

ELECTRODEPOSITION OF IRON AND IRON ALLOYS

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Iron plating is the principal material used for numerous applications due to the desirable physical properties of iron and its low cost. The early literature on iron deposition, which was concerned with both commercial applications and electrorefining, has been comprehensively surveyed in a monograph [1]. The production of electrotypes in Russia [2] and of driving bands for shells in Germany during World War I, the electroforming of iron sheets and tubes [3], and the rebuilding of worn parts [4, 5] were among the early applications of electrodeposited iron. The good magnetic properties which may be obtained with electrolytic iron led to its use by the Western Electric Company [6] in the cores of Pupin induction coils prior to the development of nickel–iron alloys with even better magnetic properties.

Another application is a process reported in 1930 [7] in which intaglio plates for printing government currency and bonds were made by depositing a nickel face backed by a heavy deposit of electrolytic iron from a hot chloride bath.

In order to conserve nickel and copper, iron plating was used during World War II to make electrotypes and to coat stereotypes [8, 9]. During the same period, the United States Rubber Company electroformed iron molds for rubber, glass, and plastics [10]. Soldering tips are plated with iron commercially, and undoubtedly there are many other small-scale applications. The electrodeposition of iron as a means of producing iron powder for powder metallurgy is an application that continues to be used [11].

Interest in iron plating persists despite the fact that many of its applications have been short-lived. This is attested by several publications on, for example, the production of iron strips [12, 13], electrowinning [14, 15], the electroforming of phonograph record stampers [16, 17], rolls and molds [18], and the use of iron for restoring worn parts [19]. Continuous iron strips produced by iron plating have been used for

composite roofing materials, low-wattage resistance heating elements, and several magnetic products such as laminated cores for coils, magnetic display boards, and magnetic shielding [20–22]. Hard iron plating was employed on aluminum pistons to enhance wear resistance, to eliminate the need for iron or steel sleeves, and to allow the use of die casting methods [23]. Over five million pistons were plated with hard iron deposits at General Motors Corporation [24]. A 1973 patent mentioned the effectiveness of intermediate thin iron deposits with low stress to obtain thick and highly stressed iron deposits on a soft material without any peeling or spalling of the iron deposits [25].

There are several reasons for this persistent interest in iron plating. Iron is cheap and abundant. It can be deposited as a hard and brittle metal which, by heat treatment, can be rendered soft and malleable, or as a soft and ductile metal to which surface hardness can be imparted by carburizing, cyaniding, and nitriding. The fatigue strength of surfaces prepared by case hardening electrodeposited iron has been reported to be equal to the best commercial rolling-element bearing materials [26]. Electrodeposited iron can be welded readily, other metals can be easily plated on it, and in the soft state it has superior drawing properties [27]. Electrodeposited iron is relatively resistant to corrosion, as would be expected from its high purity; the contrary opinion, which has been quoted in the literature [28], probably arose due to a failure to rinse deposits completely free of electrolyte traces. The throwing power of iron baths is comparable to that of nickel baths.

The production of several types of iron alloy plating has been one of the most important developments of the last two decades in the metal finishing industry. Iron–nickel alloy plating has been widely used for decorative coating [29], for the surface coating of continuous casting molds in the steel

making industry [30], and for magnetic devices [31–37]. Iron–zinc alloy plating has been used in the steel industry for the corrosion protection of iron-based materials [38] in rack-or-barrel operation [39] and continuous plating operation [40]. There have been developments in the production of iron oxides in the last decade, and some applications have been found in medical and electronics industries.

A significant problem with iron and iron alloy plating that has limited its usage to specialized or high-volume applications is that, despite usually lower costs for anodes and solutions, the expenditure for capital equipment and maintenance may be higher for an iron plating bath than for other more commonly used plating baths. Special high-temperature or corrosion-resistant equipment may be required to heat, agitate, filter, or ventilate the iron plating bath. Also, unless used regularly, the solution will oxidize gradually. The time and effort required to restore the electrolyte to an operable condition may outweigh the economic benefit of depositing a lower cost metal.

11.1 PRINCIPLES

Practically all iron is plated from acidic solutions of Fe(II) (ferrous) salts. The presence of iron in the Fe(III) (ferric) state in these baths, in an appreciable concentration, is undesirable because it lowers the cathode efficiency for depositing the metal and it may cause deposits to be brittle, stressed, and pitted. In practice, it is not difficult to maintain the concentration of Fe(III) ion at harmless levels.

Until recently, practically all iron was plated from baths containing Fe(II) sulfate, Fe(II) chloride, or a mixture of the two. Iron(II) fluoborate and Fe(II) sulfamate baths have been used to some extent. Research on plating from solutions of other iron salts has not been neglected. In 1887, Watt [41] investigated deposition from solutions of a large number of iron salts and concluded incorrectly that only sulfate baths were practical. Baths based on the iron salts of several fluorine-substituted phosphoric acids and fatty acids were investigated but did not yield satisfactory deposits [42]. Selected baths of other types are described in a later section of this chapter.

The most frequent addition to both the sulfate and chloride bath is conducting salts, such as a corresponding alkali and alkaline earth salts. Many other salts, such as those of various organic acids, have been recommended. Oxycarboxylic and dicarboxylic acids such as citric, malic, malonic, tartaric, and ascorbic have been used to prevent the formation of ferric hydroxide precipitation [43]. These acids may give codeposition of an impurity element which affects the properties of an iron deposit and may be justified in special circumstances. The simple bath combinations described next should fill most requirements and have been used generally for the production of an iron strip.

11.2 FERROUS SULFATE BATH

The Fe(II) (ferrous) sulfate bath produces deposits that are smooth and normally light gray in color. There is little tendency toward pitting, and thick deposits can be produced. Disadvantages of the bath are that it yields brittle deposits, the deposition rate is slow, and the current density at which burning occurs is about one-half that of a hot chloride bath. An advantage is that it can be operated at room temperature (about 25°C), in contrast with the ferrous chloride–calcium chloride bath.

The most common sulfate bath is the one containing the double salt, ferrous ammonium sulfate. It has been used principally for building up undersized machine parts [4, 5] and also to apply a hard facing to stereotype [8].

Iron(II) sulfate may also be used alone, or other salts such as sodium, magnesium, or aluminum sulfate may be added [1, 44]. Addition of a small amount of ammonium fluoborate to the high-pH sulfate bath is claimed to make the slimy Fe(III) hydroxide precipitate that accumulates in it more easily filterable [45].

The different added salts probably have minor specific effects on the properties of the deposits, but no data are available. The presence of ammonium ion appears to reduce the rate of air oxidation of Fe(II) ion and the internal stress.

It will be noted in Table 11.1 that the two ranges of pH are shown for the sulfate bath at 25°C. The two distinct ranges result from the fact that Fe(III) hydroxide precipitates at a pH of about 3.5, whereas Fe(II) hydroxide precipitates at a pH of about 6. In the low-pH range, even in a well-reduced bath, some Fe(III) ion is present because of air oxidation; therefore, operation at a pH too close to 3.5 results in dark-colored, excessively stressed deposits, probably caused by inclusion of basic Fe(III) salts in the deposits. Operation at a pH below the recommended minimum for the low pH-range results in lower cathode efficiency and increased deposit stress.

In the high-pH range a very low concentration of Fe(III) ion is automatically maintained [equal to the solubility of Fe(III) hydroxide], because the pH is above that at which Fe(III) hydroxide precipitates. The bath in this pH range therefore tends to be “sludgy.” The sludge does not cause significant roughness of deposits up to a few tens of micrometers in thickness, but if heavy deposits are to be produced, filtration may be required. The high-pH sulfate bath has better covering power and yields deposits that are less stressed than those from the low-pH bath. Deposits with minimum stress are obtained at pH value in the range 4.0–5.0. The internal stress of the deposit generally increases with the increase in current density.

At the higher operating temperatures, sludging due to air oxidation is rapid at high pH. Therefore only the lower pH range is recommended for operation at elevated temperatures. The advantage of an elevated temperature is the higher permissible current density. The disadvantages of operating

at temperature higher than about 60°C probably outweigh any gain in permissible current density. Deposits from the sulfate bath do not become significantly ductile even if the bath is operated at the boiling point.

11.3 FERROUS CHLORIDE BATH

The important and distinctive characteristics of the chloride baths is that they permit high current density or fast deposition rates and yield ductile deposits when operated at temperatures higher than about 85°C. The most commonly used bath is a solution of Fe(II) and calcium chlorides, which has been referred to as the Fischer–Langbein solution [46]. This bath yields dark-colored, hard, highly stressed deposits at 25°C. At increasingly higher temperatures, the deposits gradually become lighter colored.

The composition of the Fischer–Langbein solution as modified by Thomas and Blum [7] and that modified in industrial use [47] are shown in Table 11.1. The lower concentrations introduced by Thomas and Blum permit the use of moderate current densities and do not lead to crystallization of the salts when the bath is cooled. The presence of calcium chloride in the hot-chloride bath leads to increases in bath conductivity and cathode efficiency and does not appear to have significant effects on the structure and physical properties of deposits [48]. The importance of the hygroscopic character of calcium chloride in reducing evaporation of

water from this type of bath and in raising boiling point seems overstressed in the literature [46]. Elimination of calcium chloride from the bath permits the use of higher ferrous chloride concentrations with resultant higher operable current densities. For rapid deposition at current density as high as 40 Adm^{-2} , a solution of ferrous chloride alone has been used at concentration from 120 to 150 g L^{-1} as Fe^{2+} [22]. For lower stressed deposits, concentrations as high as 725 g L^{-1} $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ have been used [49].

Numerous modifications of the hot-chloride bath have been described in which calcium chloride has been replaced by other alkaline earth chlorides [1, 50]. The presence of a low concentration of Mn(II) chloride has been claimed to result in deposits of finer grain size [51], and a bath containing a large amount of this salt has been recommended for plating machine parts [52]. The presence of AlCl_3 , BeCl_2 , or CrCl_2 in low concentration has been reported to render deposit that is softer and more ductile [53]. The presence of 20–100 g L^{-1} AlCl_3 has been claimed to produce better stability [54]. The maintenance of a small concentration of Fe(III), up to about 0.5 g L^{-1} , has been stated to result in better throwing power [55] and in the elimination of pitting [16]. The presence of Fe(III), however, causes deposits to be harder, less ductile, and more highly stressed than those from well-reduced baths. From the bath with concentration ratio of Fe(III) to Fe(II) below 0.09, a deposit with good quality is produced [21]. The internal stress increases with the increase in the current density or with the decrease in the

TABLE 11.1 Composition and Operating Conditions for Iron Plating Baths

Type of Solution	Composition	Operating Conditions
Sulfate	$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$: 250–300 g L^{-1}	Low pH 2.8–3.4 or high pH 4.0–5.5, 2 A dm^{-2} , 25°C pH 2.1–2.4, 4–10 A dm^{-2} , 60°C
For production of strip Chloride (Fischer–Langbein)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$: 250 g L^{-1} $(\text{NH}_4)_2\text{SO}_4$: 120 g L^{-1} $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$: 600 g L^{-1} $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$: 300 g L^{-1} CaCl_2 : 335 g L^{-1} $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$: 300–450 g L^{-1} CaCl_2 : 150–190 g L^{-1}	pH 1.4, 6.7 A dm^{-2} , 47°C pH 0.8–1.5, 6.5 A dm^{-2} , 90°C pH 0.2–1.8, 2–9 A dm^{-2} , 88–99°C
For electrotype	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$: 240 g L^{-1} KCl: 180 g L^{-1}	pH 5–5.5, 2–5 A dm^{-2} , 25–40°C
For production of strip	Ferrous chloride: 120–150 g L^{-1} as Fe^{2+}	pH 0.5–4.7, 33–40 A dm^{-2} , 98–106°C
Sulfate–chloride, for electrotype	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$: 250 g L^{-1} $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$: 42 g L^{-1} NH_4Cl : 20 g L^{-1}	pH 3.5–5.5, 5–10 Adm^{-2} , 40–43°C
For production of strip	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$: 500 g L^{-1} NaCl: 50 g L^{-1}	pH 2.5, 3–27.5 A dm^{-2} , 80°C
Sulfamate	Iron(II) sulfamate: 250 g L^{-1} Ammonium sulfamate: 30 g L^{-1}	pH 3.2–15 A dm^{-2} , 50–70°C
Fluoborate	$\text{Fe}(\text{BF}_4)_2$: 226 g L^{-1} NaCl: 10 g L^{-1}	pH 2–3, 2–10 A dm^{-2} , 55–60°C

bath temperature. The deposit with excellent ductility is obtained at higher temperature, lower pH, and high current density.

11.3.1 Fluoborate Bath

Iron plating from fluoborate solution is not new, but since a variety of fluoborate salts became commercially available, interest in their use in plating was stimulated, and several Fe(II) fluoborate baths have been described [56–60]. The composition shown in Table 11.1 has been recommended for plating stereotypes [56] and is probably satisfactory for general-purpose baths. A bath prepared from the commercially available concentrated solution will contain a small excess of fluoboric and boric acids, which are present in the concentrate. The boric acid probably has a desirable buffering action. In the iron fluoborate bath described by Kudryavtsev and Mel'nikova [59] the recommended concentration of boric acid is 18 g L^{-1} . Fluoboric acid may be used to adjust the pH.

The fluoborate bath has good stability, high conductivity, and high tolerance to metallic impurities. The disadvantage of the bath is that it is more expensive than chloride or sulfate bath. The fluoborate bath yields deposits similar in brittleness and in most other properties to those from the sulfate bath.

11.3.2 Other Baths

Solution Used for Iron Electrotypes The two baths listed in Table 11.1 were developed for making iron electrotypes [8, 9]. Although the ferrous chloride–potassium chloride bath appears to be similar to the Fischer–Langbein type, it differs from the latter in performance in yielding light-gray, stress-free deposits at 25°C . The deposits are, however, brittle. This difference in performance appears to be caused specifically by the potassium ion. The sulfate–chloride bath yields brittle deposits that are under moderate stress. It has somewhat better “covering power,” which is improved by the presence of ammonium ion, as is also the case with nickel electrotyping solutions. Both iron plating solutions operate satisfactorily at higher temperatures than are shown in the table. The upper limits of temperature were imposed because of the low softening points of wax or plastic electrotype molding media.

Solution Used for Production of Iron Strip The three baths of simple sulfate [61], chloride [22, 62], and sulfate–chloride bath [63] listed in Table 11.1 have been developed for production of continuous iron strip. These baths contained ferrous salts at higher concentration than those for rack operation and generally operated at higher current density, higher bath temperature, and higher flow rate of the solutions by using a special electrolytic cell which will be mentioned

later in this chapter. Chloride bath is favorable for this purpose because of the allowance of higher current density as high as 100 A dm^{-2} at which satisfactory deposit was obtained. A mixed fluoborate–sulfamate Fe(II) electrolyte has been used by Levy and Hutton for the deposition of high-strength iron strips [64].

Other Special-Purpose and Less Common Baths Many iron plating baths based on unusual salts or special formulations for specific purposes have been described.

Good performance was claimed by Piontelli [65], Barrett [66], Ueno [67], and Lowrie [47] for Fe(II) sulfamate baths. Current densities up to 10 A dm^{-2} and cathode efficiency up to 96% were described by Misra and Rama Char [68] in a bath containing Fe(II) sulfamate and ammonium sulfamate. The effectiveness of saccharin addition to decrease internal stress was mentioned in sulfamate–ammonium fluoride acidic bath [67]. Iron sulfamate in the concentrated solution is available commercially.

An iron bath of a mixed chloride–sulfate type containing boric acid and sodium formate has been recommended for depositing a starting plate on active basis metals such as aluminum, beryllium, or uranium [69] and for applying an intermediate layer of iron between steel and electrodeposited antimony deposit [70].

Two types of alkaline iron plating baths have been described. In one, Fe(III) is complexed with triethanolamine and ethylenediaminetetraacetic acid [71, 72]. In the other, the main constituent of the bath is Fe(III) pyrophosphate [73]. Only thin deposits have been reported from these baths. Both suffer from the disadvantage that iron does not dissolve in them anodically. Other baths based on complexes of Fe(III), such as oxalate or citrate, have been described [74]; this type of bath, however, is useful primarily for electroanalysis rather than for electroplating.

Iron powder obtained by electrodeposition is used commercially. Conditions for depositing iron in powder form have been defined by several authors [75–78]. The bath described in [76] is unusual in that it consists of an aqueous solution of Fe(III) oxide and sodium hydroxide, in which the iron is probably present as sodium ferrate. Procedures for producing iron powders by crushing brittle deposits were reviewed by Shafer and Harr [11], who report that sintered parts made from electrolytic iron powder have higher density and better physical properties than those made from nonelectrolytic powders.

The electrodeposition of binary and ternary iron alloys has been reviewed in several articles [79–82]. Twenty-two elements, including carbon, have been electrodeposited with iron. Electrochemical investigations of anomalous deposition behavior in iron alloy systems have been discussed in many papers [83–86]. The bath composition and operating conditions for the production of iron alloy deposits are presented in Table 11.2.

TABLE 11.2 Bath Composition and Operating Conditions of Iron Alloy Plating

Alloy	Purpose and Reference	Bath Composition	Operating Conditions	Characteristics
Iron-nickel	Decorative [88]	NiSO ₄ ·6H ₂ O: 150 g L ⁻¹ NiCl ₂ ·6H ₂ O: 90 g L ⁻¹ FeSO ₄ ·7H ₂ O: 20 g L ⁻¹ H ₃ BO ₃ : 45 g L ⁻¹ Stabilizer and brightener Nickel sulfate: 16 g L ⁻¹ Nickel chloride: 40 g L ⁻¹ Ferrous sulfate: 1 g L ⁻¹ Boric acid: 25 g L ⁻¹ Sodium saccharin: 0.375–3 g L ⁻¹ Sodium lauryl sulfate: 0.2 g L ⁻¹ Nickel sulfamate: 0.75 mol L ⁻¹ Ferrous chloride: 0.25 mol L ⁻¹ Boric acid: 0.5 mol L ⁻¹ Sodium dodecyl sulfate: 0.5 g L ⁻¹ Ascorbic acid: 1 g L ⁻¹ Saccharin: 2 g L ⁻¹	60°C, pH 3.5, 4 A dm ⁻²	Fe–50%Ni, hardness: 508 Knoop
	Magnetic [37]		26°C, pH 2.5, 1.5 A dm ⁻²	Fe–80%Ni (705 nm thick), Hc: 0.25 Oe
	Invar [97]		50°C, pH 2.5, 10 A dm ⁻²	Fe–39%Ni: thermal expansion coefficient of 8.1 × 10 ⁻⁶ /°C, 4–5 × 10 ⁻⁶ /°C (after annealing at 680°C)
	Invar [99]		50°C, pH 2.5, 4 A dm ⁻²	Fe–42%Ni: thermal expansion coefficient of 6.6 × 10 ⁻⁶ /°C, 6.1 × 10 ⁻⁶ /°C (after annealing at 680°C)
Iron-zinc	Corrosion protection [40]	FeSO ₄ ·7H ₂ O + ZnSO ₄ ·7H ₂ O: 500 g L ⁻¹ Na ₂ SO ₄ : 30 g L ⁻¹ CH ₃ COONa·3H ₂ O: 20 g L ⁻¹ C ₆ H ₈ O ₇ : 5 g L ⁻¹ Ferrous chloride: 0.8 mol L ⁻¹ Zinc chloride: 0.8 mol L ⁻¹	50°C, pH 2.5, 3 A dm ⁻²	
	Corrosion protection [121]	Ammonium chloride: 100 g L ⁻¹ ZnO: 0.15–0.4 mol L ⁻¹ Ferrous gluconate: 0.05–0.075 mol L ⁻¹ KOH: 6.6 mol L ⁻¹	50°C, pH 2.5, ~4 A dm ⁻²	
	Corrosion protection [122]		25°C, pH > 14, 50–800 mA cm ⁻²	

(continued)

TABLE 11.2 (Continued)

Alloy	Purpose and Reference	Bath Composition	Operating Conditions	Characteristics
Iron-platinum	Magnetic [120]	FeCl ₂ : 0.11 mol L ⁻¹ PtCl ₂ : 0.3–30 mmol L ⁻¹ NaCl: 0.5 mol L ⁻¹	20°C, pH 2.5, -0.4 to -0.8 V (SCE)	L1 ₀ -FePt
Iron-cobalt	Antifriction [115]	FeCl ₂ : 227 g L ⁻¹ CoCl ₂ ·6H ₂ O: 8 g L ⁻¹ H ₃ BO ₃ : 10 g L ⁻¹ NH ₄ Cl: 75 g L ⁻¹ NaCl: 75 g L ⁻¹ NH ₄ BF ₄ : 10 g L ⁻¹ CoSO ₄ ·7H ₂ O: 0.10 mol dm ⁻³ CoCl ₂ ·6H ₂ O: 0.10 mol dm ⁻³ FeSO ₄ ·7H ₂ O: 0.02 mol dm ⁻³ H ₃ BO ₃ : 0.50 mol dm ⁻³ NH ₄ Cl: 0.50 mol dm ⁻³	50°C, pH 1, 5–40 A dm ⁻²	Fe-6%Co, hardness: 640 Vickers
	Magnetic [106]	NiSO ₄ ·6H ₂ O: 0.005–0.045 mol dm ⁻³ Cobalt sulfate: 0.03–0.0875 mol dm ⁻³ Nickel sulfate: 0.2 mol dm ⁻³ Ammonium chloride: 0.28 mol dm ⁻³ Boric acid: 0.4 mol dm ⁻³	40°C, pH 2.9, 1.5 A dm ⁻²	Heating under 2 kOe Co ₉₃ Fe _{5,5} , Bs: 1.6 T, Hc: 0.5 Oe
Iron-cobalt-nickel	Magnetic [115]	Sodium lauryl sulfate: 0.01 mol dm ⁻³ CoSO ₄ ·7H ₂ O: 0.01–0.05 mol L ⁻¹ NiSO ₄ ·6H ₂ O: 0.2 mol L ⁻¹ FeSO ₄ ·7H ₂ O: 0.01–0.05 mol L ⁻¹ H ₃ BO ₃ : 0.4 mol L ⁻¹	20°C, pH 2.5–3.0, 3–20 mA cm ⁻²	Co ₆₅ Ni ₁₂ Fe ₂₃ , Bs: 2.1 T, Hc: 1.2 Oe, permeability: 600 at 1 MHz, ρ: 21 μΩ-cm
	Magnetic [116]	Iron(II) sulfamate: 0.5 mol L ⁻¹ Cobalt(II) sulfamate: 0.5–0.75 mol L ⁻¹ Ammonium metavanadate: 0.4 mol L ⁻¹ Boric acid: 0.4 mol L ⁻¹ Sodium borate: 0.25 mol L ⁻¹ L-ascorbic acid: 0.025 mol L ⁻¹ Saccharin: 1 g L ⁻¹ Surfactant: 0.5 vol %	25°C, pH 2–3.5, 5–50 mA cm ⁻²	Electrodeposition under 600 Oe, Bs: 2.15 T, Hc: 1 Oe, permeability: 200 at 1 GHz, fr: 1.85 GHz, ρ: 50 μΩ-cm
Iron-cobalt-vanadium	Magnetic [118]	K ₂ Cr ₂ (SO ₄) ₄ ·25H ₂ O: 326 g L ⁻¹ Nickel sulfate: 84 g L ⁻¹ Ferrous sulfate: 56 g L ⁻¹ Glycine: 150 g L ⁻¹	45–55°C, P H3.0, 40 mA cm ⁻²	Fe52.3Co46.5V1.2, Bs: 2.2 T, Hc: 6Oe
Iron-chromium-nickel	Corrosion protection [142]		20°C, pH 2–2.2, 8.5 A dm ⁻²	9.8–11%Cr, 7.3–6%Ni

Iron-phosphorus	Corrosion protection [123]	Fe Cl ₂ :4H ₂ O: 240 g L ⁻¹ KCl: 180 g L ⁻¹ Hypophosphorus acid FeSO ₄ :7H ₂ O: 1.0 mol L ⁻¹ (NH ₄) ₂ SO ₄ : 0.1 mol L ⁻¹ C ₆ H ₇ O ₆ : 0.1 mol L ⁻¹ NaH ₂ PO ₂ H ₂ O: 0.01 mol L ⁻¹	40°C, pH 2, 40 A dm ⁻²	Fe-0.4%P
	Magnetic [124]	FeSO ₄ :7H ₂ O: 0.07 mol L ⁻¹ KBH ₄ : 0.3 mol L ⁻¹ KNaC ₄ H ₄ O ₆ :4H ₂ O: 0.6 mol L ⁻¹ (NH ₄) ₂ SO ₄ : 0.08 mol L ⁻¹ NaOH: 0.4 mol L ⁻¹	25°C, pH 2.5, 1 A dm ⁻²	Fe-6%P, Hc: 20e
Iron-boron	Magnetic [126]	FeSO ₄ :7H ₂ O: 0.07 mol L ⁻¹ KBH ₄ : 0.3 mol L ⁻¹ KNaC ₄ H ₄ O ₆ :4H ₂ O: 0.6 mol L ⁻¹ (NH ₄) ₂ SO ₄ : 0.08 mol L ⁻¹ NaOH: 0.4 mol L ⁻¹	30°C, pH 12.5, 1 A dm ⁻²	Fe-8%B, Hc: 3.60 e, saturation magnetostriktion: 27 × 10 ⁻⁶
Iron-carbon	Antifriction [132]	FeSO ₄ :7H ₂ O: 40 g L ⁻¹ L-ascorbic acid: 3.0 g L ⁻¹ Citric acid: 1.2 g L ⁻¹	50°C, pH 2.5, 3 A dm ⁻²	Fe-1%C, hardness: 800 Vickers
Iron-carbon-boron	Antifriction [134]	Fe Cl ₂ :4H ₂ O: 1.0 mol L ⁻¹ Malic acid: 5 mmol L ⁻¹ Boric acid: 0.65 mol L ⁻¹ Dimethylamineborane: 50 mmol L ⁻¹	50°C, pH 3.5, 5 A dm ⁻²	Fe-0.2%C-0.11%B, hardness: 700 Vickers, KIc: 1400 N mm ^{-3/2}
Iron-carbon-phosphorus	Antifriction [135]	Iron(II) chloride: 0.15 mol L ⁻¹ Citric acid: 6.2 mmol L ⁻¹ L-ascorbic acid: 1.7 mmol L ⁻¹ Phosphinic acid: 0.15 mol L ⁻¹	50°C, pH 3.5, 30 mA cm ⁻²	Fe-1.1%C-7%P, Hardness: 6700 Vickers, KIc: 400 kg mm ^{-3/2}

Note: Bs: magnetic flux density, Ms: saturation magnetization, Hc: coercive force.

The greatest interest in iron binary alloys in recent years, as indicated by the number of publications, has been in iron–nickel alloy plating. Iron–nickel alloy deposit is favorable to decorative and protective deposit as undercoats of thin chromium deposit, because the operating costs can be reduced to a level lower than that required for nickel plating [87, 88]. The alloy deposits are used for appliance hardware, tubular furniture, plumbing goods, jewelry, and wire products. Most baths used for decorative nickel–iron alloy plating contain nickel sulfate, nickel chloride, ferrous sulfate, boric acid, and a brightener as well as a hydroxycarboxylic acid stabilizer, such as citric acid, to prevent the oxidation of ferrous ions. Saccharin or specific aromatic sulfonamides are used as primary brighteners and give codeposition of sulfur in the deposits. Heterocyclic amine, nitrils, and secondary acetylenic alcohol have been used as secondary brighteners. These brighteners tend to increase the stress and hardness. A nickel content ranging from 10 to 45% has no detrimental effect on brittleness, leveling characteristics, or subsequent chromium plating. Bath temperature, ferric ion concentration, and the buffering ability of the added stabilizer affect the leveling and cathode efficiency. Alloy deposits have been used as replacements for bright nickel in mild or moderate service conditions since the corrosion protection of the alloy deposits is equivalent to that of comparable nickel/chromium deposits [88, 89].

Iron (4–10%)–nickel alloy deposits have been used for the inner surface coatings of continuous casting molds to prolong mold life, to improve product quality, and to reduce the running cost. The same is true of other coatings of chromium plating, thick and tapered nickel coating, and multiple-layer coatings of nickel/nickel–phosphorus/chromium plating [90]. Alloy deposits have twice the hardness and half the elongation of nickel plating and the same thermal expansion coefficient as the copper mold base. One paper mentioned that iron–nickel alloy deposits prolong mold life to about 1.2–1.7 times that attained with nickel plating or multiple-layer coating [91].

Iron (20%)–nickel alloy (Permalloy) deposits have been the subject of considerable interest for their use in magnetic devices such as thin-film recording heads, magnetic yokes in printer heads, bubble memories, shielding, logic devices, and magnetic cores in microsolenoids because of their magnetic flux density of 1.6 T [92, 93]. When employed for discrete elements, they are frequently deposited as a full film and the magnetic pattern is then defined with an etch resist [94]. One paper mentioned a micromachining technique for producing a microcantilever, three-dimensional microcoil with an integrated magnetic core, a magnetically driven microvalve, and a microturbine using an electroforming technique of iron–nickel alloy deposits [95]. The bath compositions and operating conditions for the production of magnetic iron–nickel alloy plating were surveyed in literature [96] and are presented in Table 11.2. The deposition of an iron–39% nickel alloy with a low expansion coefficient (Invar) was

achieved from a sulfamate bath [97] and has been discussed for use of waveguides [98]. The linear expansion coefficient depends on the Fe content and heating conditions after electrodeposition. Coefficients close to that of the bulk material have been reported for iron–42% nickel alloy deposits heated at 600°C [99]. An active area of research in iron–nickel alloy deposits centers on the improvement of magnetic properties by codeposition of a third element such as phosphorous [100], arsenic [101], sulfur [102], molybdenum [103], copper [104], cobalt [105–108], chromium [109], or indium [110]. Another active area centers on developing techniques to control the composition so that it stays within a tighter range. Most baths used for this purpose contain saccharin, which results in a decrease in grain size and coercive force [96]. Permalloy deposits with a coercive force below 1 Oe [37], which is lower than that of iron deposits, is obtained. The effects of current waveforms, such as a pulsating current, a reversing current, or a sinusoidal alternating current superimposed on a direct current, on the cathode efficiency, composition, or phase structure of the alloy deposits have been mentioned in the literature [111–114].

Iron–cobalt–nickel alloy electrodeposits have attracted increasing attention for their use in magnetic applications, such as magnetic recording heads, micro–magnetic actuators, and thin–film inductors, because of their magnetic characteristics. A systematic study on the relationships between the composition, phase structure, and magnetic characteristics of coercive force for iron–cobalt–nickel ternary alloy electrodeposits was carried out in 1998 [115], and the alloy composition and plating conditions required to get the magnetic and electrical characteristics appropriate for a magnetic recording head application have been found. High magnetic flux density of 2.1 T, low coercive force of 1.2 Oe, permeability of 600 at a frequency of 1 MHz, and resistivity of 21 $\mu\Omega\text{-cm}$ were obtained for a $\text{Co}_{65}\text{Ni}_{12}\text{Fe}_{23}$ alloy electrodeposited from an electrolyte containing an organic compound but without any sulfur-containing additives. Body-centered cubic (bcc) and face-centered cubic (fcc) lattices and mixtures of the two are formed in this alloy system. It was pointed out that the relationships between the composition, phase structure, and magnetic characteristics of coercive force strongly depend on the content of sulfur originating from the sulfur-containing additives in the electrolyte. Great success in using iron–cobalt–nickel alloy electrodeposits as magnetic recording heads in magnetic storage systems has been achieved in Japan. An iron–cobalt–nickel alloy electrodeposited from an electrolyte not containing any organic compounds, including sulfur-containing additives, showed a high magnetic flux density of 2.15 T, a low coercive force of around 1 Oe, a resonance frequency of 1.8 GHz, a real permeability of around 1000, and a resistivity of 50 $\mu\Omega\text{-cm}$ [116]. A giant magnetoresistance (GMR) of about 4.5% has been reported for iron–cobalt–nickel/copper multilayered electrodeposits [117].

Iron–cobalt–vanadium alloy electrodeposits with a magnetic flux density of 2.2 T and a coercive force of 6 Oe have been reported, and research on this alloy system has been seen in the last decade [118, 119]. The plating of iron–platinum alloys with an $L1_0$ ordered structure has attracted increasing attention for its use in high-density perpendicular recording media as well as cobalt–platinum alloy [120].

The production of iron–zinc alloy deposits was one of the most important developments for the corrosion protection of iron-based materials [38, 121, 122]. Iron(0.2–0.5%)–zinc alloy plating is conducted by rack-and-barrel operations [39]. Single-layer deposits of iron (15–25%)–zinc alloys have been used commercially in Japan for the inside surfaces of fenders, doors, trunk lids, and other unexposed automotive body parts because of their good weldability, formability, and corrosion resistance after painting [40]. Iron–rich iron–zinc alloy deposits with an iron concentration exceeding 40% have been used for upper layers on zinc-rich iron (20%)–zinc or zinc–nickel alloy deposits to give good corrosion resistance since the deposits have good paint adhesion and compatibility with cationic electropainting [40].

For several years, iron–0.4% phosphorus alloy plating has been used for upper layers on zinc–iron or zinc–nickel alloy deposits to enhance the paintability and phosphatability of steel strips used for automotive body parts in Japan [123]. Amorphous iron–phosphorus alloy plating with a phosphorus concentration exceeding 6% is under industrial evaluation for use in soft magnetic materials because of its low coercive force and high magnetic flux density [124, 125]. Details on a bath formulation procedure used to obtain an amorphous iron–8% boron alloy were published in 1998 [126]. Iron–boron alloy plating is under industrial evaluation for use in strain sensors and microcantilevers because of its very large magnetomechanical coupling factor, large magnetostriction, and high permeability [127].

A 1983 patent mentioned the electrodeposition of low-stress, hard iron–6% cobalt alloy deposits produced from a chloride bath with a high cathode efficiency of 96% [128].

Attempts to produce steel by co-depositing carbon in iron deposits and then performing heat treating were reported even in the early literature on iron plating. A bath reportedly used for this purpose consists of a hot ferrous chloride solution containing a relatively high concentration of glycerol, sugar, or starch [129]. Deposits are described that contain 0.7% carbon and have a hardness of 477 Brinell after heat treatment. Details on a bath formulation procedure used to obtain hard iron–1% carbon alloy deposits at a high current efficiency of above 70% were published in 1989 [130]. The bath was a ferrous sulfate solution containing small amounts of carboxylic acids as a carbon source and L-ascorbic acid to prevent the oxidation of ferrous ions in the solution. Deposits with carbon contents of 0.13, 0.56, 0.6, and 1% were obtained with oxalic, succinic, malic, and citric acids, respectively [131]. The cathode efficiency varied in the

range 70–90% according to the added carboxylic acids. The iron–carbon alloy deposits with a carbon concentration exceeding 1% had a black and bright appearance and exhibited a high hardness of above 800 Vickers [132, 133]. Oxygen incorporated in iron–carbon alloy deposits adversely affected the mechanical properties, especially toughness. The oxygen content depended on the plating conditions and the added carboxylic acid. The addition of reducing agents such as dimethylamineborane (DMAB) [134] and hypophosphorus acid [135] is effective for decreasing the oxygen content to a harmless level. Iron–carbon–boron and iron–carbon–phosphorus alloy electrodeposits prepared under optimized conditions exhibited a high hardness of HV 800 and improved toughness as estimated from the stress intensity factor. Iron–carbon alloy deposits have been under industrial evaluation for use as hard coating or alternatives to thermal surface hardening materials such as carburizing or nitriding steels because of their comparable hardness and lower levels of thermal distortion [136, 137].

One area of activity centers on attempts to electrodeposit iron–nickel–chromium alloys; electrolytes for producing stainless steel deposits for decorative or corrosion-resistant coating [138–142] are described. The alloy deposits obtained contain chromium and nickel at concentrations that vary in the ranges 2.9–29% and 8–54%, respectively, according to the type of bath and operating conditions. In general, the deposits are highly stressed and are limited to a thickness of less than 30 μm . Cathode efficiency is generally low (18–35%) [142]. Cathode efficiency rapidly drops and deposit quality deteriorates with the passage of deposition time. A paper mentioned that iron–18% chromium–8% nickel alloy deposits with a high current efficiency of 60% exhibited ferro magnetic characteristics and poor corrosion resistance [143], which differs from thermally prepared stainless steel. Amorphous iron–chromium–nickel–phosphorus–carbon alloy deposits with good corrosion resistance have been described in the literature [144]. Most baths used for iron–chromium–nickel alloy plating contain glycine, which acts not only as a pH buffer but also as a complexing agent and prevents the codeposition of basic salts.

11.4 IRON OXIDES

There has been much activity in the development of iron oxide plating for magnetic and electronic applications in the last decade. The bath composition, operating conditions, and characteristics for iron oxide deposits are presented in Table 11.3. Several types of plating processes have been developed to form iron oxides of magnetite (Fe_3O_4) and hematite ($\alpha\text{-Fe}_2\text{O}_3$). In 1984, a ferrite plating process used to form magnetite with ferromagnetic features was reported in Japan [145] and was expanded to ferrite ($\text{M}_x\text{Fe}_{3-x}\text{O}_4$, M: nickel, zinc, cobalt, manganese) [146] and garnet

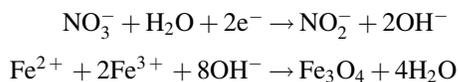
TABLE 11.3 Bath Composition and Operating Conditions of Iron Oxide Plating

Oxide	Purpose References	Bath composition	Operating conditions	Characteristics
Magnetite (Fe ₃ O ₄)	Magnetic [145]	FeCl ₂ : 1–2 mmol L ⁻¹ Air bubbling	70°C, pH 7.4	Hc: 200 Oe
	Magnetic [151]	Iron(III) nitrate: 0.01 mol L ⁻¹ Dimethylamineborane: 0.03 mol L ⁻¹	60°C, pH 2.5, –0.6 to –1.4 V (Ag/AgCl)	Ms: 320 emu/cc, Hc: 80 Oe
	Magnetic [150]	K(CH ₃ COO): 0.04 mol L ⁻¹ Fe(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O: 0.01 mol L ⁻¹	90°C, pH 6.5, –0.4 V (Ag/ AgCl)	[110]Fe ₃ O ₄ /[110] Au
Hematite (α-Fe ₂ O ₃)	Semiconductor [154]	FeCl ₃ : 5 mmol L ⁻¹ KF: 5 mmol L ⁻¹ H ₂ O ₂ : 1 mol L ⁻¹ KCl: 0.1 mol L ⁻¹	50°C, pH 2.5, –0.9–0 V (SMSE)	Bandgap: 2.2 eV (after heating at 500°C)
Zn–Fe–O	Magnetic [157]	Zinc sulfate: 1 mmol L ⁻¹ Ferrous sulfate: 10 mmol L ⁻¹	27°C, pH 4.3–4.8, –0.9 V	αFe–ZnO, Hc: 25 Oe (300 K)
Fe–Ce–O	Magnetic [158]	FeSO ₄ : 10–40 mmol L ⁻¹ CoCl ₃ : 4 mmol L ⁻¹ L-ascorbic acid: 1.1–4.5 mmol L ⁻¹ NH ₄ SO ₄ : 4 mmol L ⁻¹ (NH ₄) ₂ SO ₄ : 10 mmol L ⁻¹	60°C, –4 mA cm ⁻²	Ms: 160 emu/cc, Hc: 50 Oe

(Y₃Fe₅O₁₂) [147]. A nickel–zinc ferrite layer prepared with the ferrite plating process is under evaluation for use in an electromagnetic noise suppressor for printed circuit boards [148] because of its high permeability of 40 at a frequency of 1 GHz and resonance frequency of 1.2 GHz [149]. The ferrite plating process consists of the oxidation of Fe(II) ions adsorbed on substrates. The electroplating of magnetite is classified into two different processes of anodic and cathodic depositions in electrolytes containing Fe(II) ions. The ferrite plating process is classified as anodic deposition, where the magnetite is synthesized by the oxidation of Fe(II) ions adsorbed on the conductive substrate, as represented by the potential–pH diagram [150]:



An alternative method is cathodic deposition in an electrolyte containing Fe(II) and nitrate ions [151]. Oxygen sources such as nitrate ions and molecular oxygen are indispensable for forming oxides. The deposition reaction with the nitrate ions is believed to be as follows [152]:



The magnetite layer deposited by cathodic deposition exhibits a saturation magnetization of 0.61 T and a coercive force of 11.9 kA m⁻¹. A magnetite layer with almost the same magnetic characteristics can be obtained from the same solution without any external power supply, that is, by chemical deposition [152].

A plating of hematite (α-Fe₂O₃) has been developed, but heating at around 500°C is needed to form the crystalline oxide [153, 154]. Platings of zinc–iron oxide (zinc-doped magnetite and iron-doped zinc oxide) and iron–cerium oxide have been reported in the last decade [155–157]. Zinc-doped magnetite (Zn_{0.16}Fe_{2.84}O₄) exhibits excellent high-frequency characteristics, with a resonance frequency of 600 MHz and a permeability of 400 [158]. Iron-doped zinc oxide is a transparent semiconductor with room temperature ferromagnetic features, and the heated oxide layer exhibits a magnetoresistance of 0.4% at room temperature [159].

11.5 PREPARATION, MAINTENANCE, AND CONTROL

Commercial Fe(II) salts, and even reagent-grade salts, are likely to contain a significant amount of Fe(III). Therefore, it is usually necessary to reduce the Fe(III) ion before using a freshly prepared bath. This is done by adding degreased iron turnings or steel wool to the bath together with sufficient acid to lower pH to about 0.5 (sulfuric or hydrochloric acid for the sulfate or chloride bath). The reduction treatment requires 24–48 h, during which further addition of acid may be required to maintain a low pH. Alternatively, the iron(III) may be reduced by dummieing the bath at a low pH. Completion of a reduction treatment is indicated by the color of the solution, which should be a clear green, free from any yellow tint.

An operating bath, if used steadily, remains fully reduced as a result of cathodic reduction of Fe(III). If a bath is idle,

maintenance of a small excess of acid helps to prevent oxidation. Since excess acid is rapidly depleted by reaction with anodes, the anodes should be removed from a bath that will be idle more than a day or so. Cubes of gum rubber floating on the surface of the bath reduce oxidation, conserve heat, and limit evolution of spray [160]. Expanded polyethylene chips or hollow balls of polypropylene serve the same purpose and are most useful for hot plating baths. For several applications such as production of iron or iron alloy plated steel strips and electroplating of magnetic iron–nickel alloy (Pearmalloy) deposit, an anion exchange membrane [161] or regeneration tank [162] has been employed to keep ferric ion concentration below desirable level.

11.5.1 Impurities

Iron baths are similar to nickel baths in that small amounts of metallic and organic impurities may cause deposits to be brittle, stressed, or pitted. Therefore, a freshly prepared bath requires purification, which is best performed after the mentioned reduction treatment. Organic impurities are removed by adsorption on activated carbon, and the carbon is removed by filtration. If the pH of the solution during treatment with carbon is adjusted to 5.0–5.5, contaminant metals that precipitate as hydroxide in this pH range are also removed. The pH may be adjusted by adding sodium, potassium, or ammonium hydroxide or by suspending Fe(II) carbonate in the bath. High-pH treatment is not recommended for the more concentrated chloride and fluoborate baths in that rapid oxidation of Fe(II) occurs with subsequent precipitation of Fe(III) hydroxide. Metallic impurities such as copper, lead, and nickel are removed by dummying the bath at an average cathode current density of 0.5 A dm^{-2} with a corrugated cathode. Details of these procedures are similar to those described for purifying nickel baths, with the notable exception that hydrogen peroxide or other oxidizing agents often added to nickel baths during treatment with activated carbon must not be added to an Fe(II) solution.

Not much is known concerning effects of specific impurities. It was found that more than 0.2 g L^{-1} zinc in the Fe(II) chloride–potassium chloride electrotyping bath causes no harm in the hot-chloride bath [51], and iron–zinc alloy can be produced from sulfate baths [163, 164]. Low tolerance limits have been reported for copper lead, arsenic, tin, and molybdenum in the hot-chloride bath [51]. Copper at a concentration of 0.2 g L^{-1} in the hot-chloride bath has been reported to cause spongy roughness in areas where the current density is high and to decrease ductility [17]. Experience with the hot-chloride bath indicates that copper or lead concentrations above 0.1 g L^{-1} and nickel or cobalt concentrations above 0.2 g L^{-1} may result in roughness and poor throwing power in low-current-density areas ($<2.5 \text{ A dm}^{-2}$). In a sulfamate-ammonium fluoride bath, zinc ($>0.1 \text{ g L}^{-1}$), stannous (0.1 g L^{-1}), and manganese ($>0.5 \text{ g L}^{-1}$) increase the inter-

nal stress and chromium and copper ($>1 \text{ g L}^{-1}$) gave black deposit with rough surface [67]. In general, continuously worked baths tend to remain free of impurities in harmful amounts but occasionally may require treatment for reduction or purification, as already described.

11.5.2 pH

As indicated in the discussion of the various baths, control of pH is essential. The pH can be measured most conveniently with a glass electrode. When operated at pH below 3.5, the acid content of the bath is slowly depleted, because the anode efficiency is higher than the cathode efficiency: 100% and 80–99%, respectively. It is therefore necessary to add the appropriate acid to maintain the pH.

In the high-pH range, both anode and cathode efficiencies are close to 100%. Air oxidation of Fe(II), however, followed by precipitation of Fe(III) hydroxide results in a decrease in pH; it may be maintained by adding the appropriate hydroxide (KOH or NH_4OH). Iron(II) carbonate suspended in the bath has been used to control the pH in this range.

11.5.3 Surfactants

Although a highly purified and well-worked iron bath does not usually yield pitted deposits, pitting is sometimes encountered. Use of a wetting agent tends to increase deposit stress, but it may be helpful if used judiciously. Sodium lauryl sulfate has been reported by several authors to be a suitable wetting agent and seems to be compatible with all types of iron and iron–nickel plating solutions. The addition of 1 g L^{-1} of a condensate of sodium naphthalene sulfonate and formaldehyde to the Fe(II) chloride bath is reported to eliminate pitting regardless of Fe(III) content [23]. Reference has already been made to the control of pitting by maintaining a small concentration of Fe(III) in the hot-chloride bath [17]. Stirring of the solution or mechanical agitation of the cathode may also reduce pitting. A “bumping” type of motion is most effective. Air agitation should not be used because it results in excessive oxidation of Fe(II).

11.5.4 Analytical Technique

The approximate concentration of iron is determined by measurement of the specific gravity. Only an occasional analysis for iron is necessary. Standard analytical procedures are used to determine Fe(II), chloride, and sulfate [165]. The quantitative analysis of iron may be performed by titrimetry or spectrophotometry [166].

11.6 EQUIPMENT

All the iron plating solutions described, except the alkaline baths, require acid-proof material for tanks and auxiliary

equipment. Equipment similar to that used for acid pickling is satisfactory. For most rubber-coated steel tanks are adequate; they may be further lined with acid-proof brick for heavy service. Steel tanks with vinyl resin or fiber-reinforced plastic (FRP) linings are satisfactory at temperatures up to 60°C. Glass and glass-lined equipment is resistant to corrosion in sulfate or chloride electrolytes, but it is hardly rugged enough for commercial use unless precautions are taken to protect the cell surface from thermal and mechanical shock. Rubber-lined pumps and pumps constructed of impregnated carbon, Teflon, or titanium parts have given satisfactory service with the hot-chloride bath. Vinyl plastisols are satisfactory as rack coatings and stopoffs, even in the hot-chloride bath.

When the heat that developed from the passage of the plating current through the bath is sufficient or nearly so to maintain the proper working temperature, it has been found practical to inject live steam directly into the solution as the simplest means of initial heating. If there is too much condensate, heat exchangers of tantalum, titanium, zirconium, or Teflon may be used. Quartz immersion heaters can be used in all solutions and carbon immersion heaters can be used in fluoborate or fluoride solutions. If the nature of the work permits, mechanical agitation of the bath makes possible the use of higher current densities and facilitates the formation of a more even deposit.

For iron plating on large-volume articles as molds and rolls, a deep tank with a depth above 4 m is used to settle the ferric hydroxide precipitation on the bottom. A 1977 patent mentioned the process for exchanging a surface layer of a moving steel strip with iron deposit in an iron plating solution [167]. Special plating cells such as a paddle cell and rotating cathode cell have been employed for production of magnetic devices such as thin-film Permalloy (iron–nickel alloy) heads to maximize thickness uniformity. Several types of continuous plating cell [168] have been employed for production of iron strip and iron alloy plated steel strips in industrial fields. A paper mentioned the usage of rotating-strippable-drum system for production of an iron strip and the allowance of high current density as high as 40 A dm⁻² [22]. The thickness of the deposit is determined by the rotating rate of drums and deposition rate. In the drum system, a bare or chromium-plated stainless steel drum was used as cathode and iron and steel scraps were used as anode. Iron alloy plating on a steel strip have been carried out at high flow rate ranging from 0.1 to 0.4 m/s and narrow strip–electrode distance ranging from 9 to 50 mm [169, 170] by using insoluble anode. When an insoluble anode is used, an anion exchange membrane is effective in preventing the oxidation of ferrous ion in the bath if it is used for separating the plating cell into two compartments of catholyte and anolyte. A regeneration reactor [133] filled with iron scraps has been used for rapid reduction of ferric ion by circulating the used anolyte solution.

11.7 ANODES

Iron anodes of high purity, such as ingot iron, wrought iron, or Swedish iron, are preferred, but anodes of steel or cast iron have been used. High-purity iron anode is necessary to obtain ductile deposits, since a hot-chloride bath is easily contaminated by impurities contained in the anode materials. All of these dissolve with high efficiency but produce some insoluble sludge residue that may cause rough deposits. It is therefore usually desirable to bag the anodes. Glass cloth, although fragile, can be used and has been reported to be quite satisfactory when coated with phenolic resin [51]. Porous stoneware diaphragms have been used, but they are rather cumbersome and have a relatively high electrical resistance. The synthetic fabrics Orlon and Dynel are satisfactory bag materials. These fabrics are more durable when used as a cover on a frame, rather than as loose bags. Polypropylene cloth has excellent chemical resistance and durability in all iron plating baths and is commonly used in the hot-chloride electrolyte. The necessity for bagging may be obviated by continuous filtration. Passivity of iron anodes has not been reported, even in high-pH sulfate baths. For the production of iron strip and iron alloy-plated steel strips, insoluble materials such as platinum-plated titanium sheets or graphite sheets have been used as anode.

11.8 CHARACTERISTICS OF DEPOSITS

The data available in 1935 on the physical properties of electrolytic iron, including mechanical, magnetic, and electrical properties, was summarized by Cleaves and Thompson [1]. The data on mechanical and physical properties of iron and iron alloy deposits have been comprehensively surveyed in a monograph [171]. A representative selection of data on physical and mechanical properties is given in Table 11.4. In general, an iron deposit is an aggregate of columnar grains with a bcc lattice which corresponds to that of the equilibrium state at ambient temperature. In general, the hardness, tensile strength, and internal stress decrease and the elongation increases with an increase in bath temperature or a decrease in current density. Hardness ranging from 120 to 350 Vickers is obtained from a simple chloride or sulfate bath. A high hardness of 450 Vickers is obtained at a low bath temperature and high current density in a hot-chloride bath. The influence of current density and boric acid addition on the oxygen content was reported for a chloride bath [172]. Codeposited oxygen in the form of iron oxide deteriorates the hardness and ductility of iron–carbon alloy deposits [132]. Adding small amounts of hypophosphorus acid or dimethylamineborane to the iron–carbon alloy plating bath reduces the oxygen content to a harmless level, which results in the enhancement of ductility [134, 135]. The sulfur and carbon contents in iron–nickel alloy

TABLE 11.4 Properties of Iron Deposits

Iron	Bath Composition and References	pH	Temperature (°C)	Density (A dm ⁻²)	Current	Tensile Strength (kg mm ⁻²)	Elongation (%)	Hardness	Coercive Force
	Sulfate bath, Fe(NH ₄) ₂ (SO ₄) ₂ [177]	3.4	20	0.5		263			
		3.4	20	2.0		354			
		4.4	19	0.5		182			
		4.4	41	2.0		240			
	Chloride bath, FeCl ₂ (120–150 g L ⁻¹ as Fe ²⁺) [22]	3.5–4.7	100–106	400		50–56	5–15		9.5–11.0 (Oe)
	Chloride bath, FeCl ₂ ·4H ₂ O: 400 g L ⁻¹	0–3	86	20		45	2.1		19.5
	CaCl ₂ : 80 g L ⁻¹		96	10		42	3.33		18
	wetting agent: 2 mL L ⁻¹ [21]		96	20		43	4.67		17.5
	Chloride bath, FeCl ₂ ·4H ₂ O: 465 g L ⁻¹ , H ₃ BO ₃ : 38 g L ⁻¹ [24]	0.2–0.4	96	30		43	5.54	450	225
			108	20		36	2.67		17.5 (Am ⁻¹)
			70	15					
	Chloride bath, FeCl ₂ ·4H ₂ O: 1.57 mol dm ⁻³ , CaCl ₂ : 2.04 mol dm ⁻³ [175]	0	60	2.0					
		1		2.0				250	
		2		2.0				200	

(continued)

TABLE 11.4 (Continued)

	Bath Composition and References	pH	Temperature (°C)	Density (A dm ⁻²)	Current (A dm ⁻²)	Tensile Strength (kg mm ⁻²)	Elongation (%)	Hardness	Coercive Force
Iron-carbon	Sulfate-chloride bath, FeSO ₄ ·7H ₂ O:500 g L ⁻¹ NaCl:50 g L ⁻¹ [63]	2.5	80		8	46	4.3		
	Deposits from either sulfate or chloride baths annealed at 900°C [1]								
	FeSO ₄ ·7H ₂ O: 40 g L ⁻¹ , L-ascorbic acid: 3.0 g L ⁻¹ , Citric acid: 1.2 g L ⁻¹ [117]	2.5	50		3				800 (1%C)
	FeSO ₄ ·7H ₂ O: 0.14 mol L ⁻¹ Organic acid: 5.4 mmol L ⁻¹ Oxalic acid Malonic acid Acetic acid Adipic acid Succinic acid [131]	2.5	50		1				280 (0.15%C) 460 (0.2%C) 500 (0.2%C) 700 (0.6%C) 850 (1.3%C)
						15	56	5.3	
						27	64	2.7	
								40	70-90 (Brinell)

deposits were quantitatively determined for a sulfate–chloride bath containing saccharin [173]. The data in Table 11.4 show that annealing electrolytic iron at 900°C results in properties approaching those of thermally prepared iron ingot. Heating the deposits at 200–300°C has no significant effect on their properties. A high hardness of 800 Vickers has been obtained for iron–carbon alloy deposits with a carbon concentration exceeding 1% which had a martensitic phase with a body-centered tetragonal lattice. With annealing at 350°C, iron–carbon alloy deposits attained a high hardness of 1200 Vickers [174]. Iron–nickel alloy deposits have the phase structure of α -iron with bcc lattice or a γ -nickel structure with an fcc lattice or a mixture of the two, depending on the alloy composition [97, 176]. The phase structure of iron–nickel, iron–cobalt, and iron–cobalt–nickel alloy systems is slightly different than the equilibrium state of cast material, and the difference depends on the solution formulation, plating conditions, and impurities incorporated into the deposits originating from additives in the solutions. The phase structure is transformed to the equilibrium state by heating, resulting in a change in the mechanical and physical characteristics. Iron and iron–nickel alloy deposits have attracted increasing attention as components in spintronics with a semiconductor such as gallium–arsenide (GaAs), where the quality, including preferred orientation and lattice mismatch to the semiconductor is important. [178, 179]

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