Chapter 9
Chemical Deposition of Metals and Alloys from Aqueous Solutions

9.1 Introduction

The term *chemical deposition* of metals and/or alloys from aqueous solutions is usually used to refer to the production of metallic coatings or powders of various surface morphology and properties without an application of the external current source. As explained in previous chapters in the electrochemical deposition, electrons used for the reduction of metal ions are provided by an external current source. For the chemical deposition, electrons used for the reduction of metal ions are released under specific conditions from an appropriate reducing agent. These appropriate reducing agent may include compounds such as hypophosphite (NaH_2PO_2), borohydride ($NaBH_4$), formaldehyde (HCOH), ascorbic acid ($C_6H_8O_6$), etc., or metals which are less noble than the metal aimed to be deposited. These concepts of chemical deposition will be examined in details in the following text.

It is obvious from the present literature that many aspects of the chemical deposition of metals and/or alloys are ambiguous. Frequently, the chemical deposition is called as *electroless deposition*. As such, the word *electroless* is used in order to stress out that there is no application of the external electrical current to the system where the deposition takes place. In general terms, this is correct; however, clear differences among dissimilar systems are not precisely described. For example, heterogeneous processes involving a metal substrate and homogeneous aqueous solution containing ions of the more noble metal without a presence of the reducing agent, e.g., cementation of Cu on Fe, Ag on Cu, Zn on Al, and similar, are called electroless deposition. Similarly, deposition of metals from an aqueous solution containing a reducing agent for which a presence of a solid substrate (metallic or nonmetallic) is needed for smooth coatings but not absolutely required for powders is, again, called electroless deposition. Although these two processes are fundamentally different, in the present literature, they are discussed or grouped together as electroless processes. In order to clarify for the reader, in this book, all

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processes of deposition of metals and/or alloys without an application of the external current will be considered as *electroless* or *chemical* processes. To further clarify, all electroless processes are divided into the two following groups: *galvanic displacement deposition* (heterogeneous processes, exclusively) and *autocatalytic deposition* (combined homogenous and heterogeneous processes).

9.2 Types of Chemical Deposition of Metals from Aqueous Solutions

As explained in the introduction section of this chapter, there are two main types of chemical deposition of metals from aqueous solutions, and they can be distinguished as:

(a) Galvanic displacement deposition
(b) Autocatalytic deposition

Follows the detailed description of these two processes.

9.2.1 *Galvanic Displacement Deposition*

By the definition, the galvanic displacement deposition is a heterogeneous process in which the noble metal is deposited at the surface of an active metal [1]. The consequence is that the less noble (or active) metal is oxidized or dissolved in the appropriate solution. As a result, the ions of a more noble metal present in the solution are reduced leading to the deposition of the more noble metal. This situation can be described using the electrochemical half reactions in the following way.

(a) Oxidation and consequent dissolution of the less noble metal, M_1:

$$M_1^{\mathrm{o}} \rightarrow M_1^{z_1^+} + z_1\mathrm{e}^- \tag{9.1}$$

(b) Reduction and consequent deposition of the more noble metal, M_2:

$$M_2^{z_2^+} + z_2\mathrm{e}^- \rightarrow M_2^{\mathrm{o}} \tag{9.2}$$

In the galvanic displacement deposition, the electrons produced due to oxidation or dissolution of the metal M_1, as shown by the reaction (9.1), are further used for the reduction of the metallic ions of the metal M_2 (reaction (9.2)). Consequently, a combination of the reactions (9.1) and (9.2) leads to:

$$M_2^{z_2^+} + \frac{z_2}{z_1} M_1^{\mathrm{o}} \rightarrow \frac{z_2}{z_1} M_1^{z_1^+} + M_2^{\mathrm{o}} \tag{9.3}$$

The reaction (9.3) represents a generic description of the galvanic displacement deposition. This relatively simple process does not require any complicated equipment. Practically speaking, only a beaker (or a reactor) for a solution containing ions of the more noble metal and a less noble metallic substrate immersed into the solution is needed for this process to proceed. Although not very descriptive, other names for the galvanic displacement reaction used in practice include *cementation* or *immersion plating*.

Even not recognized as such, the galvanic displacement deposition of noble metals such as Au or Ag onto Fe, Zn, Cu, or similar substrates is known since the times of early Mediterranean cultures and, possibly, before. In the sixteenth century, the recovery of copper from copper mine waters by contacting dilute process streams with iron scrap was successfully achieved [2]. Since that time, many different galvanic displacement deposition processes have been developed. Examples used on industrial scale include application of aluminum, iron, or zinc powders for the removal of copper, silver, gold, or other noble metals from waste solutions. Similar approaches are used for the solution purification in hydrometallurgical plants, electronics, electrochemical experiments, etc.

9.2.1.1 Kinetics and Mechanism of the Galvanic Displacement Reaction

The kinetics of the galvanic displacement reactions is usually studied using the following generic equation:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -kC^n \tag{9.4}$$

where $\mathrm{d}C/\mathrm{d}t$ is the rate of deposition, C is the concentration of ions of the more noble metal, t is time, and n is the reaction order. Most of the galvanic displacement reactions follow the first order and, consequently, $n = 1$. k is the rate constant, and it can be expressed as:

$$k = \frac{DA}{\delta V} \tag{9.5}$$

where D is diffusion coefficient, A is the surface area on which the deposition takes place, δ is the boundary layer thickness, and V is the volume of electrolyte.

Practical application of Eqs. (9.4) and (9.5) can be illustrated on the example of aluminum metal immersed into an alkaline solution containing Cu(II) ions [3]. Deposition of copper onto aluminum from the complexed alkaline solution containing Cu(II) ions is a galvanic process resulting from the dissolution of aluminum. The dissolution of aluminum in strong alkaline solutions can be expressed with the following reaction:

$$2\mathrm{Al} + 6\mathrm{H_2O} + 2\mathrm{OH^-} \rightarrow 2\mathrm{Al(OH)_4^-} + 3\mathrm{H_2} \tag{9.6}$$

The reaction (9.6) has $\Delta G^{\mathrm{o}} = -857.946$ kJ/mol < 0, confirming that the process is spontaneous, and it represents a net reaction combined with a cathodic reaction:

$$2\mathrm{H_2O} + 2\mathrm{e^-} \rightarrow \mathrm{H_2} + 2\mathrm{OH^-} \tag{9.7}$$

and an anodic reaction:

$$\mathrm{Al} + 4\mathrm{OH^-} \rightarrow \mathrm{Al(OH)_4^-} + 3\mathrm{e^-} \tag{9.8}$$

The deposition of copper on the surface of aluminum metal, as a consequence of its dissolution, is a cathodic process that can simply be presented by the reaction:

$$\mathrm{Cu^{2+}} + 2\mathrm{e^-} \rightarrow \mathrm{Cu} \tag{9.9}$$

The whole process of copper deposition onto the aluminum metal surface can simply be described by the following equation, which is obtained by a combination of the reactions (9.7, 9.8, and 9.9):

$$4\mathrm{Al} + 10\ \mathrm{OH^-} + 6\ \mathrm{H_2O} + 3\ \mathrm{Cu^{2+}} \rightarrow 3\ \mathrm{H_2} + \ 4\ \mathrm{Al(OH)_4^-} + 3\mathrm{Cu} \tag{9.10}$$

The Gibbs energy for the reaction (9.10), $\Delta G^{\mathrm{o}} = -2195.2$ kJ/mol < 0 is negative, evidencing that the deposition of copper onto aluminum from an alkaline solution is the spontaneous process under the standard physicochemical conditions. According to the reaction (9.10), besides copper deposition, hydrogen evolution takes place as well in this process. The simultaneous hydrogen evolution during the galvanic displacement deposition of copper onto aluminum in the alkaline solutions can further significantly influence the morphology of the deposits as it will be shown in the later section.

The kinetics of the deposition of copper onto aluminum from alkaline solutions, therefore, can be expressed with the equation:

$$\frac{\mathrm{d[Cu(II)]}}{\mathrm{dt}} = -k'A\frac{[\mathrm{Cu(II)}]}{V} \tag{9.11}$$

where [Cu(II)] is the concentration of Cu(II) ions, t is time, A is the surface area, V is the volume of the electrolyte, and k' is the rate constant defined as:

$$k' = \frac{D}{\delta} \tag{9.12}$$

In Eq. (9.12), D is the diffusion coefficient and δ is the diffusion layer thickness.

The results of the deposition of copper onto aluminum can then be studied by integrating Eq. (9.11), which leads to:

$$\log\frac{[\mathrm{Cu(II)}]_t}{[\mathrm{Cu(II)}]_o} = -\frac{k'A}{2.303V}t \tag{9.13}$$

where $[\mathrm{Cu(II)}]_o$ is the initial Cu(II) concentration and $[\mathrm{Cu(II)}]_t$ is the concentration of copper ions at a specific time.

It is obvious from Eq. (9.13) that the dependence of $\log\{[\mathrm{Cu(II)}]_t/[\mathrm{Cu(II)}]_o\}$ on time should be linear. Indeed, the experimental results on the deposition of copper from an alkaline solution onto aluminum powder via the galvanic displacement reaction show that there is a linear dependence between $\log\{[\mathrm{Cu(II)}]_t/[\mathrm{Cu(II)}]_o\}$ and time as illustrated in Fig. 9.1 [3]. As can be seen from Fig. 9.1, the linear relationship was confirmed for all the investigated surface areas of the aluminum substrate. Furthermore, these results clearly show that an increase in the surface area of the substrate leads to the increase in the rate of copper deposition, which is a consequence of Eq. (9.13).

Considering that during the galvanic displacement deposition of copper the aluminum substrate is dissolved, alternatively, the rate of this process can be studied in the following way. Due to dissolution of aluminum, the concentration of Al(III) ions in the solution should increase with time. Eventually, complete aluminum substrate could be dissolved under proper conditions, during the deposition of copper. By applying Faraday's law to Eq. (9.8), the concentration of Al(III)

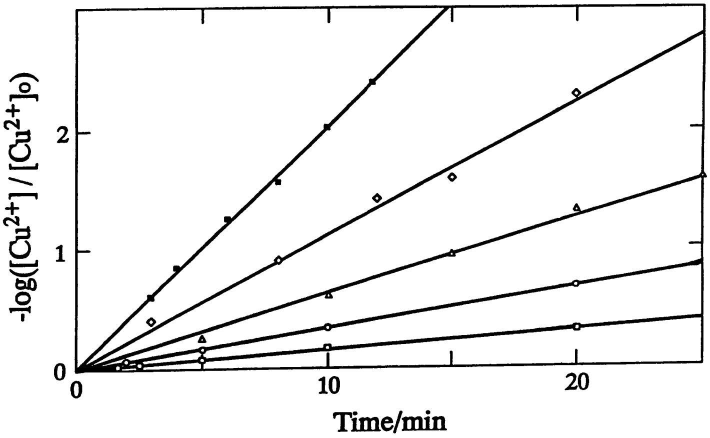


Fig. 9.1 Linear plots of – log ($[\mathrm{Cu}^{2+}]/[\mathrm{Cu}^{2+}]_o$) vs. time for various masses of Al powder: (□) 0.1116 g, (○) 0.234 g, (Δ) 0.5617 g, (◇) 1.055 g, and (■) 1.562 g (initial Cu^{2+} concentration 3.56 g/dm^3, pH 13.5) (Reproduced from Ref. [3] with permission from The Electrochemical Society)

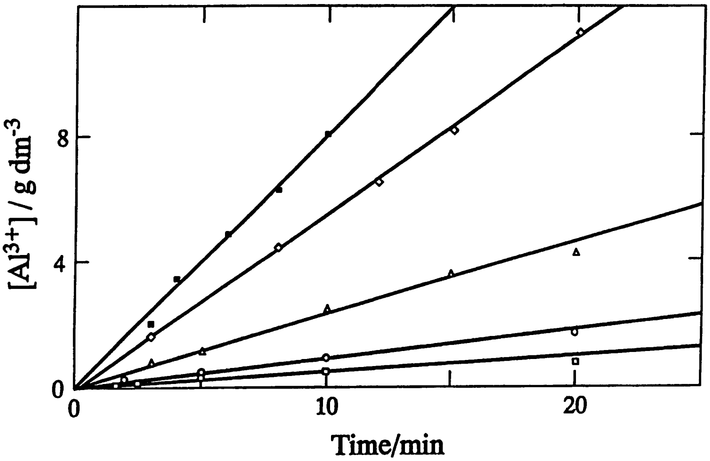


Fig. 9.2 Dependence of $[Al^{3+}]$ in solution on time for various initial amounts of Al powder: (□) 0.1116 g, (○) 0.234 g, (◊) 1.055 g, and (■) 1.562 g. (Initial Cu^{2+} concentration 3.56 g/dm3, pH 13.5) (Reproduced from Ref. [3] with permission from The Electrochemical Society)

in the solution, as a function of time, can be calculated according to the following reaction:

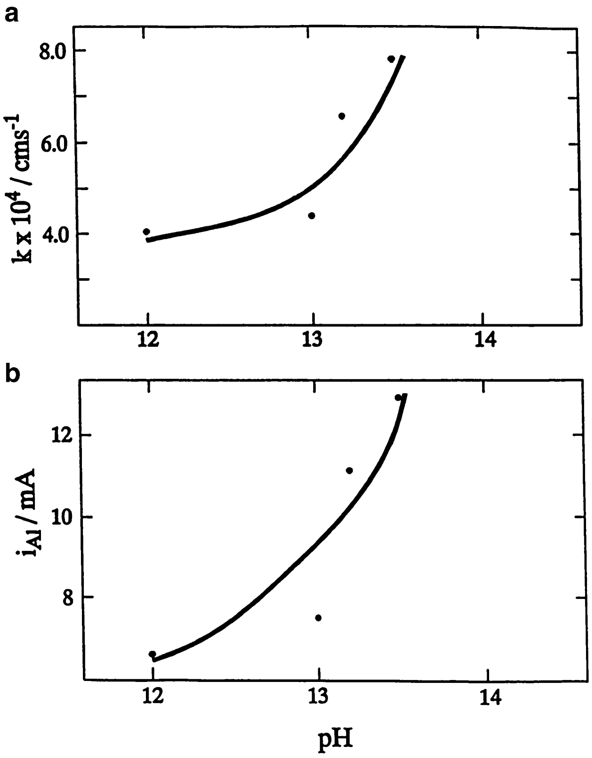
$$\left[Al^{3+}\right] = \frac{A\, i_{Al}}{F\, V\, n_{Al}} t \tag{9.14}$$

where $[Al^{3+}]$ is the concentration of the Al(III) in solution, i_{Al} is the current density of the aluminum dissolution, n_{Al} is the number of electrons, F is the Faraday's constant, and V is the volume of the electrolyte. Obviously, the concentration of aluminum ions, $[Al^{3+}]$, should linearly increase with time, according to Eq. (9.14). This is experimentally confirmed, as illustrated in Fig. 9.2. Figure 9.2 shows that there is a linear increase in $[Al^{3+}]$ with an increase in time. As in the former case, an increase in the surface area leads to an increase in the rate of dissolution, which is in the agreement with Eq. (9.14). In this way, the rate of the process described by Eq. (9.14), or similarly developed expressions for other systems, can successfully be used for studying the kinetics of the galvanic displacement reactions.

The rate of the galvanic displacement reactions depends also on pH and temperature. In general terms, when dealing with the amphoteric metals, e.g., aluminum, zinc, or similar, that act as substrates on which the deposition takes place in the alkaline solutions (above pH 8 or so), an increase in pH leads to an increase of deposition of the more noble metal. This is due to increase in the rate of oxidation or dissolution of the substrate.

For the presently analyzed Cu/Al system in the alkaline solution, the dependence of the rate of deposition on pH is presented in Fig. 9.3. The rate of deposition of Cu

Fig. 9.3 (**a**) dependence of the reaction rate constant on pH (initial Cu^{2+} concentration 3.56 g/dm^3, initial amount of Al powder 1.5 g). (**b**) Dependence of calculated current of aluminum dissolution on pH ((initial Cu^{2+} concentration 3.56 g/dm^3, initial amount of Al powder 1.5 g) (Reproduced from Ref. [3] with permission from The Electrochemical Society)



at pH below 10, practically does not take place in the investigated solution within the reasonable time frame (1 h).

Taking into consideration that on the surface of aluminum metal a thin protective film of Al_2O_3 is present, the deposition of Cu is unlikely to proceed at pH below 10. Under this condition, the Al_2O_3 film acts as a passivating layer. Consequently, the electrolyte containing the Cu(II) ions is not in contact with the aluminum metal, and the deposition does not occur. Even, if some deposition does occur, this can be attributed to the porosity of the Al_2O_3 film. An increase in pH above 10 leads to the dissolution of the passive Al_2O_3 film and the deposition of copper takes place. In the pH range from 10 to 12, the rate of copper deposition is relatively slow, while above the pH 12 it rapidly increases as shown by the results in Fig. 9.3.

In the acidic solutions, during the galvanic displacement deposition, a quite interesting behavior is observed. Annamalai et al. investigated the structure of galvanically deposited copper onto aluminum [4]. Copper deposition was performed using an acidic Cu(II) solution. The effects of Cu (II) and Cl(I) on ion concentrations, temperature, pH, and agitation were systematically investigated. Chloride ions are known to have a beneficial effect in the removal of the aluminum oxide film and to promote the deposition process to proceed further. Generally, with an increase in the chloride ion concentration from 5 to 20 mg/L, an increase in the rate of copper deposition is observed. A further increase in the chloride ion concentration does not have an effect on the rate of copper deposition.

Influence of the kinetics on surface morphology of copper deposited via galvanic displacement was investigated by Annamalai and Murr [5]. Deposition of copper was performed from the acidic Cu(II) solution on iron substrate. An increase in the Cu(II) concentration from 0.5 to 5 g/L led to a decrease in the rate of copper deposition.

The dependence of the rate of deposition on pH within the range between 1 and 4 passes through a maximum at pH = 2 [4]. A further increase in pH leads to a decrease in the rate of copper deposition onto aluminum. Although in the region of pH up to 1 and perhaps 2 the behavior can be quite unpredictable, depending on the system, it can be generally postulated that *during the galvanic displacement deposition in the acidic solutions, an increase in pH leads to a decrease in the rate of deposition*. In the region of pH below 2, the behavior cannot be generally predicted. It will depend on any particular system. In some systems, passivation may occur and in others a pronounced dissolution.

In the acidic solutions, generally, a decrease in pH leads to an increase in the rate of dissolution of the less noble metal as stated above. Consequently, in the acidic solutions, a decrease in pH should lead to an increase in the rate of deposition of the more noble metal. This is seen on the examples of copper cementation on iron, aluminum, or zinc, and a schematic presentation is given in Fig. 9.4.

In the acidic conditions, at lower pH, the oxide film on the substrate is easier dissolved and removed. In this way, more active sites of the less noble metal which act as a reducing agent of the more noble metal ions are produced. As a result at lower pH in the acidic solutions, a higher rate of the deposition is usually observed. With an increase in pH, dissolved metal ions from the less noble substrate (e.g., Fe, Al, Zn, or similar) are susceptible to hydrolysis. This can simply be described with the following generic reactions:

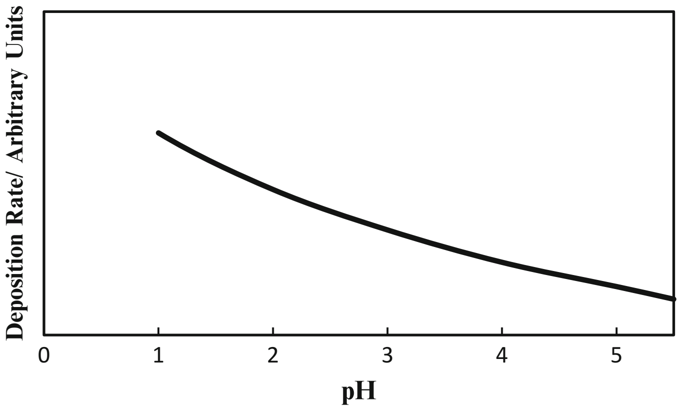


Fig. 9.4 A schematic presentation of the dependence of the rate of deposition as a function of pH in the acidic solutions

1. Dissolution of the less noble metal:

$$\mathrm{Me} \rightarrow \mathrm{Me}^{z+} + \mathrm{ze}^{-} \tag{9.15}$$

2. Hydrolysis of the less noble Me^{z+} ions:

$$\mathrm{Me}^{z+} + \mathrm{x\,H_2O} \rightarrow \mathrm{Me(OH)}_{x}^{(z-x)+} + \mathrm{x\,H}^{+} \tag{9.16}$$

The hydrolysis products, e.g., $\mathrm{Me(OH)}_{x}^{(z-x)+}$,can be adsorbed at the less noble metal surface. Consequently, less active sites are available for the further deposition of a more noble metal. Under these conditions, the rate of deposition is significantly reduced. As a consequence, the surface morphology of the deposited more noble metal can significantly be influenced. This aspect is discussed in later sections.

As in other chemical processes, temperature significantly influences the rate of deposition during the galvanic displacement. The rate of metal deposition generally increases with an increase in temperature, which is a consequence of the Arrhenius' equation:

$$\mathrm{Rate} = A\exp\left(\frac{-E_{\mathrm{a}}}{RT}\right) \tag{9.17}$$

where A is the pre-exponential factor, E_{a} is the activation energy, R is the universal gas constant, and T is the temperature at which the reaction takes place. The logarithmic expression of Eq. (9.17) should be linear:

$$\ln(\mathrm{Rate}) = \ln A - \frac{E_{\mathrm{a}}}{R}\frac{1}{T} \tag{9.18}$$

which is schematically presented in Fig. 9.5.

Most of the experimental results indeed show the dependence illustrated in Fig. 9.5. However, in some cases, such as galvanic deposition of copper onto iron from the acidic solutions [5, 6], the experimental results show a different behavior. As schematically shown in Fig. 9.6, linear dependences of ln (Rate) on $1/T$ with two different slopes were experimentally obtained for the same system, i.e., galvanic deposition of copper onto iron.

Obviously, in the range of lower temperatures (up to 40 °C), a higher activation energy is required for the galvanic displacement deposition. This behavior is attributed to the possibility that the galvanic deposition may be surface reaction controlled, i.e., chemical reaction or pore diffusion [6]. In the higher temperature range, a lower activation energy is obtained. It was postulated that under these conditions the deposition reaction is boundary layer diffusion controlled.

Based on the results from Karavasteva [7], it seems that the kinetics and consequently the surface morphology of the deposited copper via the galvanic displacement reaction onto zinc, iron, and aluminum are strongly influenced by

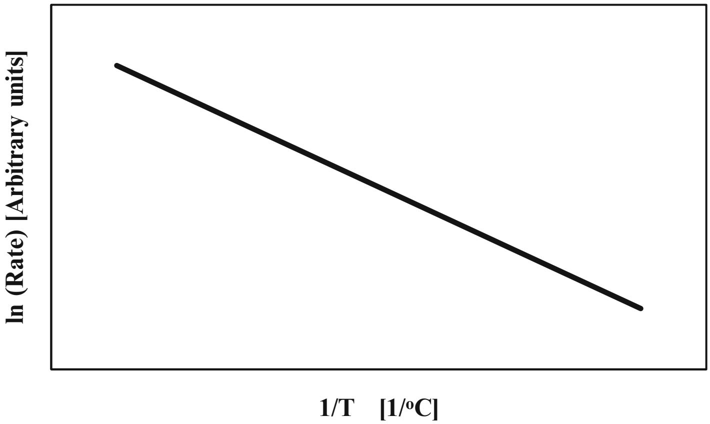


Fig. 9.5 Schematic presentation of the dependence of ln (Rate) on 1/*T*, according to the Arrhenius' equation

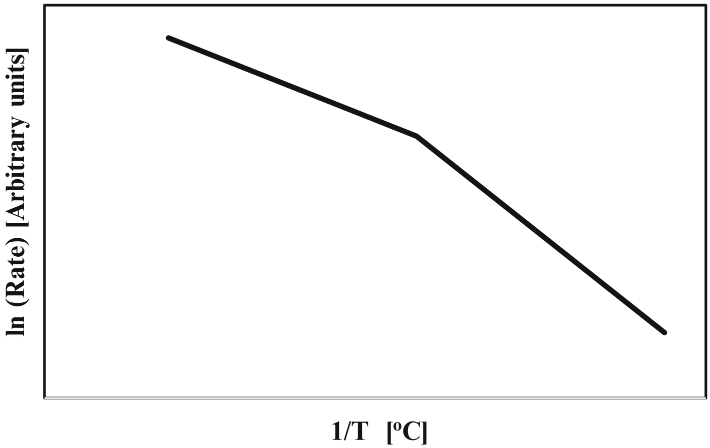


Fig. 9.6 A schematic presentation of the dependence of ln (Rate) on 1/*T* for the galvanic deposition of copper onto iron according to the results of Ref. [4–6]

the nature of the substrate. The deposition of copper on these substrates was performed from an acidic Cu(II)-containing solution at pH = 1 and 60 °C. Rates of deposition of copper onto investigated substrates, according to the results of Karavasteva, are generically presented in Fig. 9.7.

According to Fig. 9.7, the rate of deposition of copper onto different substrates decreases in the following order:

$$\mathrm{Al} < \mathrm{Fe} < \mathrm{Zn} \tag{9.19}$$

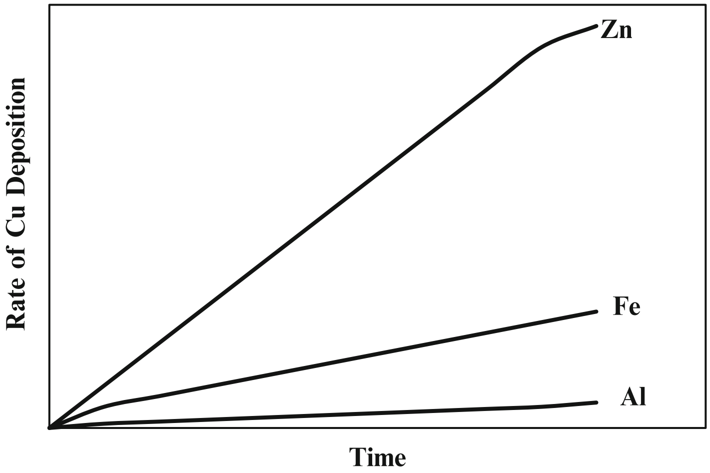


Fig. 9.7 A generic presentation of the dependence of the rate of copper deposition on time on Al, Fe, and Cu substrates according to the results of Karavasteva [7]

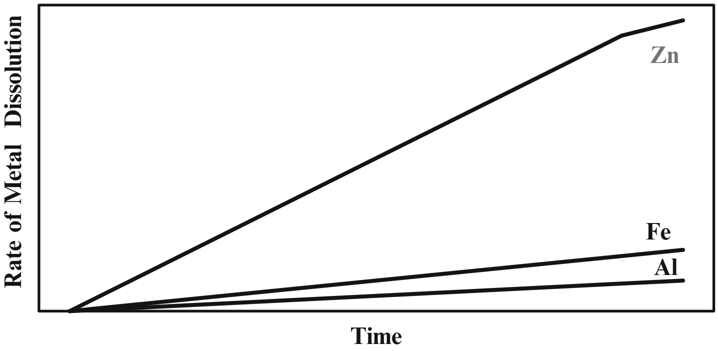


Fig. 9.8 A generic presentation of the dependence of the rates of dissolution of Al, Fe, and Cu substrates on time according to the results of Karavasteva [7]

Obviously, the rate of deposition of copper is the slowest on the aluminum surface followed by iron and zinc, respectively. The rate of copper deposition is a consequence of the rate of the dissolution of metallic substrates on which the reaction takes place. Similarly, as above, dependencies of the rate of the dissolution of aluminum, iron, and zinc on time are schematically given in Fig. 9.8.

The rate of dissolution of zinc in the investigated solution is the fastest following iron and aluminum, respectively. This is in a very good agreement with the results presented in Fig. 9.7.

9.2.1.2 Surface Morphology of Metals Produced via Galvanic Displacement Deposition

Theoretical Considerations

As explained in the previous section, the driving force for the deposition of metals via the galvanic displacement reaction is the difference in the standard electrode potentials. In these reactions, the less noble metal acts as a reducing agent of the ions of a more noble metal. For a continuation of the galvanic displacement reactions, a necessary requirement is that metal substrate (less noble metal or reducing agent) and metal ions of the more noble metal are in contact at all times. From the thermodynamics point of view, when the surface of the less noble metal, e.g., aluminum, is completely covered with the more noble metal, e.g., copper, then the galvanic displacement reaction and consequently deposition should stop. This is an ideal case, where an assumption is made that the surface of the less noble metal (e.g., aluminum) is completely covered with the more noble metal (e.g., copper). Under this condition, there is no contact between the substrate and metal ions, and a schematic presentation for this case is shown in Fig. 9.9.

The situation presented in Fig. 9.9 can only be true when the atoms of the deposited more noble metal are ideally packed on the surface of the less noble metal. In this case, the less noble metal is not anymore exposed to the electrolyte containing the more noble metal ions. As stated above, under these conditions, the further deposition does not proceed. With an ideal packing of the atoms, probably only a few monolayers of the more noble metal can be deposited.

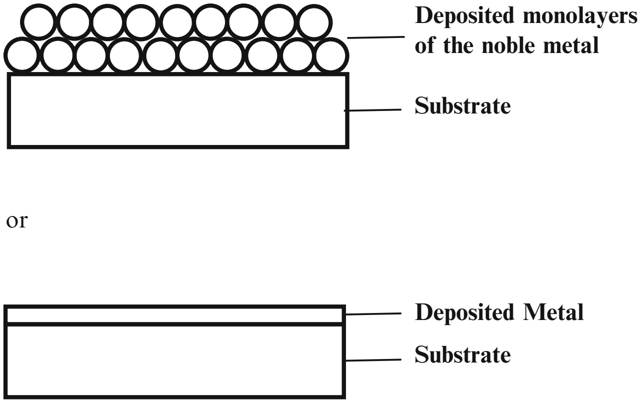


Fig. 9.9 An ideal schematic presentation when the surface of the substrate (less noble metal) is completely covered with the more noble metal

Experimental Observations

The results from real experimental settings, however, clearly show that during the galvanic displacement, reaction coatings of more noble metal significantly thicker than a *few atomic monolayers* with quite various surface morphologies are frequently obtained. The surface of the deposited more noble metal during this process can include roughening due to formation of various features, i.e., bulbous, botryoidal, dendritic, cauliflower, etc., particles. Experimental observations show that the coatings produced by the galvanic deposition are very porous. Due to porosity, the underlying, less noble metal then can easily be exposed to the electrolyte containing the ions of the more noble metal. Of course, as frequently observed in the practice, these coatings are very limited in thickness due to decreased surface area of the less noble metal exposed to the electrolyte containing the ions of the more noble metal. This is schematically presented in Fig. 9.10.

The pores are randomly distributed within the deposited metal. The existence of pores allows the electrolyte to get in contact with the substrate (less noble metal). While in contact with the electrolyte, the less noble metal dissolves producing electrons, as generically presented by the reaction (9.1). The electrons produced according to the reaction (9.1) are transferred through metal and further used for the reduction of ions of the more positive metal as described by the reaction (9.2). In this way, growth of the film of a more positive metal will further proceed. The deposition of the more noble metal and crystal growth will appear faster on the spots where pores exist compared to the pore-free sites, as schematically shown in Fig. 9.10.

In order to remove the surface oxide films and to allow the galvanic displacement deposition, an addition of the specific agents is required. In this way, the useful effect of chloride ions was reported in the literature [4]. In terms of the surface morphology, when there were no chloride ions present, galvanically deposited copper onto aluminum from acidic solutions was bulbous or botryoidal, mostly consisting of single segments [4]. This was attributed to the absence of chloride ions. Consequently, under this condition, only a few active sites are available on the

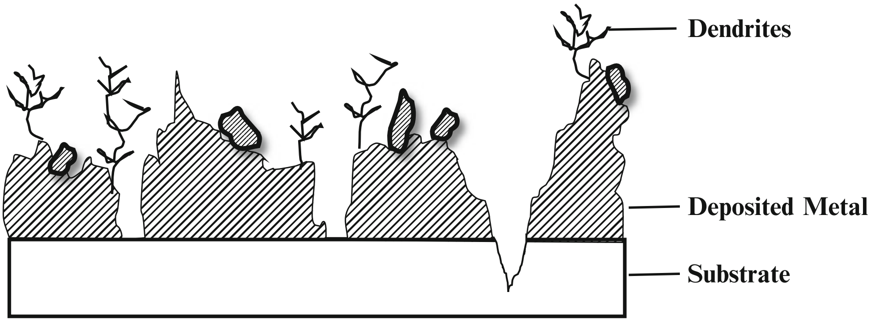


Fig. 9.10 A schematic presentation of the surface roughening during the prolonged immersion of the less noble metal substrate and deposition of the more noble metal via the galvanic displacement

aluminum surface, allowing further deposition of copper. An increase in the chloride ion concentration leads to a better removal of the aluminum oxide film and production of more uniform deposits of copper. The results of this work showed a clear transition in the surface morphology of the deposited copper bulbous or botryoidal to a crude form of dendrites and leaflike secondary arms. An increase in the agitation unavoidably leads to an increase in the rate of deposition, assuming that all other parameters, e.g., Cu(II) concentration, surface area, chloride ion concentration, and temperature, are constant. Based on the results from Annaamalai et al. [4], it seems that under these conditions various forms of copper dendrites are obtainable at different rates of agitations.

An increase in temperature leads to an increase in the rate of copper deposition from the acidic solutions onto aluminum. At temperatures up to about 40 °C, usually botryoidal or bulbous deposits of copper are obtained. A further increase in temperature leads to the deposition of the dendritic deposits. The dendrites formed above 40 °C are not compact, and they are fine and small according to the findings of Annamalai et al. [4]. The slower rate of reduction of Cu^{2+} onto iron [5] was observed at lower temperatures, and it contributed to the formation of deposits with no significant roughness. These deposits were relatively smooth. At higher rates of reduction (higher temperatures), the surface roughness of the deposited copper significantly increased, leading in production of large bulbous crystals.

The effect of copper ion concentration on the surface morphology of deposited metal was also investigated [4]. Generally, the rate of copper deposition on the concentration of Cu(II) ions passes through a maximum at about 300 mg/L [4]. The SEM images showed formation of dendritic deposits in all concentrations of Cu (II) used in this work. The authors argued that different dendrites are obtainable at various concentrations of Cu(II) ions. Presumably if the experiments of this work were properly carried out, there are no significant effects of the Cu(II) ion concentration on the surface morphology of the deposited copper: all deposits of copper onto aluminum were dendritic. During the galvanic deposition from acidic solution on iron substrate, long dendritic structures of copper were seen at higher deposition rates (lower Cu(II) concentrations) [5]. At the intermediate rates (with Cu (II) concentrations within the range 1–2 g/L), bulbous or botryoidal copper deposits were obtained. A lowest rate of copper deposition was observed with Cu (II) concentration of 5 g/L. In this case, the copper deposits exhibited a relatively flat and smooth surface.

An increase in pH in the acidic solutions, during the galvanic deposition of copper onto aluminum, leads to the formation of different deposits according to Annamalai et al. [4]. While at lower pHs, dendritic deposits were obtained, at pH close to 4, a honeycomb structure of the deposited copper is observed, evidencing that the amount of the aluminum surface is noticeably limited and, consequently, the rate of the dissolution of aluminum is significantly reduced.

It seems that the surface morphology of the deposited copper onto Al, Fe, or Zn is strongly influenced by the rate of dissolution of these metals and by the nature of these substrates [7], as noted in the previous section. Globular crystallites 1–4 μm in size are obtained on aluminum, while a coherent layer of fine crystallites less than

1 μm is deposited on iron and dendritic deposits with a high porosity are produced on zinc. The results suggest that a high rate of dissolution leads to a deposition of metals with a dendritic surface morphology. On the other hand, it seems that not only the rate of dissolution of the substrate but its structure would influence the surface morphology of the deposited metal.

A prolonged immersion of the less noble metal into the solution containing ions of the more noble metal due to deposition via the galvanic displacement reaction obviously leads to the significant surface roughening. Depending on the substrate and on the deposition product and conditions of the process (pH, temperature, composition of the electrolyte, stirring, etc.), various types of deposits, e.g., bulbous, botryoidally shapes, regular geometric shapes, cauliflower, dendritic, etc., may occur during this process. For the clarification of these issues, the reader is directed to the publications [1, 3, 8, 9] and references therein.

An experimental evidence of the surface roughening is shown in Fig. 9.11. Based on the SEM results shown in Fig. 9.11, a prolonged immersion of an

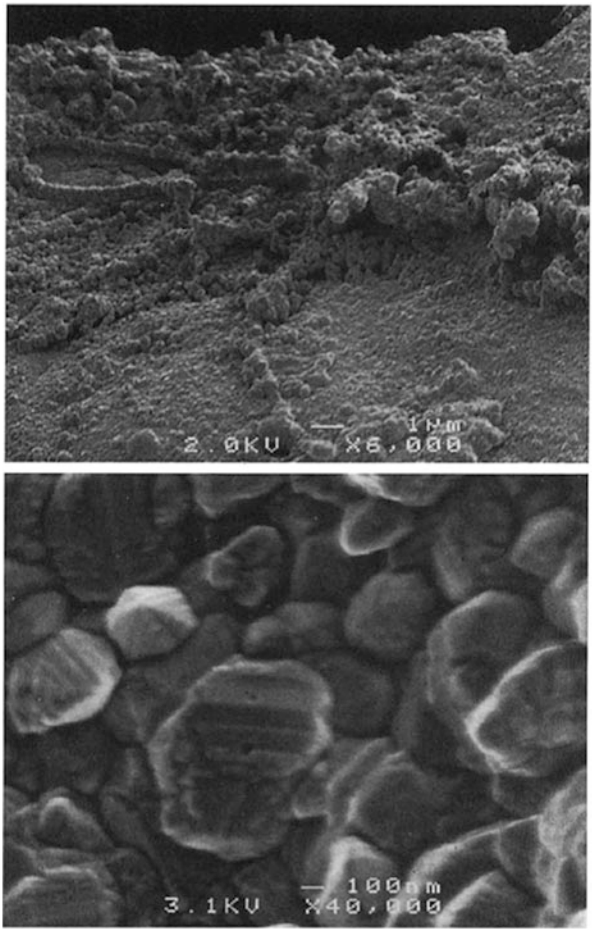


Fig. 9.11 SEM images of copper deposited onto aluminum substrates upon immersion in the alkaline Cu(II) solutions via the galvanic displacement reaction (Reproduced from Ref. [3] with permission from The Electrochemical Society)

aluminum substrate into alkaline Cu(II)-containing solutions leads to the significant roughening of the deposited copper. It seems that the surface roughening appears randomly. Probably, this is dependent on the transfer of the electrons produced due to dissolution of the less noble metal (aluminum) and on the surface concentration of the Cu(II) ions. This further suggests that the diffusion, temperature, mixing, local pH, etc., may significantly influence the surface morphology of galvanically deposited metal. Perhaps, further investigations will give a clearer picture of these issues.

Production of Metal Powders via Galvanic Displacement Deposition

Production of powders via the galvanic displacement reaction is described in literature [8]. Due to the surface roughening and unpredictable crystal growth, a prolonged immersion of a less noble metal during the galvanic displacement deposition produces particles of various sizes and shapes. A poor adhesion of the deposited metals makes it easy to separate them from the substrate. Several examples of galvanically produced powders are presented in the following figures. In Fig. 9.12 are shown dendritic powders of bismuth produced via the galvanic displacement deposition on flat aluminum substrates from a complexed Bi(III) citrate–EDTA solution at pH 2 [10].

Similarly, dendritic bismuth powders can successfully be obtained on the aluminum substrate from an acidic $K[BiI_4]$ solution at pH 1, as shown by the SEM images in Fig. 9.13.

Silver powders can be grown onto aluminum surface using the galvanic displacement reaction and different electrolytes [9]. Two examples are shown in Fig. 9.14. In Fig. 9.14 are shown the SEM images of silver powder produced onto aluminum surface from alkaline (a) and acidic (b) solutions. Based on these SEM

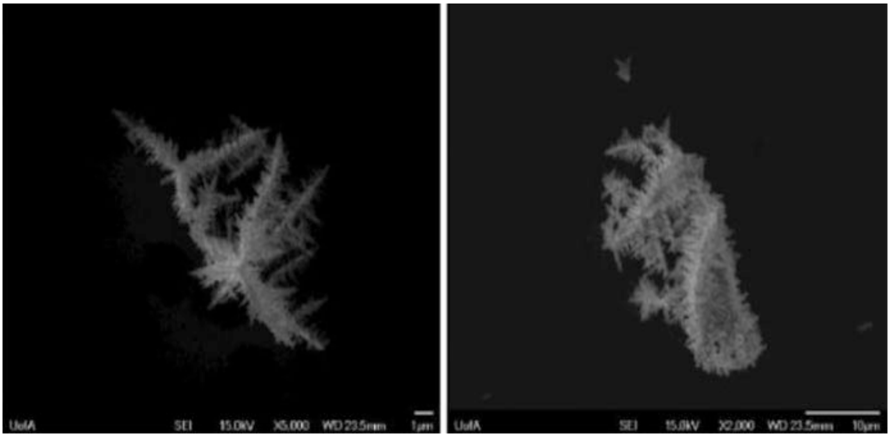


Fig. 9.12 SEM images of Bi powders produced from a complexed Bi(III)–citrate–EDTA solution at pH 2 and room temperature on aluminum metal substrate (Reproduced from Ref. [10] with permission from The Electrochemical Society)

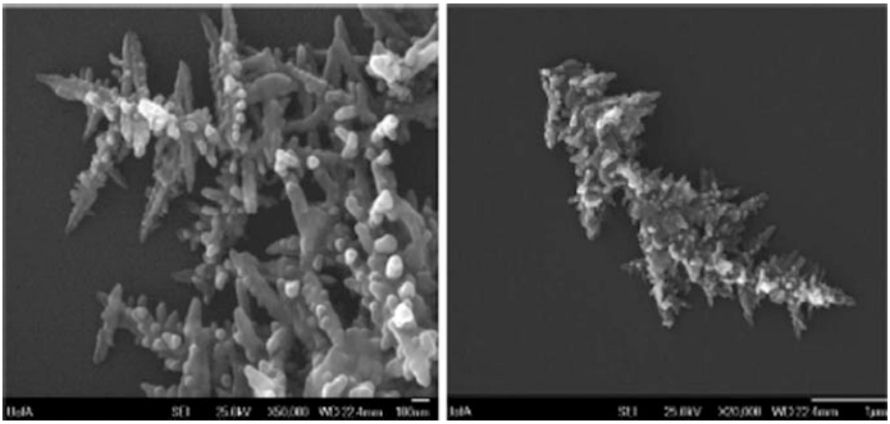


Fig. 9.13 SEM images of bismuth powders produced on aluminum surface from an acidic $K[BiI_4]$ solution at pH 1 and room temperature via the galvanic displacement (Reproduced from Ref. [10] with permission from The Electrochemical Society)

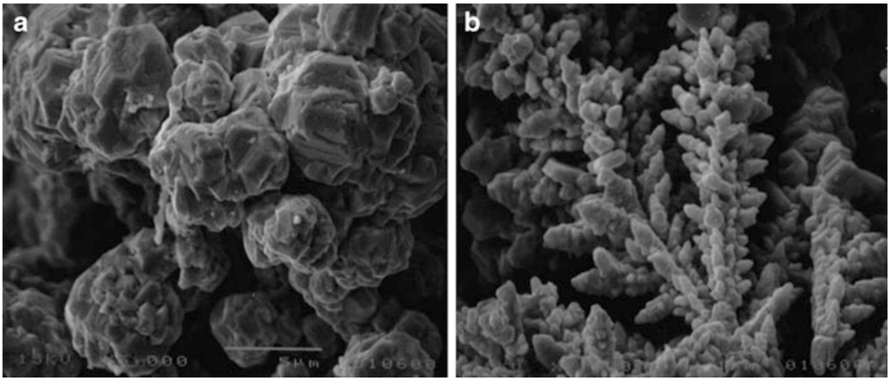


Fig. 9.14 Silver powders produced via the galvanic deposition from (**a**) 0.01 M $AgNO_3$ dissolved in diluted NH_4OH (pH 10, 22 °C) and (**b**) 0.01 M $AgNO_3$ dissolved in 0.5 M citric acid solution (pH 10, 22 °C) on an aluminum substrate (Reproduced from Ref. [9] with permission from The Electrochemical Society)

images, it seems that pH can significantly influence the shape of the particles produced. In the alkaline solutions, bulbous particles of silver were produced (Fig. 9.14a). However, as shown in Fig. 9.14b, an immersion of the aluminum foil into acidic Ag(I) solutions produces the dendritic silver powders.

In Fig. 9.15 are shown SEM images of silver produced with an immersion of niobium substrates into highly alkaline Ag(I) solutions above 90 °C. Agglomerated silver particles are clearly visible from these images. Deposition of silver onto niobium surface via galvanic displacement shows that unavoidably present oxide film at the surface of the substrate can be successfully removed. A production of powdery deposits suggests that oxide film is unevenly removed from the niobium surface.

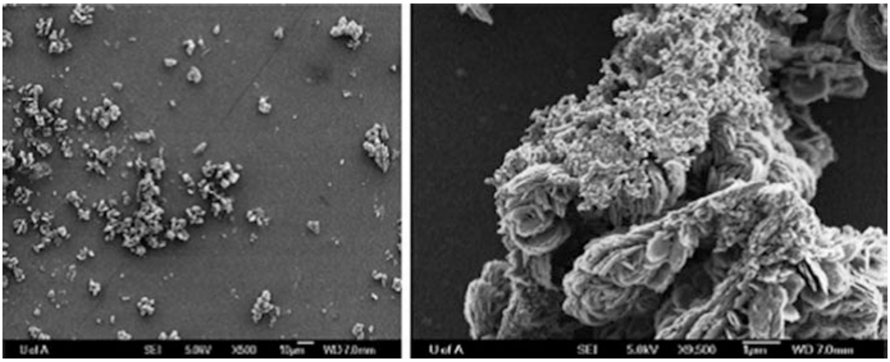


Fig. 9.15 SEM images of silver surface obtained by the immersion of Nb into alkaline Ag (I) solution for 30 s (pH 14, temperature 90–95 °C) (Reproduced from Ref. [11] with permission from The Electrochemical Society)

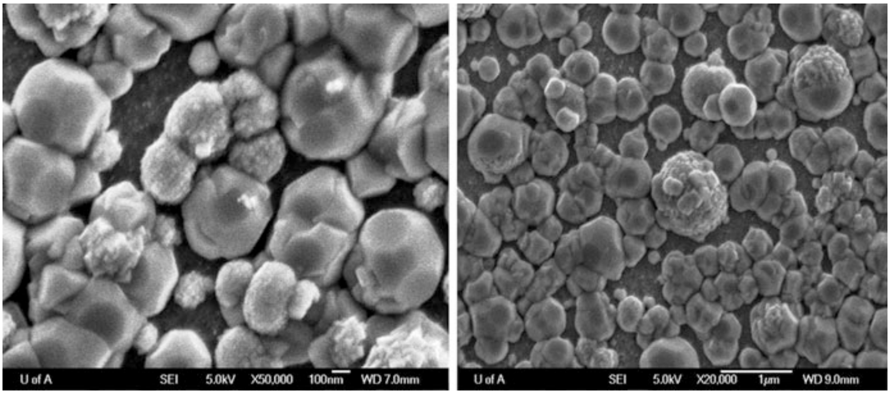


Fig. 9.16 SEM images of copper deposited onto niobium from alkaline Cu (II) solutions (pH 14, temperature 90–95 °C, deposition time 1 min)

The SEM images in Fig. 9.16 show a better surface coverage with the metal deposited (copper) in comparison with the results presented in Fig. 9.15 (silver). Bulbous copper particles (Fig. 9.16) are more densely distributed at the niobium surface than silver particles shown in Fig. 9.15. This result suggests that the niobium oxide film is more efficiently removed in the alkaline Cu(II) solutions.

Porous coatings of copper onto aluminum are shown by the SEM images in Fig. 9.17. These samples were obtained by an immersion of aluminum powders into alkaline Cu(II) solutions [3]. Due to porosity of the deposited copper, the electrolyte penetrates through pores and reacts with aluminum. In this way, simultaneous reactions of aluminum dissolution, hydrogen evolution, and copper deposition occur. A complete dissolution of aluminum and a production of hollow copper particles are shown in Fig. 9.17.

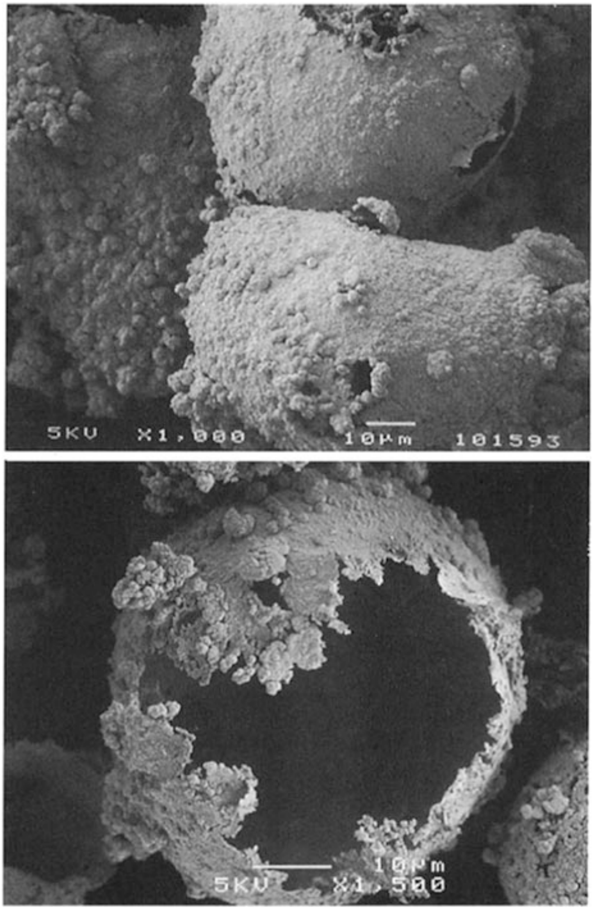


Fig. 9.17 SEM images of the hollow copper particles produced by the galvanic deposition of copper onto aluminum powder in Cu (II) alkaline solutions (pH 14, room temperature) (Reproduced from Ref. [3] with permission from The Electrochemical Society)

A sufficiently long exposure of the less noble substrate into a solution containing the ions of the more noble metal may lead to the significant surface roughening due to porosity of the deposited metal. Presence of oxide films at the surface of the less noble metal may not only delay the initial stages of the deposition but as well lead to the production of very rough deposits. A breakdown of an oxide film is usually achieved by an addition of specific additives. Due to an uneven removal of the oxide film, the deposition will not take place uniformly onto the whole surface immersed into the electrolyte. In addition, due to hydrolysis, one should take into consideration that in some electrolytes oxide films may form at the surface of the less noble metal, which further complicates deposition and formation of smooth deposits.

Changes in the operating conditions may influence the surface roughening of the deposited metal. It is obvious that a decrease in pH in the acidic solutions, for most of the metals serving as substrates, leads to an increase in their dissolution rate. In the case of the amphoteric metals, serving as substrates, an increase in pH in the alkaline solutions also leads to an increase in their dissolution rates. As well, it is generally observed that an increase in temperature leads to an increase in the dissolution rate for most of the metals. The dissolution of the less noble metal is the required condition providing the electrons for the reduction of the ions of the more noble metal and its deposition. Consequently, under the conditions where an increased rate of the dissolution of the less noble metal is observed, significant surface roughening takes place. The deposited more noble metals as can be seen from the scanning electron microscopy analysis exhibit formation of various shapes including powders, as shown in Figs. 9.11, 9.12, 9.13, 9.14, 9.15, 9.16, and 9.17.

9.2.1.3 Galvanic Displacement Deposition onto Semiconductor Substrates

The analysis presented here can further be applied to the metallization of semiconductor substrates via galvanic displacement. Metallization of semiconductors is very important in the electronic industry and as such was investigated for a relatively long time. A few examples are presented as follows.

Deposition of copper onto both p- and n- germanium substrates can be successful when the process is carried out from both acid and alkaline Cu(II)-complexed solutions [12]. The process, which proceeds via galvanic displacement, is described with the following reaction:

$$Cu^{2+} + Ge + 2H_2O \rightarrow GeO_2 + Cu + 2H^+ + H_2 \tag{9.20}$$

with $\Delta G^o = -87.944$ kJ/mol < 0.

An XRD analysis of such produced samples showed the presence of both Cu and GeO_2 phases. The SEM images of copper-coated germanium are shown in Fig. 9.18.

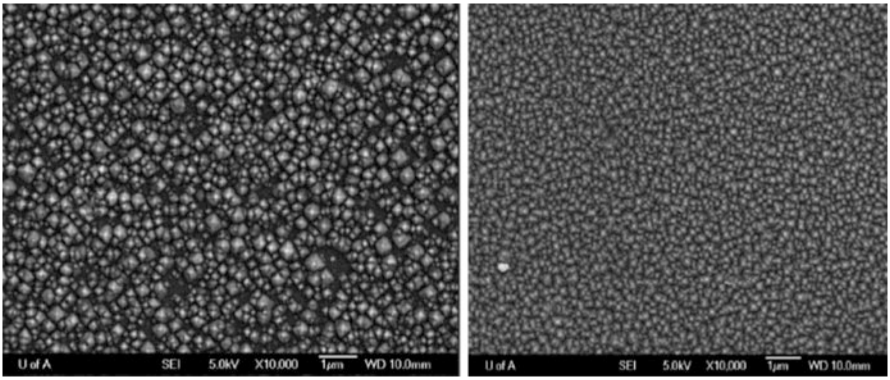


Fig. 9.18 SEM images of copper deposited from an acidic Cu(II) citrate solution (pH 2) onto n-Ge (*left*) and Ge substrate (*right*) (10 min immersion time) (Reproduced from Ref. [12] with permission from Elsevier)

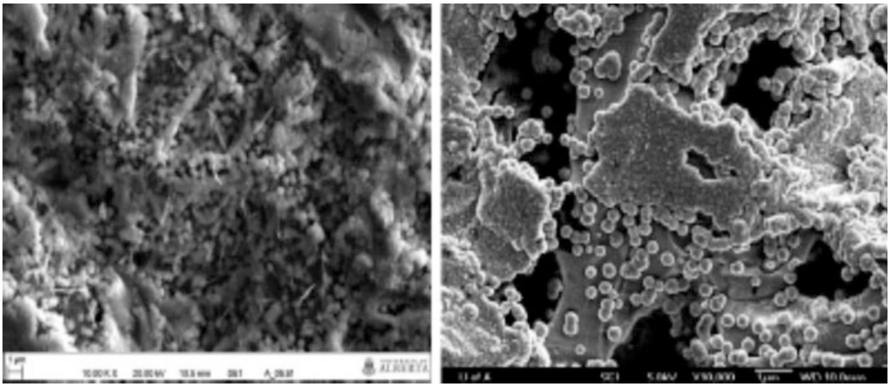


Fig. 9.19 SEM images of copper deposited from an alkaline Cu(II) solution (pH 14) on n- (*left*) and p- (*right*) Ge substrates (10 min immersion time) (Reproduced from Ref. [12] with permission from Elsevier)

As shown in Fig. 9.18, there is a quite uniform deposition of copper on both n- and p- germanium substrates. However, these images clearly show that larger particles of Cu are produced on n- germanium substrates in comparison to that of the p-Ge, leading in this way to a different surface morphology. The differences in the surface morphology of these two samples were attributed to the presence of different dopants (impurities) in the n- and p- Ge substrates [12].

The surface morphology of deposited copper onto germanium substrates is as well very much influenced by pH [12]. As shown by the SEM images in Figs. 9.18 and 9.19, the surface morphology of the deposited copper from alkaline solutions (pH 14) is quite different than that obtained from the acidic Cu (II) solutions (pH 2).

By a comparison of the SEM images from Figs. 9.18 and 9.19, it is obvious that the roughness of the deposited copper is more pronounced for the samples produced in the alkaline (pH 14, Fig. 9.19) than for those produced in the acidic solutions (pH 2, Fig. 9.18). As found by the XRD analysis [12] and as well as described by the reaction (9.20) above, GeO_2 is produced during the galvanic displacement deposition. The GeO_2 can be dissolved in the alkaline solutions which further leads to an increased rate of the Ge dissolution (oxidation). An increase in the rate of germanium dissolution, due to production of the electrons, further leads to an increase in the rate of copper deposition. Consequently under the alkaline conditions, surface roughening of the deposited copper should be pronounced as shown in Fig. 9.19.

Silver and gold can, as well, be deposited on germanium substrates [12]. It seems that the presence of GeO_2 and simultaneous hydrogen evolution (reaction (9.20)) can further influence the surface morphology of the deposited metals. Production of powdery silver deposits was demonstrated by a prolonged immersion (24 h) of the germanium substrate into acidic Ag(I) solutions. This is illustrated in Fig. 9.20, where dendritic silver powders deposited onto germanium substrates are shown.

Metallization of silicon semiconductor substrates is usually performed using the fluoride-based solutions [13]. In this case, unavoidably present SiO_2 film at the

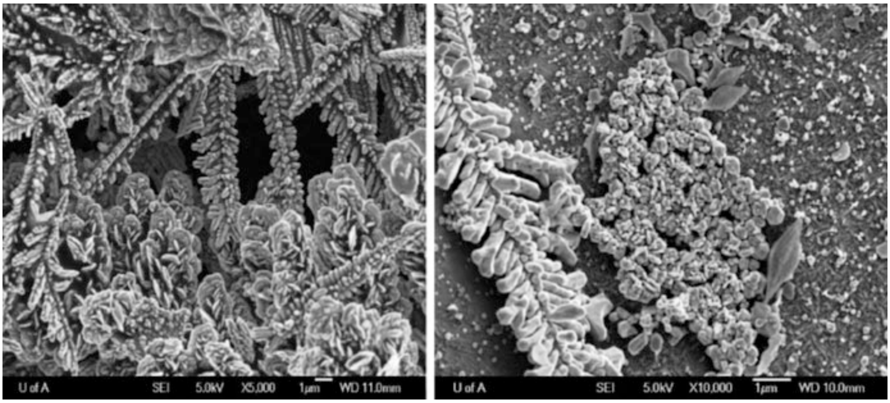


Fig. 9.20 Dendrites of silver produced on germanium substrates from an acidic Ag(I) solution (pH 2) (Immersion time 24 h) (Reproduced from Ref. [12] with permission from Elsevier)

surface of the silicon substrate is successfully removed by the fluorides present in the electrolytes. Deposition of silver onto both p-and n- silicon substrates was observed visually upon immersion into alkaline and *fluoride-free* Ag(I) solution at 85 °C [14]. Deposition of silver onto silicon proceeds via the galvanic displacement reaction which can be described by the following reaction:

$$\mathrm{Si} + 4\mathrm{OH}^- + 2\mathrm{Ag(NH_3)}_2^+ \rightarrow \mathrm{SiO}_3^{2-} + 2\mathrm{Ag} + \mathrm{H_2O} + 4\mathrm{NH_3} + \mathrm{H_2} \quad (9.21)$$

with $\Delta G^{\mathrm{o}} = -523.958$ kJ/mol < 0.

Or, considering the presence of the SiO_2 film at the surface of silicon wafers, the overall reaction describing the deposition of silver can be written as:

$$\mathrm{SiO_2} + \mathrm{Si} + 6\mathrm{OH}^- + 2\mathrm{Ag(NH)_3)}_2^+ \rightarrow 2\mathrm{SiO}_3^{2-} + 2\mathrm{Ag} + 2\mathrm{H_2O} + 4\mathrm{NH_3} + \mathrm{H_2} \quad (9.22)$$

with $\Delta G^{\mathrm{o}} = -507.176$ kJ/mol < 0.

SEM images of silver-coated silicone at 85 °C are presented in Fig. 9.21. As these results show, silver is deposited on both n- and p-silicon substrates. No significant differences in surface coverage with silver among n- and p-Si substrates are noticeable from these SEM images.

Practical applications of the galvanic displacement reaction, when smooth or continuous coatings are required, are, obviously, quite limited. It seems that only very thin coatings limited to several tens of nm with a smooth surface morphology can be achieved by this method. This aspect should be very carefully kept in mind for the modern electronics or biomedical applications. Contrarily, when hydrometallurgical applications are in question, i.e., solution purification, the galvanic displacement deposition is frequently a method of choice. This method is used

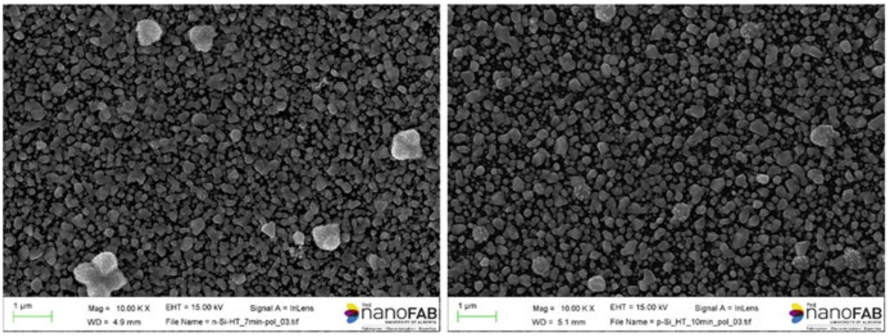


Fig. 9.21 SEM images of silver deposited at 85 °C on n-Si substrate (*Left*: 7 min immersion time) and on p-Si substrates (*Right* 10 min of immersion time) (Reproduced from Ref. [14] with permission from The Electrochemical Society)

for the removal of heavy or noble metals in the environmental applications. In both of these cases, i.e., hydrometallurgical or environmental applications, where the surface morphology of the deposited metal is not crucial, the galvanic displacement reaction can be a quite successful approach.

9.2.1.4 General Conclusions of the Galvanic Displacement Deposition in Terms of Surface Morphology

The surface morphology of deposited metals during the galvanic displacement depends on the rates of dissolution of the less noble metal and crystallization of the more noble metal. In terms of the surface morphology, following general conclusions can be made:

(a) Smooth and uniform coatings can be obtained only when the oxide film is successfully removed from the surface of the substrate.
(b) Smooth coatings can be obtained only for short deposition times and at lower deposition rates.
(c) When dealing with amorphous metals as substrates, e.g., Al, Zn, or similar in the alkaline solutions, deposition of smooth coatings is possible in solutions at lower pH (below 12).
(d) In the acidic solutions, deposition of smooth coatings takes place at higher pH (above 2).
(e) In terms of temperature, smooth coatings can be obtained at lower temperatures.
(f) A prolonged immersion of the less noble substrate into solutions containing ions of the more positive metal, due to poor adhesion and porosity of the deposited metal, unavoidably leads to the surface roughening.

(g) The surface roughening and production of powders of various sizes and shapes is strongly influenced with changes in temperature, pH, diffusion, surface concentration of the more noble metal ions, agitation, etc.

To conclude, the surface roughening during the deposition via the galvanic displacement reaction occurs either by a prolonged immersion or when an increased rate of the dissolution of the less noble metal is observed.

9.2.2 Autocatalytic Deposition

9.2.2.1 Basic Considerations

Autocatalytic deposition is the most widely used type of plating of metals from aqueous solutions, without an application of the external electrical current or potential. This process is frequently called *electroless* or *chemical deposition*, although, these terms do not precisely describe the *autocatalytic* deposition.

The autocatalytic deposition proceeds only on the catalytically active surfaces. Initiation of the autocatalytic deposition is achieved by a proper choice of catalysts, reducing agents and stable solutions containing metal ions aimed to be reduced. In many cases, such as deposition on ceramics, polymers, and other nonmetals, prior to metallization, the surfaces must be properly sensitized and/or activated in order to achieve a successful process [1, 15–17]. Similar procedures are used as well for some metallic surfaces on which the initiation of the autocatalytic deposition of a specific metal does not take place. The character of the reactions during the autocatalytic deposition and morphology of the deposit is significantly influenced by the catalytic activity of the metal particles formed in the reaction between metal ions and appropriate reducing agent.

For the autocatalytic deposition, both ions of the metal aimed to be deposited and a reducing agent are present in the homogeneous solutions in the aqueous phase. The reducing agents provide electrons for the reduction of metal ions and a consequent metal deposition. In general terms, reducing agents must be soluble and reasonably stable in the plating solution. Many reducing agents of metal ions are available in the practice. A choice of the reducing agent depends on the nature of the metal being deposited and on the properties of the final product. For example, compounds such as sodium hypophosphite ($Na_2H_2PO_2$), sodium borohydride ($NaBH_4$), and dimethyl amine borane (DMAB – $(CH_3)_2NH{\cdot}BH_3$) have quite successfully been used for the deposition of metals such as Ni, Co, Pd, Pt, etc. Hydrazine (N_2H_4) was reported as a successful reducing agent of Co(II), Ag(I), Ni(II), Pd(II), etc., ions. Formaldehyde (H_2CO) was used for a long time for the reduction of Cu(II) or Ag(I) ions. Ascorbic acid ($C_6H_8O_6$) was used for the reduction of Ag(I) or Au(I) ions. For a comprehensive review of the reducing agents used in the autocatalytic deposition, the reader is referred to the published monographs and references therein [1, 16].

9.2.2.2 Reducing Agents and Catalysts in the Autocatalytic Deposition

The reducing agent and a proper catalyst for the initiation of the autocatalytic deposition play very important roles in order to achieve the desired properties of the final product. In general terms, observations for commonly used reducing agents and respective catalysts, based on the published literature [1, 16, 17], are summarized as follows:

(a) The initiation of the deposition with borohydride ($BH_4^{\,-}$) as a reducing agent is realized using Pd, Pt, Ag, and Cu sites as catalysts.
(b) The initiation of the deposition with hypophosphite ($H_2PO_2^{\,-}$) as a reducing agent is realized using Ni, Co, Pd, and Pt catalysts. Silver or copper cannot be used for this purpose.
(c) The initiation of the deposition with formaldehyde (H_2CO) as a reducing agent is realized using Ag, Cu, Pd, and Pt as catalysts.
(d) Other reducing agents, e.g., hydrazine, dimethyl amine borane (DMB), ascorbic acid, etc., show in general terms quite similar behavior as that described for borohydride and hypophosphite; however, some differences are observed, depending on the metallic ion being reduced.

Many of the commonly used catalysts, e.g., Pd, Pt, Ni, etc., are considered as hydrogenation–dehydrogenation sites [16]. If the hypophosphite is used as a reducing agent, then on silver or copper surfaces dehydrogenation does not occur and consequently there is no catalytic deposition.

After the initial stage of the metal ion reduction on the catalytic sites, a further metal plating and film growth proceed via the so-called autocatalytic mechanism. Simply, the reduction of metal ions is autocatalyzed by the metal being deposited.

9.2.2.3 Kinetics and Mechanisms of Autocatalytic Deposition

The autocatalytic deposition proceeds by a controlled chemical reaction that is catalyzed by the metal or alloy being deposited [1]. This process can be presented with the following reaction:

$$M^{z+} + R^{n-} \rightarrow M + R^{z-n} \tag{9.23}$$

where M^{z+} is the ion of the metal M and $R^{n-}$is the reducing agent participating in the reaction. Consequently, according to the reaction (9.23), metallic ions M^{z+} are reduced to metal M, while the reducing agent R^{n-} is oxidized to R^{z-n}. Many examples of this type of deposition are described in the literature [1, 15–17].

The empirical rate law for the autocatalytic deposition according to the reaction (9.23) can be presented by the following equation:

$$-\frac{\mathrm{d}C^{\Delta}_{\mathrm{M}^{z+}}}{\mathrm{d}t} = KC^{\alpha}_{\mathrm{M}^{z+}}\ C^{\beta}_{\mathrm{R}^{n-}}\ \exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) \tag{9.24}$$

where $C_{\mathrm{M}}{}^{z+}$ is the concentration of the metallic ions used in the deposition, $C_{\mathrm{R}}{}^{n-}$ is the concentration of the reducing agent, α and β are the reaction orders of the respective species, K is the frequency factor from the Arrhenius law, E_{a} is the activation energy, T is the absolute temperature, and R is the universal gas constant. The individual time derivatives $\mathrm{d}C_{\mathrm{M}}{}^{z+}/\mathrm{d}t$ and $\mathrm{d}C_{\mathrm{R}}{}^{n-}/\mathrm{d}t$ are referred to as the rate of reaction with respect to the species M^{z+} and R^{n-}, while $\alpha+\beta$ is the overall reaction order.

The explicit rate law must be derived for each individual system. In general terms, these equations, besides mentioned concentrations of the metal ions and reducing agents, should contain as well parameters related to the concentrations of the complexing agents, additives, inhibitors, etc. With an assumption that the concentrations of the complexing agent of M^{z+} ions, inhibitors, additives, and other constituents of an autocatalytic plating solution are ideal, the most important factors determining the rate of the deposition are the concentrations of M^{z+} and R^{n-} ions and temperature. An increase in the $C_{\mathrm{M}}{}^{z+}$, $C_{\mathrm{R}}{}^{n-}$, and T generally leads to an increase in the rate of deposition according to Eq. (9.24). The additives such as stabilizers, inhibitors, and similar affect the rate of deposition. The stabilizers and/or inhibitors are used to reduce the rate of deposition in order to obtain a deposit with desired physicochemical or morphological characteristics. The effects of these compounds in more details can be found in the literature [1, 16].

From the present discussion, it is obvious that at lower concentrations of both metal ion and reducing agent, or at lower temperatures, the deposition will proceed smoothly. When the concentration of reducing agent is increased and at significantly higher temperatures, the rate of deposition or, more precisely, the rate of reduction of metal ions rapidly increases and provokes the *bath instability*. In order to produce a continuous metal film/coating, the deposition in the bulk solution must be avoided.

Bath Instability

The *bath instability* is a term that is frequently used in the published literature to describe the conditions where the deposition of the desired coating is significantly diminished. Under these conditions, significant roughening of the metal deposit, and more frequently, deposition of powders, not only at the surface but, as well, in the bulk solution, is observed. Schematically, this is presented in Fig. 9.22 as a dependence of the rate of deposition on temperature. It is to be noted that dependences of the rate of deposition as function of $C_{\mathrm{R}}{}^{n-}$ exhibit a similar trend.

Although, the general rate of the reduction of metal ions should increase with an increase in $C_{\mathrm{M}}{}^{z+}$, $C_{\mathrm{R}}{}^{n-}$, and T, even at the point of the so-called bath instability is reached, the rate of deposition of metal at the desired surfaces significantly

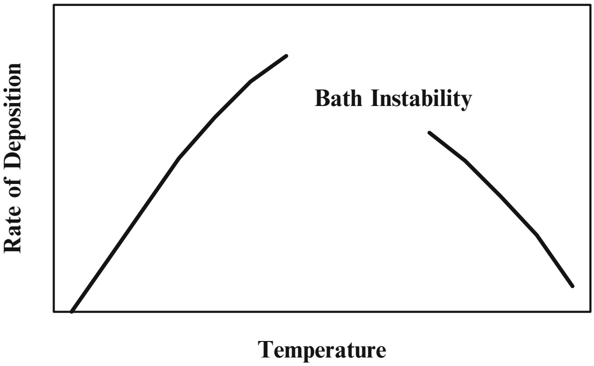


Fig. 9.22 A schematic presentation of the rate of deposition as a function of temperature

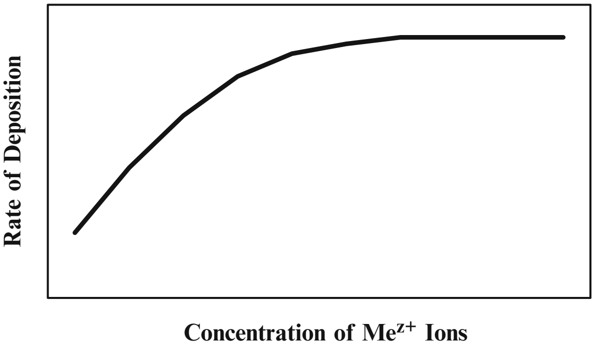


Fig. 9.23 A schematic dependence of the rate of deposition of metal Me on the concentration of its ions in solution. An assumption is made that the concentration of the reducing agent and temperature are optimal

decreases, as shown in Fig. 9.22. At the point when the bath instability is achieved, the deposition of powders in the bulk solutions takes place, rather than on the desired surface. As well, in terms of the surface morphology, significant roughening may occur under these conditions. Therefore, in considering these three variables, i.e., $C_M{}^{z+}$, $C_R{}^{n-}$, and T, on the rate of reduction of metal ions, the following can be summarized:

(a) A relatively small increase in $C_M{}^{z+}$ when $C_R{}^{n-}$ and T are kept constant may lead to a slight increase in the rate of deposition and insignificant surface roughening. A significant increase in the $C_M{}^{z+}$ may not influence the rate of reduction. This is schematically presented in Fig. 9.23.
(b) An increase in $C_R{}^{n-}$ when $C_M{}^{z+}$ and T are kept constant usually leads to the significant increase in the rate of the reduction of metal ions. As explained above, this leads to the so-called bath instability. Under these conditions, powdery deposits can frequently be obtained.
(c) When the $C_M{}^{z+}$ and $C_R{}^{n-}$ are kept constant, an increase in temperature unavoidably leads to an increase in the rate of metal ion reduction. Due to the bath instability, an increase in the surface roughening and formation of powdery deposits is easily observed.

Mechanisms of Autocatalytic Deposition

An understanding of the mechanisms of the autocatalytic deposition is crucially important in order to achieve the desired surface morphology and other physicochemical properties of the deposits produced using this approach. So far, five different mechanisms of the autocatalytic deposition have been proposed and they are listed below [1]:

- Atomic hydrogen mechanism
- Hydride ion mechanism
- Electrochemical mechanism
- Metal hydroxide mechanism
- Universal mechanism

For the review of all these mechanisms, the reader is referred to the Ref. [1]. In summary of the proposed listed mechanisms, it is, based on the experimental observations and the present knowledge, quite unlikely that the *atomic hydrogen* and *hydride ion* mechanisms are applicable in the description of the autocatalytic deposition. The *universal* mechanism is not applicable, since every single autocatalytic deposition (e.g., Ni, Co, Pd, Pt, Ag, Au, Cu, Bi, etc.) must have a specific mechanism, and a generalization is quite difficult to achieve. It seems that the *metal hydroxide* and up to some extent the *electrochemical* mechanisms are the only mechanisms that can explain most of the characteristics of the autocatalytic deposition of metals and alloys. The discussions of the mechanistic aspects of autocatalytic deposition in details is out of the scope of the present book; however, the metal hydroxide mechanism [1, 16–18] seems as the most acceptable way to explain the properties including the surface morphology of the deposits produced via the autocatalytic deposition. The metal hydroxide mechanism is based on the fact that under the conditions of autocatalytic deposition there is an unavoidable pH rise at the surface where the reaction in question takes place. Due to hydrolysis, hydrolyzed species can form and further be absorbed and/or reduced at the surface. This mechanism explains quite well the *bath instability* and formation of powders within the bulk electrolyte. When other parameters are constant, in general terms, an increase in pH of the solution leads to an increase in the rate of deposition, as schematically presented in Fig. 9.24.

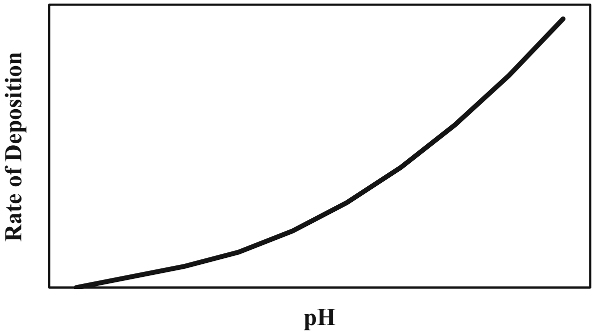


Fig. 9.24 A schematic dependence of the rate of autocatalytic deposition on pH

An increased concentration of the reducing agent, pH, and an elevated temperature significantly contribute to the hydrolysis of the metal ions causing the formation of hydroxyl complexes, hydroxides, and even oxides [19]. The autocatalytic deposition of a metal M from a homogenous liquid solution, using a reducing agent R^{n-}, is described with the reaction (9.23). In the autocatalytic deposition, the hydrolysis phenomena, as has already been published before [1, 16, 18, 19], play a very significant role in the reduction of metallic ions from aqueous solutions. Due to an increase in pH, the following reaction may occur:

$$M^{z+} + \mathrm{xOH}^- \rightarrow M(\mathrm{OH})_{\mathrm{x}}^{(\mathrm{z-x})+} \tag{9.25}$$

The hydrolyzed metallic species $\left(M\left(\mathrm{OH}\right)_{\mathrm{x}}{}^{(\mathrm{z-x})+}\right)$ are further reduced in the presence of an appropriate reducing agent (R^{n-}) to metal according to the reaction:

$$M_{\mathrm{x}}^{(\mathrm{z-x})+} + R^{\mathrm{n}-} \rightarrow M + R(\mathrm{OH})_{\mathrm{x}}^{(\mathrm{z-x-n})+} \tag{9.26}$$

These hydroxides and/or oxides, formed into the bulk solution, serve as sites, which are further reduced to the metallic state with an appropriate reducing agent. Because various sizes of particles can be produced, it is obvious that the further growth of the metallic powder is autocatalytic. Furthermore, because the formation of hydrolyzed metallic species is significantly determined by pH, it seems that the degree of hydrolysis can significantly influence the shape of powder particles.

By all means, further studies are required to clarify the mechanisms of the autocatalytic deposition. The observations suggest that every single reaction (autocatalytic deposition) must have its own mechanism. In this way, all the generalizations must be avoided, no matter how many of the autocatalytic processes are analogous or similar.

9.2.2.4 Surface Morphology of the Coatings Produced by the Autocatalytic Deposition

Most widely studied autocatalytic deposition systems include nickel, copper, silver, gold, cobalt, and palladium [1, 16]. In order to produce uniform coatings with a relatively smooth surface morphology, it is obvious that the surface coverage with the active catalysts, e.g., Pd, is uniform and sufficiently dense. A nonuniform distribution of the catalysts at the substrate will unavoidably lead to a formation of noncontinuous deposits and, frequently, produce coatings with a noticeable roughness and other surface irregularities.

With an assumption that the surface of the substrate is uniformly covered with the catalyst and that the initial stage of the metal ion reduction proceeds uninterruptedly, further film growth and its surface morphology is influenced exclusively by the parameters of autocatalytic deposition. The rate of metal ion reduction with the appropriate reducing agent at the initial stage of the deposition progressively increases with time until the continuous film is formed on the surface of the substrate. Ideally, at this point, the rate becomes constant. However, in the real experimental settings, the rate of deposition may continuously change with time and depending on the microstructure of the growing film, diffusion, and adsorption of different ions or molecules.

An increase in the deposition time leads to the increase in the grains of the deposited metal and alloy. This is frequently seen in the autocatalytic deposition of nickel, cobalt, copper, silver, etc. The effects of plating variables including the composition of the solution on autocatalytic deposition of cobalt using hydrazine as a reducing agent were systematically investigated [18]. For this purpose, cobalt was deposited on palladium-activated copper. Cobalt film produced at lower deposition rates replicated the surface morphology of the polycrystalline Cu substrate. At lower plating rates, the deposits were smooth and shiny. XRD analysis of these deposits found that Co had a hexagonal close-packed (hcp) structure. An increase in the pH, temperature, or N_2H_4 concentration or a decrease in Co^{2+} concentration, however, leads to an increase in surface roughness as shown in Fig. 9.25.

At relatively high pH values ($>$12.8), higher N_2H_4 concentrations, and higher temperatures ($>$70 °C), the cobalt reduction rate increased rapidly. Deposits obtained under these conditions exhibit significant roughness and the formation of dendrites occurs. Furthermore, due to the bath instability, the reduction of cobalt is observed in the bulk solution, even without the presence of any metallic substrate. In such a case, pure Co powder is obtained. The SEM micrographs show that the Co powder produced under these conditions was dendritic in terms of surface morphology (Fig. 9.26). XRD analysis found that the Co powder contained 70 % Co with the hcp and 30 % Co with the fcc structure.

Similarly, formation of powders of different metals with various surface morphologies during the autocatalytic deposition was reported in the literature [8, 9]. Generally, during the autocatalytic deposition, powders are produced due to the bath instability (higher pH, increased temperature, and higher concentrations of the reducing agent).

The substrate and the nature of the reducing agent may significantly influence the surface morphology of the deposited film. Autocatalytic deposition of gold onto Ni-B and Ni-P surfaces was comparatively investigated using hydrazine, hydrazine sulfate, sodium borohydride, and ascorbic acid as the reducing agents of Au(I) ions [20]. In terms of the substrate, autocatalytic deposition of gold using these reducing agents was preferably observed on Ni-B surfaces. On Ni-P substrates, only ascorbic acid and somewhat sodium borohydride were successful. Deposition of gold using hydrazine or hydrazine sulfate onto Ni-P surfaces was not observed.

While the deposition of gold using ascorbic acid as a reducing agent occurred within the temperature range from 20 to about 50 °C, with other reducing agents, the deposition was observed above 65 °C. The rate of gold deposition generally increased with temperature for all reducing agents used in this work. Using hydrazine, hydrazine sulfate, or sodium borohydride, rates of gold deposition were significantly higher in comparison with the rate of deposition when ascorbic acid was used as a reducing agent. In the case of the ascorbic acid, the bath instability as

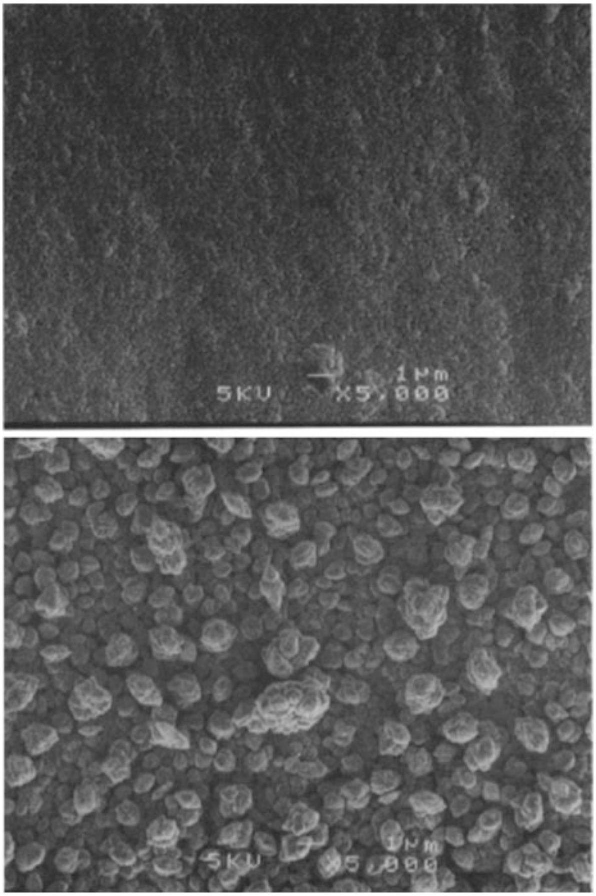


Fig. 9.25 SEM images of cobalt autocatalytically deposited onto copper activated with palladium *Top*: pH 12.3, $[N_2H_4] = 0.032$ mol/dm^3, $[Co(II)] = 0.08$ mol/dm^3, 62.5 °C, *Bottom*: pH 12.73, $[N_2H_4] = 0.32$ mol/dm^3, $[Co(II)] = 0.08$ mol/dm^3 72 °C (Reproduced from Ref. [18] with permission from The Electrochemical Society)

a function of temperature appeared at about 50 °C. For the deposition of gold with hydrazine, hydrazine sulfate, or sodium borohydride, the bath instability appeared at about 85–90 °C.

As the SEM image in Fig. 9.27 (right) shows, the Ni-B substrate was not uniformly covered with gold using sodium borohydride as a reducing agent. Rather, relatively large gold grains ranging from about 1 μm to more than 10 μm are clearly visible. The underlying Ni-B substrate with the cauliflower surface morphology and produced via autocatalytic deposition is, as well, clearly seen. At a larger magnification (Fig. 9.27 left), a significant roughness of the gold surface is visible.

A better coverage of the Ni-B substrates was achieved when hydrazine sulfate (Fig. 9.28), hydrazine (Fig. 9.29), and ascorbic acid (Fig. 9.30) were used as the reducing agents. As these figures show, there is a significant influence of the reducing agent on the surface morphology of the deposited gold. The surface roughness of gold deposited onto Ni-B substrate as a function of the reducing agent decreases in the order:

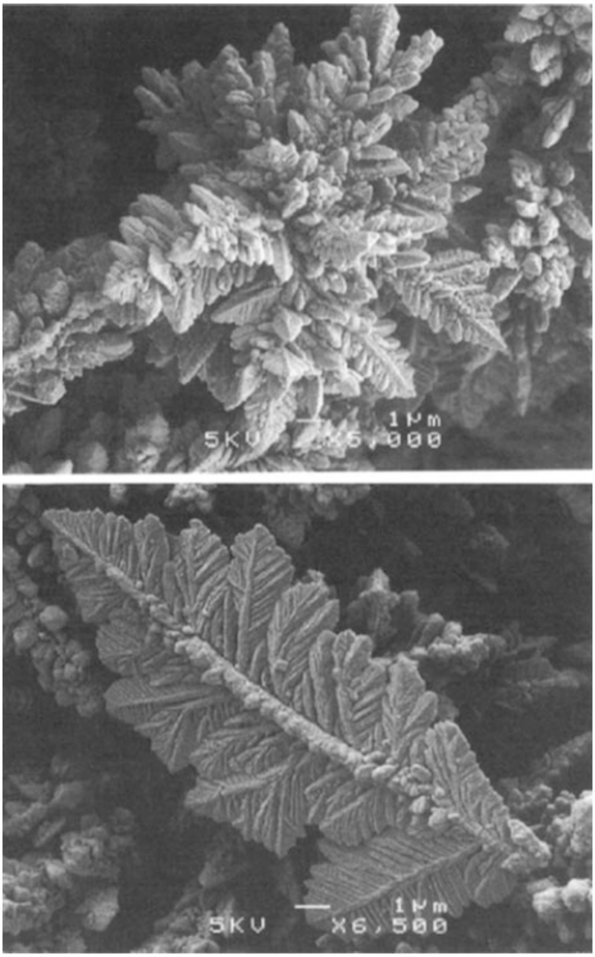


Fig. 9.26 SEM images of cobalt powder produced in bulk solution at 75 °C, pH 12.9, [Co(II)] = 0.08 mol/L, $[N_2H_4] = 0.32$ mol/L (Reproduced from Ref. [18] with permission from The Electrochemical Society)

$$\text{Ascorbic Acid} < \text{Hydrazine Sulfate} < \text{Hydrazine} < \text{Sodium Borohydride} \tag{9.27}$$

It is important to note that the crystallite size, as calculated according to the XRD analysis [19], as a function of the reducing agent, follows the same order as described by the relation (9.27).

Of course, it is widely known that the additives may significantly influence the bath stability and consequently the surface morphology of autocatalytically deposited metals and alloys. According to the published literature, there are many different formulations for the autocatalytic deposition of metals and/or alloys which are used in the applications. As well, each of these formulations uses quite different additives, and there is not yet a meaningful scientific explanation and/or

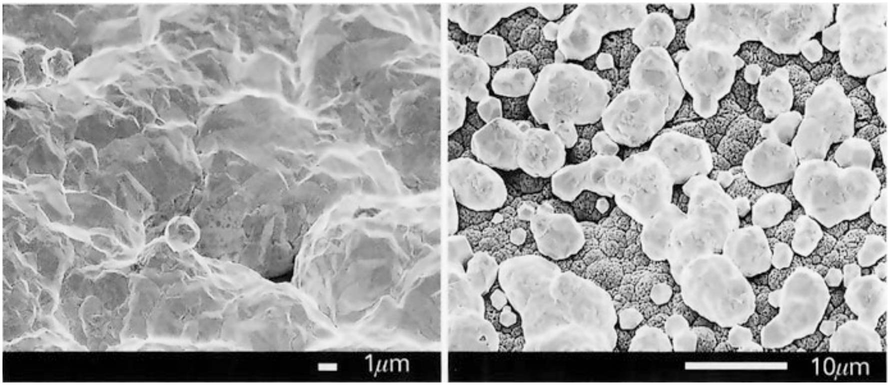


Fig. 9.27 SEM images of gold deposited onto Ni-B substrate using sodium borohydride as a reducing agent at 75 °C (Reproduced from Ref. [20] with permission from The Electrochemical Society)

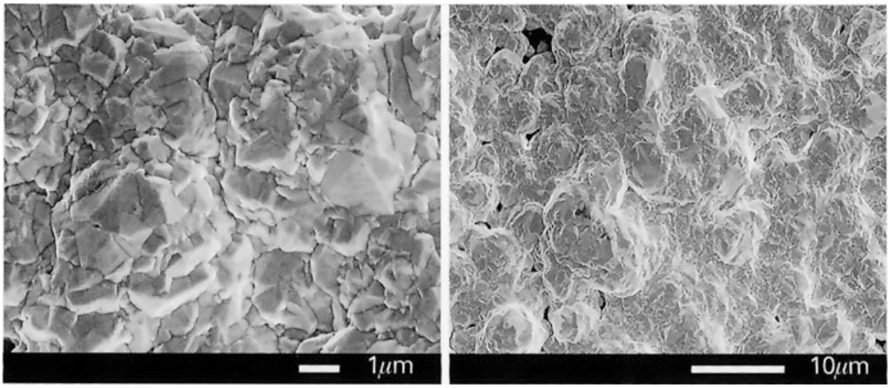


Fig. 9.28 SEM images of gold deposited onto Ni-B substrate using hydrazine as a reducing agent at 75 °C [20] (Reproduced by the permission of The Electrochemical Society Inc)

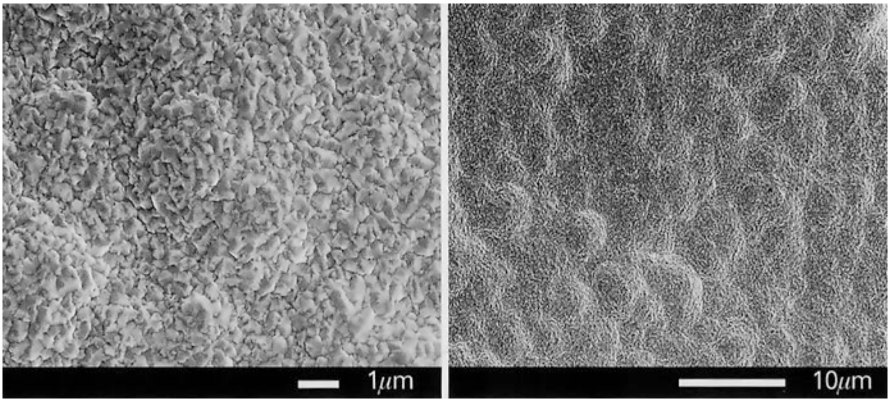


Fig. 9.29 SEM images of gold deposited onto Ni-B substrate using hydrazine sulfate as a reducing agent at 75 °C [20] (Reproduced by the permission of The Electrochemical Society Inc)

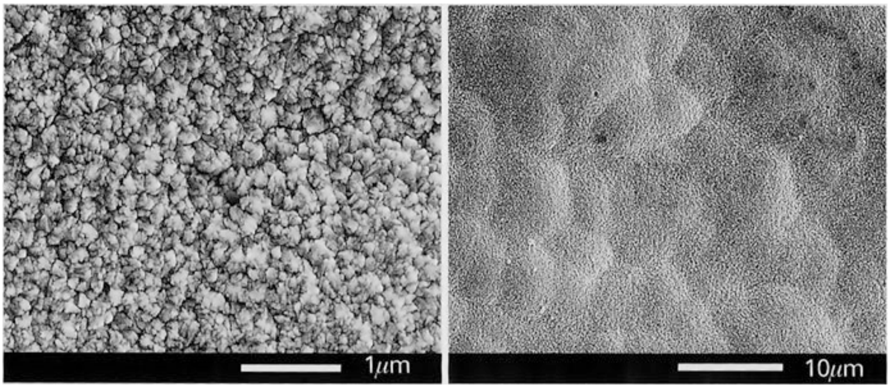


Fig. 9.30 SEM images of gold deposited onto Ni-B substrate using ascorbic acid as a reducing agent at 75 °C [20] (Reproduced by the permission of The Electrochemical Society Inc)

trend of their effects on the autocatalytic deposition. It seems that every single additive generally has a specific effect on a particular plating system. When applied to another plating system, the same additive shows a quite different behavior.

9.2.2.5 General Conclusions of the Autocatalytic Deposition in Terms of Surface Morphology

What causes the surface roughening and formation of powdery deposits? According to the observations from the practice or from the experiments, the appearance and surface morphology of metals and alloys produced during autocatalytic deposition is significantly influenced by the rate of the reduction of metal ions. These observations are briefly summarized as follows:

(a) Formation of smooth coatings can be obtained at lower concentrations of ions of the metal being deposited and/or reducing agents and at lower temperatures.
(b) An increase in the concentrations of either metal ion or reducing agent would lead to an increase in the rate of deposition and most likely to the appearance of the surface roughness at the microlevel.
(c) Significant increase in the concentration of the reducing agent if the concentration of metal ions and temperature are kept constant may lead to a noticeable surface roughening of the deposit.
(d) If both concentrations of the reducing agent and temperature are kept constant and temperature is significantly increased, an extensive surface roughening of the deposited coating and even formation of powdery deposits in the bulk solution may readily occur.
(e) If the concentration of the reducing agent and temperature are kept constant within the reasonable time frame, an increase in the concentration of the metal ions increases the rate of the reduction, but not significantly. The surface roughening may occur at the microlevel and coatings produced under these conditions are usually dull.

The influence of the deposition parameters on the surface morphology of chemically deposited metals and alloys is significantly more complex than that described for its electrodeposition counterpart. The surface morphology of chemically deposited metals and alloys depends on many parameters such as concentrations of the metal ions and reducing agent, pH, temperature, and mixing. Further studies are definitely required for a more systematic and precise description in order to achieve the desired physicochemical properties and a required surface morphology.

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