissolved

in liquids as a source of depositing metals. As the reactions involved in the process are chemical and electrochemical, thermodynamic and kinetic principles relevant to electroless plating are also summarized by giving emphasize on the hydrogen evolution reaction and its relation to the catalytic selective surfaces. Section 1.7 is devoted to mixed potential theory, which is extensively used to explain the kinetics of electroless deposition. In Section 1.8, the role of deposition parameters and bath constituents in the electroless nickel deposition processes is outlined.

## 1.2 CHEMISTRY OF ELECTROLESS PLATING

The history of electroless plating dates back to 1844; there are very comprehensive book chapters and reviews that cover the history of this plating method (Riedel 1991; Popov et al. 2002; Mallory and Hajdu 1991). Here, only the major milestones and a brief review on the progress of electroless plating will be given. Wurtz (1844) observed that nickel ions can be reduced by hypophosphite ions. The first bright electrodeposits were obtained in 1911 by Breteau (Breteau 1911). In 1916, Roux received the first patent on electroless Ni plating. However, these baths either decomposed spontaneously or very slow. In 1946, Brenner and Riddell (1946) described the proper conditions for obtaining electroless deposition. The main contribution of Riddell and Brenner was to understand and define the kinetic conditions to keep these thermodynamically unstable baths from spontaneous decomposition. Today, many metals and alloys can be electroless deposited relying on the principles put forth by Riddell and Brenner. In the periodic table given below (Table 1.1), the metals and metalloids that can be deposited by electroless method are outlined. Though the table indicates that many elements have the ability to be deposited on different substrates, major coatings produced by electroless method are those of Ni-P, Ni-B, Cu, and Ag, among which Cu- and Ni-based ones have the widest technological application area.

**TABLE 1.1**  
**Metals and Metalloids That Can Be Electroless-deposited**

1																	2		
H																	He		
3	4													5	6	7	8	9	10
Li	Be													B	C	N	O	F	Ne
7	9													11	12	14	16	18	20
11	12													13	14	15	16	17	18
Na	Mg													Al	Si	P	S	Cl	Ar
23	24													27	28	31	32	35	40
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
39	40	45	48	51	52	55	56	59	58	64	65	70	73	75	79	80	84		
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
85	86	89	91	93	96	(98)	101	103	106	108	112	115	116	122	128	127	131		
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86		
Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
133	137	139	178	181	184	186	190	192	195	197	201	204	207	209	(210)	(211)	(222)		
87	88	89	104																
Fr	Ra	+Ac	Rf																
(223)	(226)	(227)	(267)																

Source: Kanani, N., *Electroplating Basic Principles*, Elsevier, Burlington, VT, 2004.

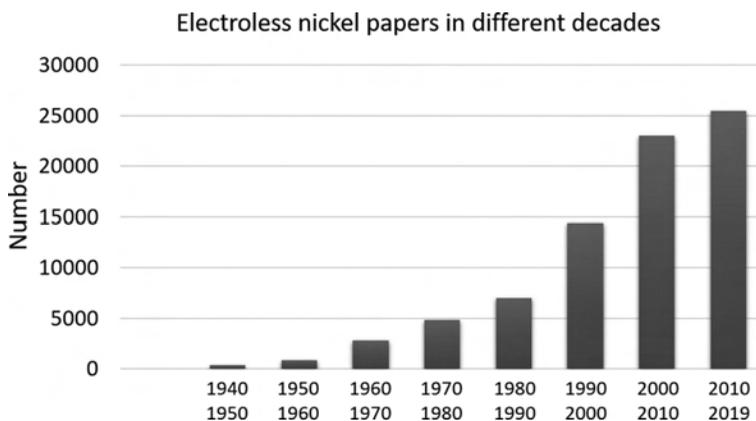
The readers interested further in the history of electroless plating and the major contributors to the development of electroless baths may refer to the papers published by Shipley (1984) and Brenner (1984) on the history of the commercialization of electroless plating beyond the discovery of electroless nickel (Shipley 1961; Brenner 1984).

A very comprehensive study on the progress of electroless plating until 2010 can also be found in the book of Zhang (2016). After the collection of the number of papers and patents from different databases, they classified electroless deposition process stages as early stage of development (mid-1940s to 1959), slow growth period (1960–1979), rapid development period (1980–1999), and fundamental mechanistic studies and development of nanoelectroless plating (2000–present).

According to this study, during the first two periods of slow growth is a kind of incubation period. In these stages, studies on the development of the stability of baths, efforts for application of electroless plating to larger scales, development of methods for electroless deposition of other metals (especially copper), and commercial applications in small scale have occurred.

Increase in the scientific interest on the mechanism of electroless plating, determination of interesting physical and chemical properties of electroless deposits (mechanical, magnetic, chemical resistance, etc.), extension of large-scale electroless plating to different industrial fields, development of ternary and multicomponent alloys and composites, and participation of China and India in the research and developments in the plating field are discussed in the same papers as the main reasons of the rapid development stage. Figure 1.1 shows the number of papers published on electroless nickel deposition since 1940.

Today, more than thousands of electroless plating facilities around the world have extended the use of electroless plating in different industry sectors (mainly automotive, petrochemical, and electronics) and estimated 15 billion USD output value in the world market (Zhang et al. 2014), which makes this deposition method an important player in the surface treatment field. The unique properties of this deposition method



**FIGURE 1.1** Number of papers and US patents published on electroless nickel deposition since 1940 (from Zhang (2014).)

such as geometry-independent homogeneous deposition on any kind of substrate; possibility of deposition in amorphous and/or nanocrystalline, composite, and nanocomposite state; ability to be deposited in alloy form; possibility of deposition on conductive and nonconductive powders, and fibers; and deposition on selected areas are some of the reasons for continuing expansion of R&D activities and industrial use of electroless nickel (EN) plating.

### 1.3 COMPARISON OF ELECTROLESS PLATING WITH OTHER ELECTROLYTIC METAL DEPOSITION PROCESSES

Electroless metal plating is an autocatalytic process that proceeds in accordance with the electrochemical kinetic principles. This property differentiates this method from other metal deposition processes that use metal ions as source of plating. Namely, in electroplating, we supply the electrons required for the reduction of metal ions using an external power supply, or in galvanic displacement/immersion metal plating, the electrons required for the reduction of the metal ions are supplied through corrosion of the metal substrate. In electroless plating, the electrons required for the reduction of the metal ions are supplied by the oxidation of the chemical compound, (reducing agent) present in the solution.

When compared from the thermodynamic point of view, the driving force for immersion plating or galvanic displacement is the potential difference between half-cell (single electrode) reactions, the addition of which is the total reaction. Let's consider copper deposition on steel when immersed in an acidic sulfate solution containing copper ions. In this case, there are two half-cell cathodic reactions and one half-cell anodic reaction; i.e., hydrogen evolution reaction and reduction of copper ions are the two half-cell cathodic reactions, both of which gets the electrons required for the reduction from the dissolution reaction of iron (anodic half-cell reaction). Thus, the reduction of copper ions in the solution is only possible when the iron surface is exposed; once the surface is covered with copper, the reaction stops. Deposition process starts all over the surface that is in contact with the copper ion-containing solution.

Electrolytic metal plating on the other hand does not choose substrate material as long as it is conductive; for example, it is possible to electrodeposit zinc on iron, although electrode potential of zinc is far more electronegative than iron, because the energy required for the reduction of the metal ions in the solution is supplied externally with the help of a power supply. In these systems, a positive electrode (anode) is required to complete the circuit. The need for an anode in the system turns it into a line of sight process, which means the deposition process shows a strong dependence on its position relative to the anode. On the edges, we have thicker coatings, and so we cannot deposit inside holes, although the solution containing the metal ions to be deposited is in contact with the substrate metal. In electroless plating, the deposition starts and proceeds at the same rate all over the substrate as long as metal ions and reductant are present, which is one of the major advantages of the technique. However, a certain combination of substrate metal and reductant is required for the realization of the process. The reasons for this selectivity will be explained in the following sections.

## 1.4 THERMODYNAMIC ASPECTS OF ELECTROLESS DEPOSITION

Electroless deposition of metals is an electrochemical process that proceeds according to the principles of thermodynamics and kinetics of electrochemical reactions. Today, it is well known that the driving force of this spontaneous electroless deposition process is the potential difference between minimum two half-cell (single electrode) reactions, namely anodic half-cell and cathodic half-cell reactions and proceeds under mixed potential control.

The reduction of metal ions constitutes the main cathodic half-cell of the overall reaction. For the realization of the reduction reaction spontaneously, an anodic reaction (anodic half-cell) that will supply the electrons needed for the reduction of metal ions is required. The number of reducing agents suitable for electroless plating is rather limited. The major reducing agents used in electroless deposition and their standard potentials are given in Table 1.2.

The standard electrode potentials of the cathodic half-cell reactions can be extracted from electromotive force (EMF) series. Simply, for the standard electrode potential ( $E_0$  or  $E_{rev}$ ) for the cathodic half-cell reaction for nickel is presented in Equation 1.1:



**Equation 1.1:** Standard electrode potential of  $\text{Ni}_{+2}/\text{Ni}_0$  reaction

This potential is valid for standard conditions, namely for nickel ion activity of 1, 298 K and 1 atm. As very well known, when the conditions are away from standard conditions, new values can be calculated by using Nernst equation. The potential  $E$  of the  $\text{Me}^{+n}/\text{Me}$  electrode is a function of the activity ( $a$ ) of metal ions in the solution (Equation 1.2):

$$E = E_0 + \frac{RT}{nF} \ln a_{\text{Me}^{+n}}$$

**Equation 1.2:** Nernst equation

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**TABLE 1.2**

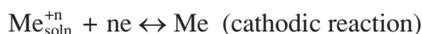
### Main Reducing Agents Used in Electroless Deposition and Their Standard Electrode Potentials

Name	Chemical Formula	Available Electrons	Standard Electrode Potential (V)	Used for deposition of
Sodium hypophosphite	$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$	2	-1.57 in alkaline/-0.5 acidic	Ni, Co
Sodium borohydride	$\text{NaBH}_4$	8	-1.24 alkaline	Ni, Co
Dimethylamine borane	$(\text{CH}_3)_2\text{NH} \cdot \text{BH}_3$	6	-1.18 alkaline	Ni, Co, Ag
Formaldehyde	HCHO	2	-1.11 alkaline	Cu, Ag
Hydrazine	$\text{N}_2\text{H}_4$	4	-1.16 alkaline	Cu

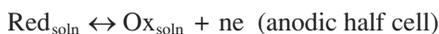
Source: Riedel, W., *Electroless Nickel Plating*, Finishing Publication Ltd, London, UK, 1989.

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When we write half-cell electrode reactions (Equations 1.3 and 1.4) that constitute the total reaction, we can calculate the free energy or electrode potential of the total reaction (Equation 1.5) that will tell us whether these reactions are prone to proceed.



**Equation 1.3:** Cathodic half-cell reaction



**Equation 1.4:** Anodic half-cell reaction



**Equation 1.5:** Total of anodic and cathodic half cell reactions

Simply, if  $\Delta G$  of the total reaction is negative, the reaction proceeds spontaneously in the written direction. Because the relation between standard free energy and the standard electrode potential is  $\Delta G = -nFE_0$ , the reaction proceeds in the written direction if  $\Delta E$  of the total reaction is positive.

The thermodynamic calculations either by using chemical or electrochemical rules indicate that when the metal ions to be reduced are introduced into a solution that contains appropriate reductants, reactions are thermodynamically possible. However, it is fortunate that the rate of these reactions is very low and they require overcoming of large activation energy barriers to proceed at an appreciable rate. Thus, from the thermodynamic point of view, the electroless metal plating solution can be described as metastable that can be made to proceed at an appreciable rate by decreasing the activation energy barrier for the reaction. The decrease of the activation energy barrier for the reaction is achieved by the introduction of a catalytic substrate surface into the bath (Ni, Pt, Pd, etc.). The role of catalytic processes on electroless plating will be further discussed in kinetics section.

Thermodynamics is also an important tool in designing or developing electroless baths. For the reasons explained further in this book, we may require electroless nickel plating baths with different pH values extending from acidic to basic. In these cases, for the deposition process to occur, nickel must be in ionic form. Potential-pH diagrams based on thermodynamic calculations can be used for the selection of proper complexing and chelating agents. For example,

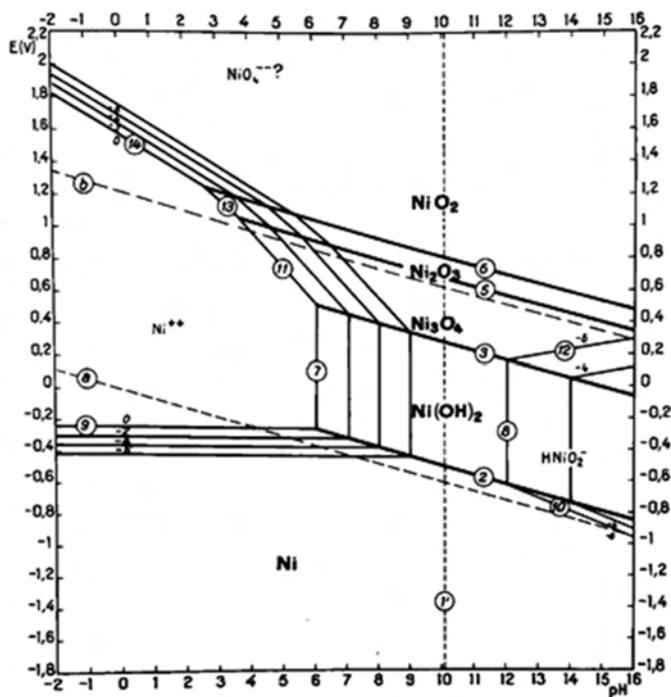
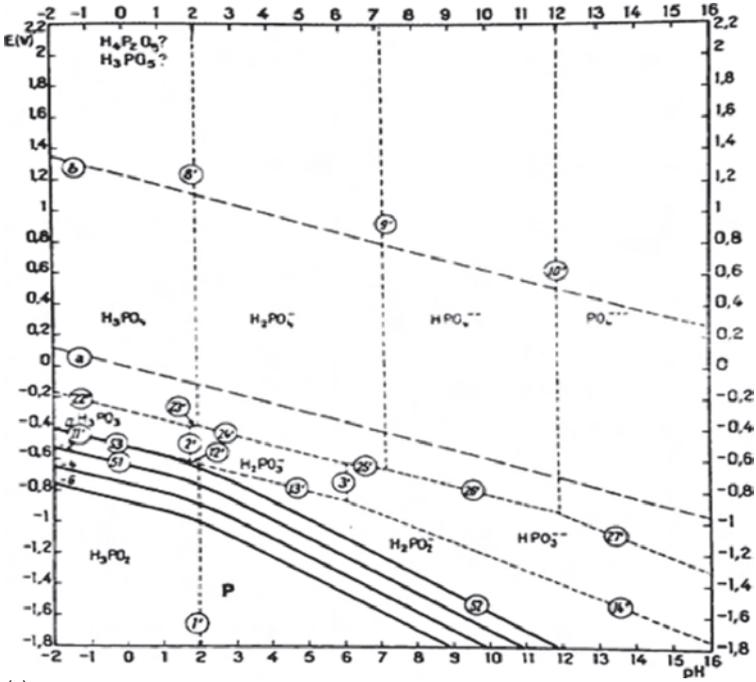


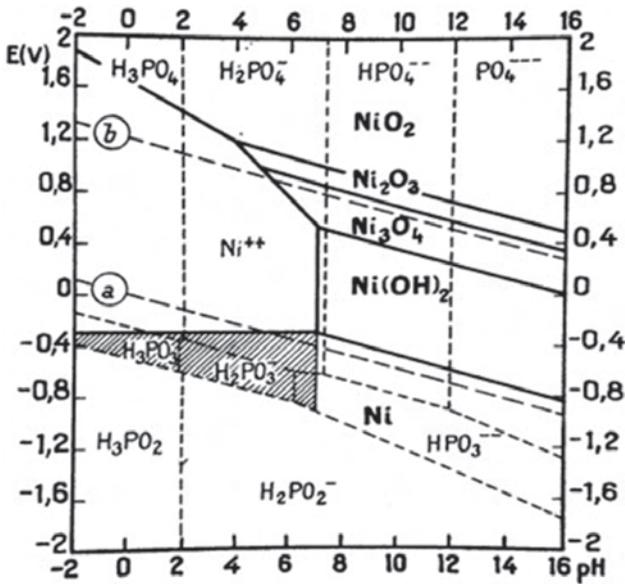
FIGURE 1.2 Potential-pH diagrams of Ni-H<sub>2</sub>O.

the reductant (sodium borohydride) for electroless Ni-B plating require alkaline environments to function; thus, nickel should also be in ionic form under these conditions, which is not possible in water-based solutions without complexing and chelating agents (Figure 1.2). However, we can achieve the required ionic form that can be reduced with this reductant that contains nickel by forming nickel-amine complexes.

Similarly, the pH and environment oxidation potential dependence of the reductant agents can also be determined by using the potential-pH diagrams. For example, the stability region of reductants in Ni-P and Ni-B baths can be determined by using P-H<sub>2</sub>O and B-H<sub>2</sub>O potential-pH diagrams. An example of the usage of potential-pH diagrams for Ni-P system is presented in Figure 1.3. In this diagram, Ni-H<sub>2</sub>O potential-pH diagram calculated for 0.6 g/L Ni<sup>+2</sup> is superimposed on P-H<sub>2</sub>O diagram (Pourbaix 1966). The hatched region of this diagram clearly indicates that it is thermodynamically possible to reduce nickel ions by the oxidation of hypophosphites to phosphites or phosphates.



(a)



(b)

**FIGURE 1.3** (a) P-H<sub>2</sub>O potential-pH diagram. (b) Superimposed Ni-H<sub>2</sub>O and P-H<sub>2</sub>O diagram (for Ni<sup>2+</sup> concentration of 0.6 g/L). (From Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Vol. 1, Pergamon Press, London, UK, 1966.)

## 1.5 CONTRIBUTION OF HYDROGEN EVOLUTION REACTION TO ELECTROLESS PLATING

Some interesting aspects of electroless deposition are:

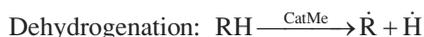
- Only some substrate metals act as a catalyst,
- The restricted number of reductants, and
- Hydrogen evolution in almost all of them.

Among these, hydrogen evolution attracted a significant interest not only because of its generation mechanism but also its possible contribution to the catalytic activity of specific metals and also on the specificity of the reductants.

Five different mechanisms are proposed for the explanation of hydrogen evolution and its relation to metal and metalloid deposition in electroless metal plating. These are pure electrochemical (Elze 1960; Minjer 1975; Müller et al. 1960), metal hydroxide (Cavallotti and Salvago 1968; Salvago and Cavallotti 1972), hydride ion, atomic hydrogen (Hersch 1955; Lukes 1964), and modified atomic hydrogen or dehydrogenation mechanisms (Nikiforova and Sadakov 1967; Donahue 1972; Gorbunova et al. 1973). Among these mechanisms, two of them, namely dehydrogenation (“universal mechanism” as named by Meeraker (Van der Meeraker 1981)) and metal hydroxide mechanism (Cavallotti and Salvago 1968) are the most widely used and accepted mechanisms that have the ability to explain most of the observations in the electroless deposition.

Universal mechanism combines electrochemical reactions with the atomic hydrogen mechanisms and introduces additional dehydrogenation and recombination reactions to the anodic reaction sequences. The general scheme of anodic and cathodic reactions for electroless plating according to this mechanism is given below (Van Den Meerakker 1981), where RH is the reductant such as formaldehyde, hypophosphite or borohydride. *CatMe* in Equation 1.6 stands for catalytically active metal surface.

Anodic reactions:



**Equation 1.6:** Dehydrogenation of the reductant during electroless metal deposition



**Equation 1.7:** Oxidation of the reductant radical during electroless metal deposition



**Equation 1.8:** Recombination of to give hydrogen gas molecules during electroless metal deposition

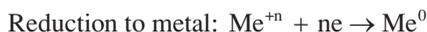


**Equation 1.9a:** Oxidation of in alkaline electroless metal deposition solutions



**Equation 1.9b:** Oxidation of in acidic electroless metal deposition solutions

Cathodic reactions:



**Equation 1.10:** Reduction of metal ions during electroless metal deposition

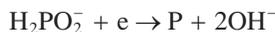


**Equation 1.11a:** Hydrogen evolution reaction in alkaline electroless metal deposition solutions

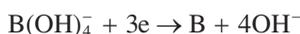


**Equation 1.11b:** Hydrogen evolution reaction in acidic electroless metal deposition solutions

In solutions where hypophosphite, aminoborane, and sodium borohydride are used as reductants, the co-deposition of phosphorus (Equation 1.12) or boron (Equation 1.13) is the other cathodic process.



**Equation 1.12:** Reaction that results in co-deposition of P in electroless nickel – phosphorous deposition solutions

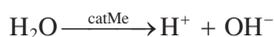


**Equation 1.13:** Reaction that results in co-deposition of B in electroless nickel – boron deposition solutions

According to the reaction sequences given above, dehydrogenation step (Equation 1.6) that leads to the formation of reductant (R) and hydrogen radicals determines the catalytic nature of the process. Initiation of electroless deposition on a metal substrate that does not have the ability to catalyze this reaction is not possible. The metals (such as Pt, Pd, Ni, and Co) that act as catalytic surfaces for the electroless deposition process are also good hydrogenation and dehydrogenation catalysts and the poisons for this reaction, such as thiourea and mercaptobenzothiazole, act as stabilizers for almost all electroless deposition processes. When we look at the same reaction scheme from the reductant perspective, a proper reductant for the electroless process should involve dehydrogenation step on the catalytic metal surface (reaction 1.6) during its oxidation so that the reduction of metal ions occurs directly on the substrate surface. All of the reductants used in the electroless deposition processes possess this property.

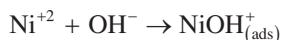
Another evidence that supports the deterministic role of reaction 1.6 is the higher efficiencies of deposition for metals with higher catalytic activity (Pd, W, Au, Mo, and Re) for dehydrogenation reaction. For example, in the case of Pd, a higher efficiency (100%) can be obtained when compared to Ni-B (45%) efficiency because of the higher catalytic activity of Pd toward dehydrogenation reaction (Van Den Meerakker 1981).

The other mechanism that also found acceptance especially for the case of Ni-P deposition from acidic electrolytes is the metal hydroxide mechanism put forth by Salvago and Cavallotti (Cavallotti and Salvago 1968; Salvago and Cavallotti 1972). According to this mechanism on the catalytic surface of nickel, ionization of water occurs (Equation 1.14)

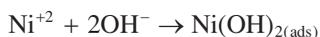


**Equation 1.14:** Ionization of water on catalytic nickel surface

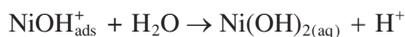
Then, nickel ions at the surface hydrolyze to give nickel hydroxo complexes



**Equation 1.15:** Hydrolysis reaction between nickel and hydroxyl ions to give hydroxo complexes

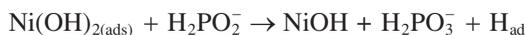


**Equation 1.16:** Hydrolysis reaction between nickel and hydroxyl ions to give nickel hydroxide ad atoms

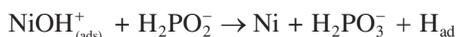


**Equation 1.17:** Hydrolysis of nickelhydroxo complexes to give nickel hydroxides and hydrogen ions.

As a result of the reaction of the hypophosphite ions with these hydrolyzed species, metallic nickel, atomic hydrogen, and orthophosphide ions are produced

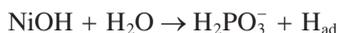


**Equation 1.18:** Reaction of hypophosphite ions with nickel hydroxide ad atoms to give orthophosphide ions and atomic hydrogen



**Equation 1.19:** Reaction of hypophosphite ions with nickel hydroxocomplexes to give metallic nickel, orthophosphide ions and atomic hydrogen

According to this mechanism, one of the sources of hydrogen evolution is the combination of atomic hydrogen that is formed in Equations (1.18 and 1.19). The other sources of hydrogen as put forth by this mechanism are the reaction of monovalent NiOH that is formed in accordance with reaction 1.18 with water (Equation 1.20) and/or direct reaction of hypophosphite ions with water (Equation 1.21).

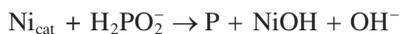


**Equation 1.20:** Reaction of hypophosphite ions with mono valent nickel hydroxides complexes to give atomic hydrogen



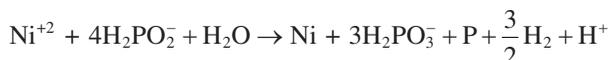
**Equation 1.21:** Reaction of hypophosphite ions with water to give molecular hydrogen.

Accordingly, the requirement of catalytic metallic surface come into play not only for reactions 1.14 and 1.20 but also for the reduction of hypophosphite ions to elemental phosphorous (Equation 1.22).



**Equation 1.22:** Reduction reaction of hypophosphite ions on catalytic nickel surface to give elemental phosphorous.

The overall reaction with proper stoichiometry is given as (Djokic 2014):



**Equation 1.23:** Overall reaction between nickel and hypophosphite ions to give Ni-P deposits and hydrogen gas.

## 1.6 KINETICS OF ELECTROLESS DEPOSITION PROCESSES

Kinetic aspects of electroless deposition are twofold: Kinetics of electrochemical reactions and nucleation and growth kinetics of the electroless deposited metals. In this section, the principles of electrochemical reaction kinetics relevant to electroless metal plating will be outlined. The second aspect is the kinetics of nucleation and growth will be briefly introduced in the section about the role of additives on electroless metal plating baths.

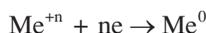
As explained in the previous sections, electroless deposition of metals is an electrochemical process under mixed potential control, which means that the process (at least the steps that involve electron transfer) proceeds, obeying electrochemical kinetic principles. Because of the electrochemical nature of the process, the rate of electroless deposition can be expressed as current and interrelated to the mass

of electrodeposit by using Faraday's law (Equation 1.24). In this equation,  $w$  is the amount of deposited metal (in grams),  $A$  is the atomic mass (in grams),  $I$  is the deposition current (in amperes),  $t$  is the deposition time (in seconds),  $n$  is the number of electrons transferred, and 96487 is the charge in coulombs required for the deposition of equivalent of a metal.

$$w = \frac{A \cdot I \cdot t}{n \cdot 96487}$$

**Equation 1.24:** Faraday's law

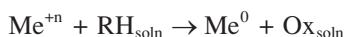
Electroless deposition process consists of half-cell reactions (Equations 1.25 and 1.26) and an overall reaction (Equation 1.27), the rate of which depends on the properties of each half-cell reaction.



**Equation 1.25:** Cathodic half-cell reaction



**Equation 1.26:** Anodic half-cell reaction

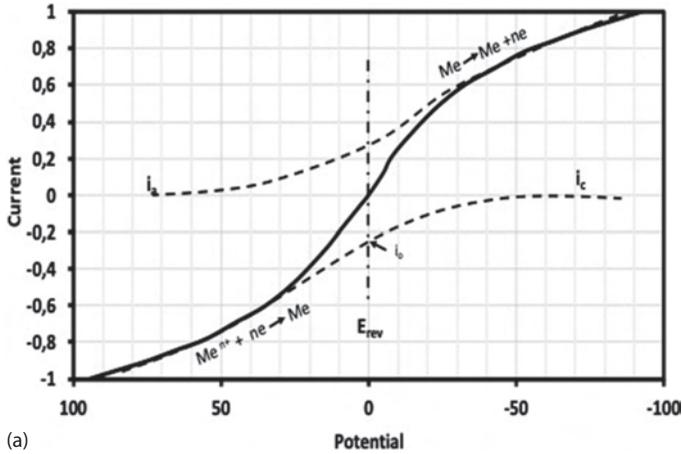


**Equation 1.27:** Overall reaction between metal ions and the reductant.

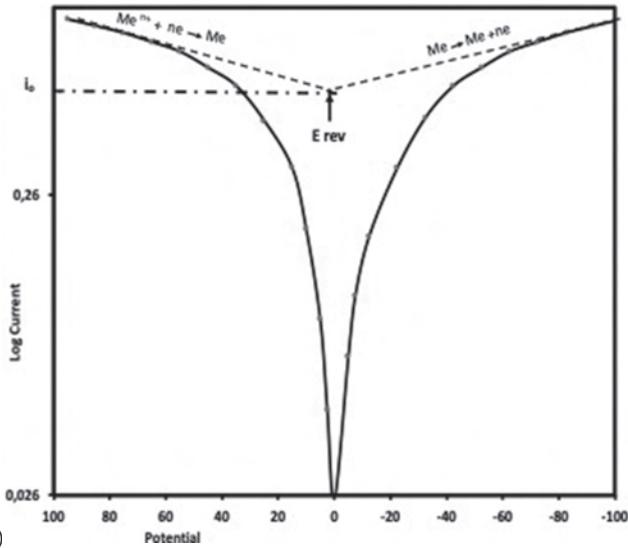
The potential difference between the anodic and cathodic reactions is the driving force of the spontaneous overall reaction. Because the system consists of two electrochemical half-cell reactions with a potential difference that will polarize them accordingly, mixed potential theory can be applied. For a better description of the mixed potential theory, the kinetics of half-cell reactions will be summarized first.

### 1.6.1 KINETICS OF HALF-CELL REACTIONS

The coordinates of equilibrium conditions at a reversible potential can be shown graphically by using potential and current axis in linear or semi-logarithmic scales (Figure 1.4a and b). On the potential axis, the reversible potential extracted from thermodynamics (EMF series and Nernst equation) is marked, and on the current axis, the rate of the reaction at equilibrium ( $i_0$ ) is marked. Because at  $E_{\text{rev}}$ , the rate of forward and reverse reaction are equal to each other and  $i_0$  ( $i_a = i_c = i_0$ ). The calculation of  $i_0$ , exchange current density, is not straight forward because, at these equilibrium conditions, there is no net charge transfer (hence, mass loss or gain); thus, these values can be calculated theoretically or by changing the equilibrium (polarization). By polarizing this half-cell reaction to either cathodic or anodic direction, a net current starts to pass showing dependence on the magnitude of the energy (overvoltage,  $\eta$ ) applied for changing the equilibrium.



(a)



(b)

**FIGURE 1.4** Schematic linear (a) and semi-logarithmic (b) representation of polarization curves.

At equilibrium:  $\eta = 0, \quad i_c = i_a = i_0$

**Equation 1.28:** Definition of equilibrium conditions of a half-cell reaction.

On cathodic polarization:  $\eta_c = E_{rev} - E_p \quad i_c > i_a \neq i_0 \quad i_{net} = i_c - i_a$

**Equation 1.29:** Definition of the conditions for cathodic polarization of a half-cell reaction.

On anodic polarization:  $\eta_a = E_{rev} - E_p$   $i_a > i_c \neq i_o$   $i_{net} = i_a - i_c$

**Equation 1.30:** Definition of the conditions for anodic polarization of a half-cell reaction.

If the reaction is under activation control (in case where the slowest step is the electron transfer), the relation between the rate of the reaction ( $i_{net}$ ) and overvoltage obeys the Butler-Volmer equation. Equation 1.31 represents the Butler-Volmer equation for anodic polarization. In this equation,  $\eta$  is the overvoltage (the difference between the polarized potential and reversible potential),  $b_a$  and  $b_c$  are the anodic and cathodic Tafel slopes, respectively.

$$i_{net} = i_a - i_c = i_o \exp\left(\frac{\eta}{b_a}\right) - i_o \exp\left(\frac{\eta}{|b_c|}\right)$$

**Equation 1.31:** Butler-Volmer equation for an anodically polarized half-cell.

As can be followed from the schematic (Figure 1.4b) for overvoltages in the range of 30–50 mV, a linear relation between  $E$  and  $\log i$  is started to be observed because the contribution of cathodic component ( $i_c$ ) starts to become insignificant for anodic polarization and vice versa. For the anodic polarization case (Equation 1.31), the equation can be simplified by canceling the second exponential term (Equation 1.32). The same methodology can be applied for cathodic polarization case (Equation 1.33).

$$i_{net} = i_a - i_c = i_o \exp\left(\frac{\eta}{b_a}\right)$$

**Equation 1.32:** Simplified Butler-Volmer equation for an anodically polarized half-cell.

$$i_{net} = i_c - i_a = -i_o \exp\left(\frac{\eta}{|b_c|}\right)$$

**Equation 1.33:** Simplified Butler-Volmer equation for a cathodically polarized half-cell.

Taking logarithms of Equations (1.20 and 1.21) and solving them for  $\eta$ , the well-known Tafel equation is obtained:

$$\eta = a \pm b \log|i|$$

**Equation 1.34:** Tafel equation

where  $a$  and  $b$  are constants and  $|i|$  is the absolute value of  $i_{net}$ ,  $\pm$  sign stands for anodic and cathodic processes, respectively. The theoretical values of these constants for activation-controlled cathodic reactions are:

$$a_c = \frac{2.303 RT}{\alpha nF} \log i_o$$

**Equation 1.35:** Tafel equation constant  $a$

$$b_c = \frac{2.303 RT}{\alpha nF}$$

**Equation 1.36:** Tafel equation constant  $b$

In these relations (Equations 1.35 and 1.36),  $\alpha$  is the transfer coefficient  $R$  for gas constant,  $n$  is the number of electrons transferred, and  $F$  is the Faraday constant.

On the other hand, the derivative of Butler-Volmer equation (Equation 1.31) leads to the slope ( $d\eta/di$ ) for  $\eta \rightarrow 0$  V, and named as charge transfer resistance  $R_{ct}$ , that allows calculation of the rate of the half-cell reaction (exchange current density,  $i_o$ ) without extension of cathodic or anodic polarization.

Besides activation (charge transfer) control, half-cell reactions can also be controlled by diffusion (concentration) polarization. In these cases, the slowest step during the realization of the reaction is the mass transport of the reacting species to the electrode solution interface. Butler-Volmer equation for combined polarization of a cathodic reaction is presented in Equation (1.37). In this equation,  $i_{lim}$  stands for limiting current.

$$i_c = \frac{i_o \exp\left[\frac{-(1-\alpha)nF}{RT}\eta_c\right]}{1 - \frac{i_o}{i_{lim}} \exp\left[\frac{-(1-\alpha)nF}{RT}\eta_c\right]}$$

**Equation 1.37:** Butler-Volmer equation for combined (activation + diffusion) polarization controlled cathodic half-cell reaction. In this equation  $i_{lim}$  stands for limiting current.

$$\text{if } i_{lim} < i_o \exp\left[\frac{-(1-\alpha)nF}{RT}\eta_c\right]$$

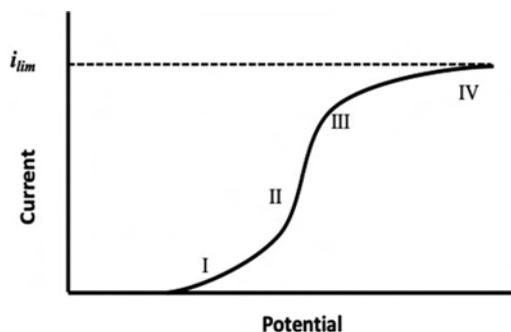
*denominator of equation 1.37 goes to 1 (activation control)*

**Equation 1.38:** Definition of conditions for activation control in the combined Butler-Volmer equation

*denominator goes to 1- activation controlled*

$$\text{if } i_{lim} > i_o \exp\left[\frac{-(1-\alpha)nF}{RT}\eta_c\right]$$

*$i_{lim} = i$  reaction 1.37 becomes potential independent (diffusion control)*



**FIGURE 1.5** Four regions that can be observed during polarization of a half-cell reaction to one direction (anodic or cathodic). I: linear region (slope gives  $R_{ct}$ ); II: exponential region (slope gives Tafel slope); III: mixed control region; IV: diffusion controlled region.

$i_{lim} = i$  and the reaction becomes independent of potential, diffusion control

**Equation 1.39:** Definition of conditions for diffusion control in the combined Butler-Volmer equation

$$i_{lim} = \frac{nFD}{\delta} C_b$$

**Equation 1.40:** Definition of limiting current.

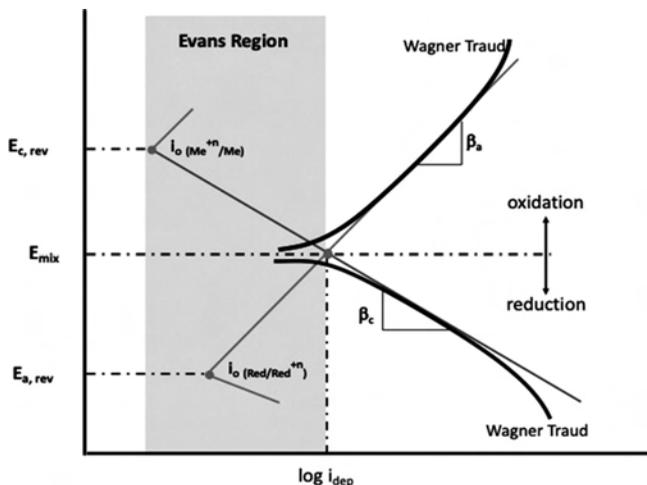
Depending on the magnitude of  $i_{lim}$ , Equation 1.37 is converted into activation-controlled (condition 1.38) or diffusion-controlled state (condition 1.39). Limiting current by definition is a function of diffusion coefficient ( $D$ ), number of electrons transferred ( $n$ ), diffusion layer thickness ( $\delta$ ), and concentration of diffusing species ( $C_b$ ).

A half-cell reaction that starts with activation control and proceeds with mass transport control on a linear scale upon polarization is schematically presented in [Figure 1.5](#).

From the evaluations of the half-cell reactions that are under activation control, the most effective parameters on the kinetics of the reaction are exchange current density, i.e., the rate of the reaction at equilibrium, the number of electrons transferred, and  $\alpha$ , transfer or symmetry coefficient that indicates the symmetry of the activation energy barrier for activation-controlled reactions. All these parameters reflect the values of the constants in Tafel equation. Simply, the lower the value of Tafel constants, the higher is the rate of the reaction upon polarization. On the other hand, the most effective parameters for transport-controlled reactions are the diffusion coefficients ( $D$ ), the thickness of diffusion layer ( $\delta$ ), and the bulk concentration of diffusing species in the solution ( $C_b$ ).

## 1.7 MIXED POTENTIAL THEORY

Mixed potential theory is first established by Wagner and Traud for the explanation of kinetics of corrosion in their classical paper “On the Interpretation of Corrosion Processes through the Superposition of Electrochemical Partial Processes and on the Potential of Mixed Electrodes,” in 1938.



**FIGURE 1.6** Schematic representation of spontaneous polarization (gray-shaded, Evans region) and forced polarization regions.

According to this theory, two half-cell reactions that occur in the same solution on the same electrode will be anodically and cathodically polarized because of the potential difference between them, obeying Butler-Volmer equation till a new “equilibrium” state is reached at  $E_{mix}$  (gray-shaded region in Figure 1.6). During this stage, some sites on the substrate metal will act as anodic sites and the others will act as cathodic sites, and the slower half-cell reaction will control the overall reaction rate (see Figure 1.8a–c).

This is not a real equilibrium because net changes are occurring at  $E_{mix}$ . The polarization that occurs spontaneously cannot be followed experimentally. However, it can be determined by further polarizing them externally from  $E_{mix}$  potential, assuming that they will still obey Butler-Volmer equation upon further polarization (region described by Wagner and Traud) or calculated by using relevant kinetic parameters.

Although this theory has been put forth for electrochemical corrosion reactions, it has been verified that most of the electroless deposition processes also obey the principles of mixed potential theory (Paunovic 1983; Flis and Duquette 1997). This is not an unexpected outcome because of the similarity between electrochemical corrosion and electroless metal deposition reactions. Both of them consists of minimum two half-cell reactions (cathodic and anodic), these reactions occur on the same substrate, both of them are spontaneous and they are driven by a potential difference between anodic and cathodic half-cells.

The self-polarized spontaneous polarization region can be calculated or schematically drawn for presenting roles of different parameters on the polarization behavior (Evans diagrams). The self-polarized spontaneous polarization region can be calculated by using Equations (1.19 and 1.20), if  $i_0$  values,  $E_{rev}$  values, and Tafel slopes for both anodic and cathodic reactions are known.

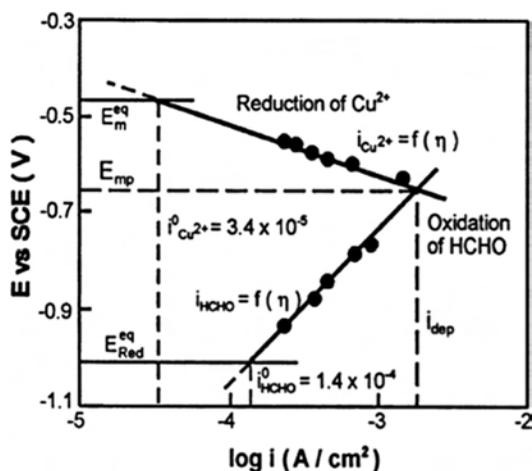
Another way of determining the spontaneous region of polarization and the rate of reactions at  $E_{mix}$  is to use polarization curves obtained by polarization from  $E_{mix}$ . The rate of reactions at  $E_{mix}$  can be determined by extrapolating the linear regions

of anodic and cathodic polarization curves (Tafel extrapolation method), assuming that they still obey Butler-Volmer equation upon polarization from  $E_{mix}$ . In cases where  $E_{rev}$  values of anodic and cathodic reactions are known by further extrapolating anodic and cathodic polarization curves to  $E_{rev}$ , one can determine one of the most important kinetic parameters, the exchange current density ( $i_0$ ).

Another way of determining the reaction rate at  $E_{mix}$  is to use low potential approximation. The same approach for the determination of exchange current density (Equation 1.36) can be used simply by replacing  $i_0$  with deposition rate ( $i_{dep}$ ).

During the application of mixed potential theory concepts to electroless deposition, polarization curves for each half-cell reaction can be obtained separately that allows the determination of kinetics of each half-cell reaction that constitutes total reaction. This is realized by investigating the polarization behaviors of cathodic and anodic half-cell reactions in the absence of reductants and in the absence of metal ions, respectively (Figure 1.7) (Paunovic 1968). The possibility of polarizing each half-cell electrode reaction is the advantage of electroless deposition systems when compared with corrosion. In this manner, the polarization of each half-cell reaction that occurs spontaneously, when the reductants and oxidants are present in the same solution, can be followed and determined (Figure 1.7). By using this method of obtaining polarization behavior of the half-cells that constitutes the electroless deposition process, factors affecting the kinetics of the process can be determined. For example, the role of additives, exchange current densities of different catalytic substrates, concentration of reductants, and so on, in the kinetics of the half-cell reactions can be successfully evaluated by this methodology.

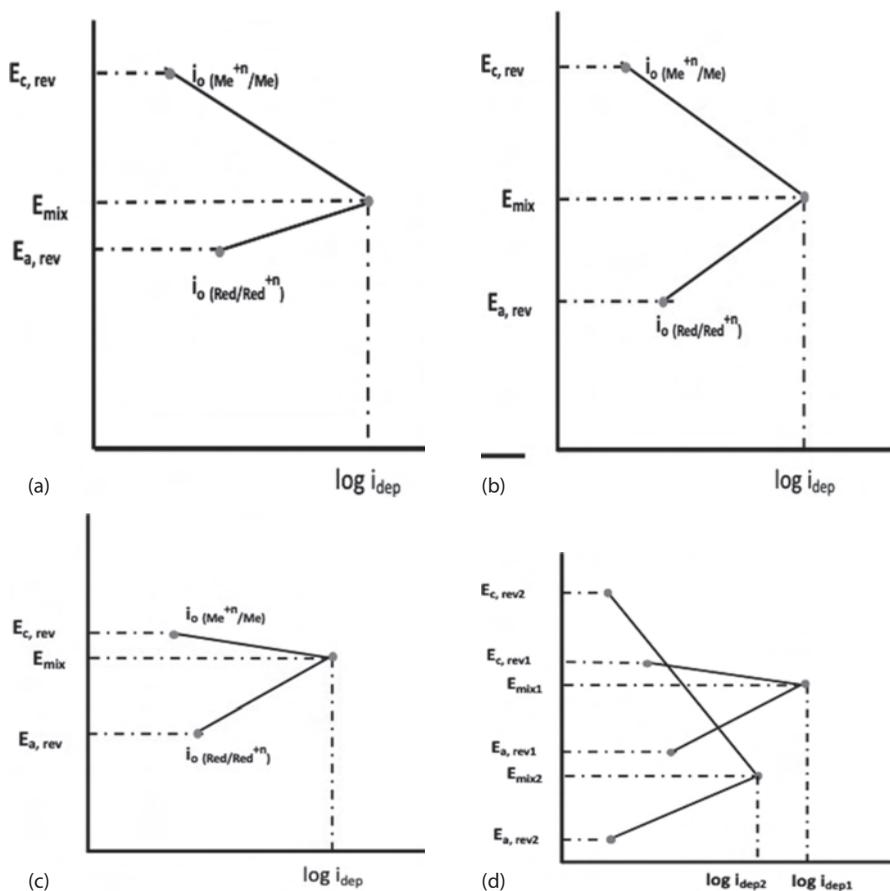
Evans diagrams (the schematic diagrams representing the spontaneous region) are a very effective way of presenting the role of several parameters on the kinetics of electroless deposition processes, such as the rate of controlling half-cell reaction,



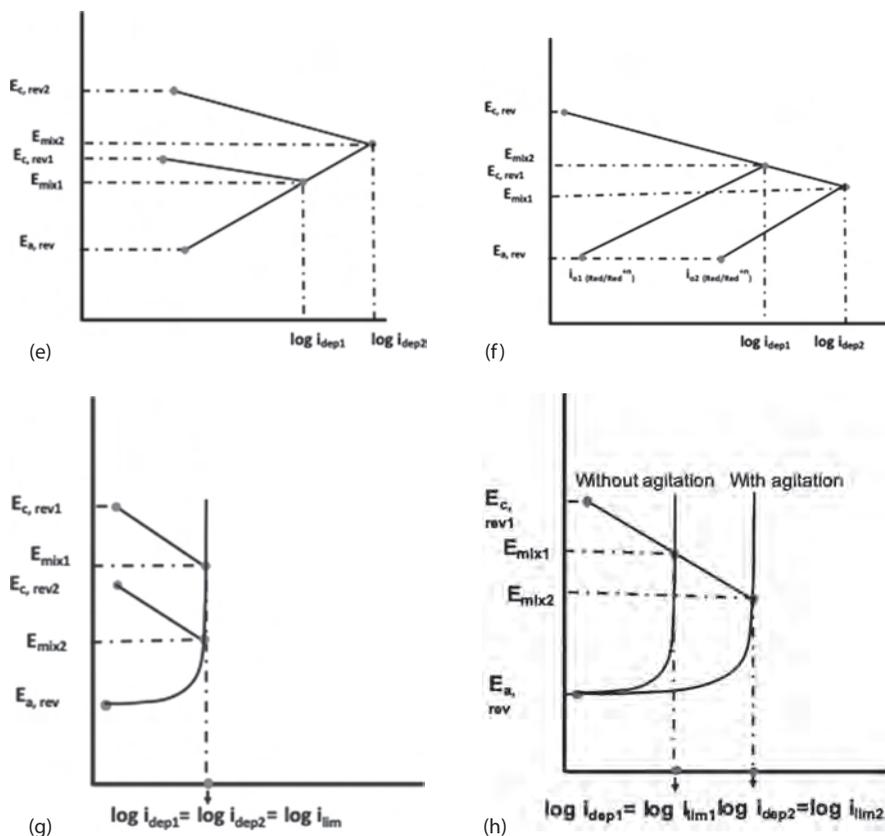
**FIGURE 1.7** Overlaid  $\text{Cu}^{2+}$  reduction and formaldehyde oxidation polarization curves (Evans diagram).  $\text{Cu}^{2+}$  reduction curve obtained for 0.1 M  $\text{CuSO}_4$  and 0.175 EDTA solution with pH 12.5 at  $25^\circ\text{C}$ . Formaldehyde oxidation curve obtained for 0.05 M HCHO and 0.175 M EDTA solution at  $25^\circ\text{C}$ . (From Paunovic, M., *Plating*, 51, 1161–1167, 1968.)

the importance of  $i_0$  in kinetics, and type of control (activation or diffusion control) and concentration changes in the electrolyte. Several examples of Evans diagrams are presented in Figure 1.8 that can be used for understanding the role of kinetic and thermodynamic parameters on electroless deposition.

In studies that investigate the validity of the mixed potential theory for electroless deposition, the deposition rates calculated from  $i_{dep}$  are in accordance with the rates determined by weight gain measurements especially for electroless copper deposition in formaldehyde (Paunovic 1968) and Ni–dimethylamine borane (DMAB; Paunovic 1983; Flis and Duquette 1997) solutions and copper and nickel in hypophosphite solutions (Martins and Nunes 2016). However, for electroless nickel coatings conducted by using hypophosphite's and reductants, the rates attained by mixed potential theory are much lower than the gravimetric ones. This special behavior observed in hypophosphite baths is generally attributed to chemical reduction of nickel ions by the active adsorbed hydrogen that forms on



**FIGURE 1.8** Evans diagram describing: (a) cathodic control; (b) mixed control; (c) anodic control; (d) a reaction with higher reaction tendency (differences between  $E_{a, rev}$  and  $E_{c, rev}$ ) that can result in lower deposition rate; (Continued)



**FIGURE 1.8 (Continued)** Evans diagram describing: (e) effect of increased cathodic reactant concentration on deposition rate by shifting  $E_{rev}$  to more positive potentials; (f) effect of exchange current density on deposition rate (higher  $i_0$  means easier polarization, higher deposition rate); (g) deposition rate does not change with the change of  $E_{c, rev}$  because of diffusion-controlled anodic reaction; (h) the role of agitation on the deposition rate of diffusion controlled reactions.

the catalytic surface through adsorption and dehydrogenation of hypophosphite ions and/or to the multistep complexity of reduction and oxidation reactions (Magagnin et al. 2011).

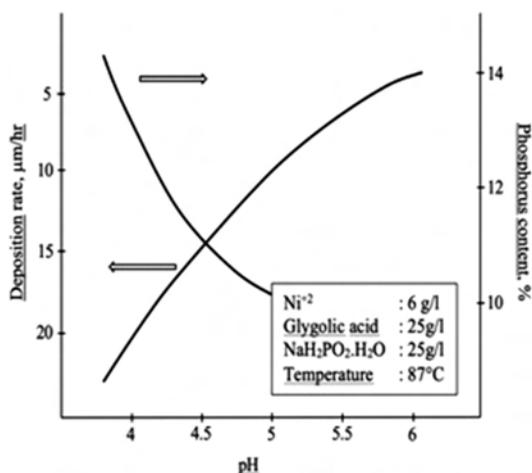
## 1.8 THE ROLE OF DEPOSITION PARAMETERS AND CHEMICAL COMPONENTS ON ELECTROLESS NICKEL COATING PROCESS

### 1.8.1 THE ROLE OF DEPOSITION PARAMETERS

Before going into details of bath components, the role of deposition parameters on the properties of the electroless nickel coatings will be summarized. The deposition parameters other than the composition of the solution are pH, temperature of the

solution and agitation. Thus, when compared to electrolytic metal plating, the variables are limited. In electrolytic metal plating, the rate of deposition can additionally be easily controlled by changing the magnitude and shape (e.g., pulse plating) of the applied voltage.

Generally, for Ni–P coatings, a decrease in the pH leads to a decrease in the deposition rate and an increase in the P content of the coating. This effect is more pronounced in acidic Ni–P baths. In acidic baths, the pH of the solutions is not generally allowed to go below 3.5–4 because the deposition rate decreases very dramatically (Figure 1.9). The reason for the decrease in deposition rate can be explained with Evans diagrams (see Figure 1.8). With the decrease of pH, the contribution of hydrogen evolution cathodic reaction increases and oxidation rate of the reductant decreases (Equation 1.7), thus leading to a decrease in the deposition rate. Generation of hydrogen ions during deposition leads to a decrease in pH during deposition. The decrease in pH not only results in lowering of the deposition rate and the increasing of P content (Figure 1.9) but also increases the stability of the bath. Additionally, by lowering the pH value, the adhesion of coating to the substrate increases, internal stress shifts to compressive direction, porosity decreases in the coatings, and the solubility of the phosphite increases (reaction product of the reductant), thus extending the life of the bath. However, as explained above, because incremental changes in pH dramatically change P content (e.g., a change in pH from 4.5 to 4 increases the P content from 9–14), very good complexing agents (buffers) are needed to keep the pH of the acidic Ni–P baths constant. This class of Ni–P electroless deposition (acidic) baths are suitable



**FIGURE 1.9** Effect of solution pH on deposition rate and P content of the coatings. (Adapted from Mallory, G.O., *The Fundamental Aspects of Electroless Nickel Plating*, In *Electroless Plating: Fundamentals and Applications*, American Electroplaters and Surface Finishing Society, New York, pp. 1–56, 1990.)

for deposition of low (3%–5%), medium (6%–9%), and high (10%–14%) phosphor-containing deposits by adjusting the deposition parameters and composition of the solution. Because the main parameter defining the P content is the pH of the solution, the use of different complexing agents (buffers) may be required for different P contents. As will be given in the other chapters of the book, P content of the coatings has a strong influence on the physical (conductivity, hardness, magnetic, thermal expansion) and chemical (corrosion resistance) properties. Ni–B baths based on DMAB show similar features as in Ni–P baths with respect to changes in pH.

The other types of Ni–P baths are alkaline; these baths are generally preferred for the deposition on temperature- and acid-sensitive materials (polymers) because it is possible to use these baths at lower temperatures (40°C–75°C) than acidic baths (85°C–90°C). The stability of these baths is lower than the acidic baths because the potential of the reductant reaction is higher compared to the ones in acidic solutions (Table 1.2). The lowest operating pH of these baths is approximately 8 and generally does not allow to deposit coating with high P and B content (DMAB). Contrary to acidic baths, the decrease in the pH of the solution does not dramatically increase the P content in these baths but lowers the deposition rate. On the other hand, Ni–B baths based on NaBH<sub>4</sub> is a special case of baths that should be treated separately because they can only be kept stable at high pH values.

Temperature is another key parameter in electroless nickel plating. As high activation energy is required for the initiation of chemical and/or electrochemical reactions on catalytic metal surface, high temperatures are required to carry out the deposition process. The rate of deposition shows an exponential relation with temperature (Mallory 1990), indicating the necessity of overcoming energy barrier for the initiation of the reaction. Generally, in acidic baths, deposition temperatures are higher than the alkaline baths. The control of deposition temperature for alkaline baths is more critical than acidic ones because increased temperatures may lead to bath decomposition.

The solution mixing or agitation is one of the parameters that have not attracted necessary attention in electroless deposition research. There are very limited studies in the literature that systematically investigated the role of transport in the kinetics of electroless nickel deposition processes. In this book, because a section is specifically devoted to ultrasonic-aided electroless deposition, the possible role of agitation on electroless deposition will be briefly discussed.

Agitation of the solution has direct effects on the realization of oxidation and reduction reactions on the metal surface through:

1. Transport of reactants and reaction products from and away from the reaction interface (avoiding the local pH changes, removal of hydrogen bubbles from the surfaces, and easier chemistry equilibration in recesses and cavities).
2. Increasing the reaction rate if reactions involve diffusion of ions (transport-controlled) by increasing the limiting current.

## 1.8.2 CHEMICAL COMPONENTS OF ELECTROLESS NICKEL DEPOSITION BATHS AND THEIR FUNCTIONS

An electroless nickel bath is basically composed of nickel ion sources and reductants (Table 1.4). Other than these components stabilizers, complexing agents and wetting agents are required for a properly functioning electroless bath. The classification of electroless nickel bath and their main constituents are presented in Table 1.3.

### 1.8.2.1 Main Components, Nickel Ion Sources, and Reductants

The main components of electroless nickel baths are nickel ion sources and reductants. Basically, any nickel salt that can dissolve in water-based solution to give nickel in ionic form can be used as nickel ion source. However, for reasons of availability, solubility, and the knowledge accumulated about their behavior because of their extensive use in electrodeposition, nickel sulfate and nickel chloride are the most widely used nickel ion sources. When depositing on aluminum and steel, chloride-containing baths are not preferred because of the risk of inducing localized corrosion on these substrates. Nickel hypophosphite is also used as nickel ion source; however, its cost is the major drawback. This nickel salt can be directly used in acidic electrolytes by adjusting the solution pH to not allow them to precipitate as hydroxides. For using these baths at high pH values (alkaline baths), complexing agents such as amines are needed.

**TABLE 1.3**  
**Classification of Electroless Nickel Bath and Their Main Constituents**

Bath Type	Pure Ni	Acid Ni-P and Ni-B	Alkaline Ni-P and Ni-B
pH	10–11	4–5.5 (low to medium P and B) 5.5–6.5 (low P and B)	8.5–14
Temperature	85–90	75–95	25–100
Deposition rate (micron/hr)	6–12	10–25	10–15
Metal source	Nickel acetate	Nickel sulfate, nickel chloride	Nickel sulfate, nickel chloride
Reductant	Hydrazine	Na hypophosphite for Ni-P Dimethylamine borane for Ni-B	Na hypophosphite for Ni-P Dimethylamine borane for Ni-B Sodium borohydride for Ni-B
Complexing agents	EDTA glycolic acid	Citric, lactic, glycolic, propionic acids, sodium citrate, succinic acid	Citric, lactic, glycolic and propionic acids, sodium citrate, sodium acetate, sodium pyrophosphate, ammonium and amine salts
Stabilizers	—	Thiourea, lead acetate, heavy metal salts, mercaptotriazoles	Thiourea, lead acetate, heavy metal salts, thio-organic salts, thallium nitrate, selenium salts
Wetting agents	Ionic, non-ionic surfactants	Ionic, non-ionic surfactants	Ionic, non-ionic surfactants