Review

Electrodeposition of Ni-Fe alloys, composites, and nano coatings—A review

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A R T I C L E   I N F O

Article history:
Received 23 April 2016
Received in revised form 25 August 2016
Accepted 30 August 2016
Available online 31 August 2016

Keywords:
Coating
Direct current
Electrodeposition
Ni-Fe
Pulsed current

A B S T R A C T

Electrodeposition is considered as an easy and cost effective technique for preparation of alloy coating. A wide variety of properties for coatings can be achieved by selecting different parameters of electrodeposition. The electrodeposited Ni-Fe coating is employed in many fields such as corrosion, wear, magnetic and electrical applications, and electrocatalytic materials. In this study, as the evaluation of previous researches will be valuable to guide future researches, electrodeposition of Ni-Fe coating was investigated from different aspects. The electrodeposition process, effective parameters, properties, and application of Ni-Fe were summarized considering the previous studies.

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http://dx.doi.org/10.1016/j.jallcom.2016.08.329
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1. Introduction

1.1. Preface

The mechanical, thermal, chemical and electrochemical interaction of a material in a given environment initiate from its surface. Therefore, the surface of a material is the most important engineering part. Among the standards which are developing continuously for production and manufacturing process, the use of surface modification technologies in the manufacturing process is inevitable. Since the surface of materials is often under threat of wear and corrosion [1], tribology and corrosion are the most essential and important fields in surface technology. The tribological and corrosion phenomena impose huge damages to economy and industry. The damages will be irrecoverable if wear and corrosion phenomena are not controlled correctly. Therefore, the surface technology can be considered as a key technology in the production engineering process. The use of appropriate surface technologies can prevent the damages or at least delay them. The selection of a proper method to create distinctive surface properties is a complex process as it includes modifying the various characteristics and properties. Furthermore, the selection of suitable process usually requires the economic and environmental investigations [2].

Electrodeposition is an electrochemical process applied for surface structure modification. The electrodeposition process is an old method in surface engineering processes which has a long history. The electrodeposition technique was firstly applied more than 2000 years ago in several hypotheses [3,4]. The production of a galvanic cell with Volta in about 1800 and then progress in electrical motors from 1800 to 1900 led to use electrodeposition technique as a cost effective process to produce a coating. In this process, a monolayer or multilayer coating is formed because of the electrochemical reactions occurred at the electrode/electrolyte interface and deposition of ions from the electroplating bath on the surface [5]. The coating may be deposited on the surface to enhance the solderability, lubricant properties, electrical conductance, corrosion resistance, and wear and thermal resistance of the substrate material. Electrodeposition process can be performed with both types of direct (DC) and pulse current (PC) [6]. In the DC method current is continuously applied to the system. However, in a PC electrodeposition process, the electrical current is alternated swiftly between two different values [7]. The properties of deposited coatings can vary because of pulsating parameters in PC electrodeposition process. The progress in electronics made it possible to control the properties of the coating by using the PC instead of DC method. The better dispersion of elements in the coating, compact and nonporous nanostructure coating, a decrease in absorption of gasses in coatings, a reduced need for organic additives and thus a decrease in environmental pollution are advantages of PC electrodeposition process.

1.2. Electroplating of Ni and Ni-Fe alloy

Because Ni and its alloys have a variety of merits such as good corrosion and wear resistance, they have been receiving a great attention in deposition applications. Almost 12% of Ni consumption in the world is allocated to the electrodeposition of Ni coating [8]. The use of Ni coating for decorative purposes is the main application of electroplated Ni coating [9]. The Ni deposits are used in the industry to improve wear and corrosion resistance, to repair eroded metals, to change the dimensions of small size pieces, to improve magnetic properties, to prepare the substrate surface for glazing or producing the organic coating, and other purposes [10]. In addition to pure Ni coating, it is possible to produce a Ni-based alloy coating by an electrodeposition process. The Ni-Fe alloy coating is used in order to decrease the cost production and also provide soft magnetic properties, good electrical conductivity, proper corrosion resistance and special optical properties [11]. This type of coating is widely used in electronic, sensors, communication and optic industries. There are several processes used to produce Ni-Fe coating as follows: sputtering, molecular beam epitaxy, evaporation and electrodeposition [12]. The special conditions of temperature and pressure, ultra-high vacuum and
consequently expensive process are disadvantages of former methods over electrodeposition. Also, the coating produced by electrodeposition process is more homogenous and has lower defects in comparison to that of produced with other coating processes [13]. Furthermore, increasing the thickness of coatings is possible and cost effective in electrodeposition while other methods prepare thin films of Ni-Fe.

Nickel-iron alloys containing from 40 to 90 wt% Fe possess very interesting magnetic properties. Particularly, the alloy containing 78.5 wt% Ni, sometimes referred to as Permalloy, has a very high permeability in small magnetic fields. The magnetic properties of this alloy can be varied to a marked extent by heat treatment. In this connection, many attempts have been made to correlate the changes in magnetic properties with the changes in structure, internal strain, etc., which are normally associated with variations in heat treatment. In past years, extensive researches have been done to draw the phase diagram and different versions have been proposed based on experimental or theoretical work. The mostly accepted diagram in Fig. 1 represents the possible phases and transformations in this system. The phase boundaries of the Fe-Ni phase diagram in Fig. 1 were determined by Deen and Woude [17] using Mossbauer spectroscopy. A eutectoid reaction was predicted suggesting that \( \alpha \) and Ni\(_{3}\)Fe were in equilibrium at low temperatures [16]. The critical ordering temperature of FeNi\(_{5}\) (516 °C at 73 at% Ni) was determined by Deen and Woude [17] using Mossbauer spectroscopy. It is claimed that FeNi and Fe\(_{2}\)Ni phases also existed in this phase diagram below the eutectoid temperature in the two-phase (\( \alpha + \gamma \)) region [16]. Little information concerning the Fe-Ni system at low temperatures exist due to the slow diffusion of Ni in Fe-Ni. Therefore, the low-temperature part of the Fe-Ni phase diagram was according to speculations. The existence of ordered phases in this diagram demonstrates the equilibrium state can be reached via annealing for very long periods. Some evidences about the ordered phases have been reported for annealing at temperatures higher than the room temperature for long periods [15,18]. Based on the experimental works, the electrodeposited Ni\(_{1-x}\)Fe\(_x\) (0.1 < \( x < 0.9 \)) alloys consist of \( \alpha \) and/or \( \gamma \) phases since the deposition condition is a non-equilibrium process [19–22].

![Fig. 1. The Fe-Ni phase diagram [23].](image1)

2. **Mechanism of Ni-Fe electrodeposition**

Codeposition of Ni and Fe from an electrolyte is believed as an anomalous deposition, where the content of the more active element in the deposit is higher, however, the ratio of ions in the electrolyte for noble element compared to active element is higher. The deposition rate of Fe, which is a more active element than Ni, is higher than that of Ni in an electrodeposition bath of Ni-Fe. Fig. 2 indicates the content of Fe versus the ratio of Ni/Fe ions in the electrolyte. According to this diagram the relationship between Fe content of alloy and Ni/Fe ion ratio of the bath is not linear. For instance, the work of Sanaty-Zadeh [24] shows that at Ni/Fe ion ratio of 1 the content of Fe in the deposit is 84 wt%. Hence, the deposition rate of Fe is greater than that of Ni indicating the anomalous deposition. In early studies, the anomalous deposition was attributed to the deposition of Fe hydroxide on the surface of the electrode which prevents reduction of Ni ions [25]. According to this mechanism, the reduction of \( \text{H}^+ \) ions on cathode surface and thus the local increase of \( \text{pH} \) value on the surface facilitates the formation of metallic hydroxides. In this case, the formation of Fe(OH)\(_2\) on the surface is more than that of Ni(OH)\(_2\) which in turn inhibits the deposition of Ni ions. Nevertheless, there are several reports which indicate the anomalous deposition occurred at very low pH values [26,27]. Accordingly, this is not reasonable to justify this behavior with above mentioned theory. In the next models, the anomalous deposition was attributed to the formation of NiOH\(^+\) and FeOH\(^+\). The formation of these intermediate compounds may be due to hydrolysis of Ni\(_{2+}\) and Fe\(_{2+}\), and discharging on the cathode surface [28]. Therefore, the high concentration of FeOH\(^+\) ions near the electrode and coverage of the surface with these ions inhibit the formation of NiOH\(^+\) ions. In a newer model suggested by Matlosz [29], the kinetic rather than the chemical reaction is emphasized. Hence, it is assumed that the reduction reaction of both Ni and Fe ions occurs in two steps as follows:

\[ \text{M(II)} + e^- \rightarrow \text{M}^{0}_{\text{ads}} \text{ step (1)} \]

\[ \text{M}^{0}_{\text{ads}} + e^- \rightarrow \text{M}^{2+} \text{ step (2)} \]

In the first step, the reduction of Fe\(^{2+}\) and Ni\(^{2+}\) ions to Fe\(^{+}\) and Ni\(^{+}\) occurs respectively, and these intermediate species are adsorbed on the electrode surface. The deposition rate of ions is controlled by the second step in which the reduction process of intermediate ions is performed [30,31]. In this step, the reduction rate of Fe\(^{+}\) compared to Ni\(^{+}\) is higher and thus many areas of the surface are covered with Fe ions. The covering of electrode
surface with Fe⁺ prohibit from the deposition of Ni ions. According to this model, the hydrogen evolution and increase in pH values near the electrode is not essential in the anomalous deposition process. This model has been confirmed by electrochemical impedance spectroscopy measurements [32].

3. Baths used in electrodeposition process of Ni-Fe coating

3.1. Sulfate and chloride baths

Sulfate-based and chloride-based baths are most widely used baths in the industry and previous investigations. From economic aspects, sulfate and chloride baths are the best choices for electrodeposition process. Beside the sulfate compounds, Ni chloride is used in a sulfate bath. The presence of Cl⁻ due to the addition of Ni chloride to the electrolyte causes dissolution of Ni anodes and increases the conductivity of the solution [8,36]. The Fe chloride and Ni chloride are usually used in sulfate baths of Ni-Fe electroplating. The absence of chlorides in electrolyte can lead to a decrease in the internal stresses of the coating. In electroplating bath in which the consumable anodes are not used, the absence of chlorides will be favorable. In comparison, in the presence of consumable anodes, chlorides and other reactive agents are used in electroplating bath [37,38]. Moreover, the chloride baths alone is also used in electrodeposition of Ni-Fe alloy. The coatings produced in chloride baths compared to the one prepared in sulfate baths is harder and have more stresses in its structure. The reason for this effect is unclear in many studies concerned the internal stress of electrodeposits [39–41]. Furthermore, the corrosion resistance of these coatings is low and some special plans should be proposed to protect from corrosion attacks [42]. It has been found that in both chloride and sulfate baths, current efficiencies were independent of Fe²⁺ concentrations, although their values in chloride baths were higher by about 20%. The higher limiting current for H⁺ in the sulfate bath rather than chloride bath was the main reason of latter. Accordingly, significant decrease in the overpotential of Ni-Fe in chloride baths attributed to the catalysis effect of chloride through the formation of a Cl⁻ bridge between the electrode and the metal ions [39,43]. The electrodeposits fabricated in sulfate baths have larger grains and less internal stress than chloride bath; however, the anode passivates and causes the metal ion concentration and solution pH to change [43].

3.2. Fluoroborate bath

The use of some special additives such as saccharine in chloride, sulfate or sulphamate baths allows deposition of some other products beside the metallic coating [20]. The presence of these products in the coating can affect the properties of the coating. For instance, the properties of coating deposited from a bath containing citrate additives can be changed due to the presence of active carbon in the composition of electroplating bath [22]. If consumable anodes such as Ni or Ni powder are used in above-mentioned baths, the dissolution rate of the consumable anode cannot compensate the decrement rate of Ni ions in the bath. Therefore, local changes in pH value and composition of bath occur that could be effective on the properties of the coating. To overcome these problems, fluoroborate baths can be used in the electrodeposition process. In this case, the problems issued from the presence of additive agents such as saccharine and sulfur will be solved. Furthermore, the dissolution of Ni and Fe powders in the bath is easy and thus the decrement of Ni ions in the composition of the bath can be compensated. In addition, the deposition rate in this bath is also high [22]. This bath has some drawbacks such as high cost and corrosivity.

3.3. Sulphamate bath

The sulphamate baths have some advantages such as high throwing power, high deposition rate, and low internal stress of deposited coating. The hydrolysis process and formation of azodisulfonate are the major defects of these baths. The high concentration of Ni sulphamate leads to decreased hydrolysis, but the intensified formation of azodisulfonate impurities. Azodisulfonate, persulfate, sulfate and sulfite are some of the impurities which may be generated in sulphamate baths. Among these impurities, the azodisulfonate is the main source of sulfur which decreases the ductility and compressive stresses [44,45].

3.4. Nonaqueous baths

The Ni-Fe alloys are usually deposited from aqueous baths. The discharging process of H⁺ ions and formation of hydrogen during electrodeposition process is the most important drawback of aqueous bath. It has been observed that hydrogen discharging in the electrodeposition process degrades some of the deposit properties. Therefore, the use of an appropriate solvent without active hydrogen or a solvent, in which the hydrogen bonds are stronger than that of water bonds, is preferred. For this purpose, the organic electrolytes are preferred over the aqueous ones. Ethylene glycol solution was used for Ni-Fe electrodeposition process. This solution has a good amphoteric and complexing properties. Because the boiling point of this solution is higher than that of water, it is possible to use at higher temperatures. In comparison to water, ethylene glycol provides a lower adhesion, better wettability, appropriate surface charge, higher viscosity and density. These properties cause the increased stability of ethylene glycol in suspensions. In this electrolyte, since the chance of hydrogen releasing decreases, a coating with low content of hydrogen can be obtained [46,47]. N,N-dimethylformamide (DMF) is another solvent, which has least or no active hydrogen, is employed for electrodeposition of Ni-Fe-Si₃N₄ coating [48]. There are no information concerning the comparison of deposition rate and properties of deposited Ni-Fe coatings in nonaqueous electrolyte with the ones deposited in aqueous solutions.

4. Additives

4.1. Boric acid

The boric acid is added to chloride and sulfate baths used in the electrodeposition process of Fe group metals. In electrodeposition process of Fe group metals, a part of the electrical current is consumed to form hydrogen. This reaction decreases the current efficiency and leads to an increase in the pH value of cathode surface and thus affects the kinetics of reduction reactions for metallic ions. Boric acid improves the range of required current density for electrodeposition process. Furthermore, the presence of Boric acid in an electroplating bath improves the appearance of the coating and decreases the coating brittleness [49,50]. Many researchers believe that boric acid acts as a buffering agent and prevents pH increment on cathode surface [51,52]. Some researchers believe that boric acid can act as a catalyst for the reduction reaction of metallic ions by the formation of some complexes with Ni [53]. This mechanism has been proven for Fe in chloride baths [54]. Zech [55] evaluated the effect of boric acid in Ni-Fe electroplating bath. This author found that boric acid act as a source to produce proton in the solution in a potential range in which reduction reactions occur and reduction of water is also possible. Therefore, the increase in the pH value of the cathodic areas occurs in nobler potentials. The presence of boric acid in an electroplating bath inhibits pH raise and
also the required potential range for the electrodeposition process is extended without hydroxide deposition.

4.2. Citric acid

Citric acid is used in Ni-Fe electroplating baths as a complexing agent. Citric acid is a complex agent for Fe\(^{3+}\), Ni\(^{2+}\) and Fe\(^{2+}\) ions. The stability of the produced complexes decreases in the order of Fe\(^{3+}\), Ni\(^{2+}\) and Fe\(^{2+}\). The addition of citric acid to the sulfate baths leads to deposition of the high content of Fe on the cathode surface; however, the current efficiency decreases significantly [56]. The results indicate that the local increase in the pH value of the cathode surface leads to the formation of hydroxide layer. In this case, citric acid quickly decomposes and provides the necessary protons. The proton reduction leads to a decrease in cathodic efficiency. In the cases the formation of hydroxide layer is not desirable (such as chloride baths in pH = 3), the content of Fe in the coating is very low and a high quantity of Fe\(^{3+}\) ions is formed in the solution. Since the stability of Fe\(^{3+}\) ions is higher than that of Fe\(^{2+}\), the Fe\(^{2+}\) ions exit from the complex mode and thus the equilibrium chemical reaction occurs in a direction to form Fe\(^{3+}\) ions [57]. The complexing effect of citrate ions shifts the reduction potential of Ni-Fe alloy to the more negative potential and increases the diffusion-limited current. The other effect is raising the nucleation sites and nucleation rate [58].

4.3. L-Ascorbic acid

L-Ascorbic acid prevents the oxidation of Fe\(^{2+}/Fe^{3+}\) during electrodeposition process. The presence of this acid in electroplating bath inhibits the formation of Fe hydroxide films. When the condition for the formation of Fe hydroxide layer in cathodic sites is ready, Ascorbic acid causes Fe discharge from hydroxide films. This behavior is often seen in sulphamate baths and it is not reported in the case of chloride medium [57]. The ascorbic acid is not effective on the chemical composition of the coating, although it prevents oxidation of Fe\(^{2+}\) ions and thus hinder decrement in the concentration of these ions [25].

4.4. Glycolic acid

Glycolic acid with sodium citrate is used in chloride baths. According to the results of previous works, the presence of glycolic acid in the bath shifted the reduction potential of Ni-Fe alloy toward more negative values. Furthermore, the nucleation rate increased with the presence of this acid in the electroplating bath. These behaviors can be explained by this fact that glycolic acid acts as a buffer and a complexing agent. In the presence of glycolic acid, some spherical nuclei are formed on the surface which they continue to grow with the same growth rate. Furthermore, the addition of this acid decreased grain size and the surface roughness [56,58,59].

4.5. Saccharin

Saccharin is used as an additive agent in electrodeposition baths of many metals and alloys. This material can act as a grain refiner and stress reliever in electroplating solutions [60]. Effect of saccharin addition on the internal stress of coating is presented in Fig. 3. Based on the plot, it is found that internal stress of Ni-Fe coating is reduced with saccharin concentration. Different mechanisms are reported for the effect of this additive on the coating properties. One of the most important mechanisms is the formation of complex compounds on the surface of the cathode and decrease in the diffusion rate of adsorbed Ni ions and thus the increase in the frequency of nucleation sites [61]. The addition of additive agents such as saccharin affects the cathodic polarization behavior. According to some investigations, the reduction potential of Ni ions shifts toward more positive values due to the addition of saccharin to the electrolyte solution. This behavior can be attributed to the barrier properties of the generated complexes against diffusion of Ni ions. High overpotential values re in a good compatibility with the increase in nucleation rate and a decrease in grain size [62]. The stress relieving in the structure can be attributed to the grain refinement. The grain refinement and increase in the volume of grain boundaries releases the energy produced due to internal stresses [59]. The study on the concentration of saccharin in the bath revealed that at low concentrations (<3 g/l) shiny surface with nano-size grains, probably induced by stress relaxation and grain refinement, is formed. Increasing the saccharin concentration to higher values caused a rough surface with bimodal size distribution [63]. The effect of saccharin concentration on the chemical composition of deposits is a controversial issue. Jin-Ku et al. [64] reported partial changes of chemical composition (from 4.60 to 4.45 wt%) with increasing saccharin from 0 to 8 g/l. On the other hand, Tabakovic et al. reported the partial change of chemical composition at concentrations greater than 0.8 g/l while the lower values had a noticeable effect on the chemical composition of deposit and increased the Fe content [22].

5. Electrodeposition methods

5.1. DC electrodeposition

Electrodeposition process can be carried out through DC, PC, and PRC methods. Fig. 4 represents different modes of electrodeposition process. So far, above three different modes have been used in electroplating of Ni-Fe coating. In DC electrodeposition process, the electrical current is continuously exerted to the system in an uninterruptible manner. This method is the conventional and old method that have used for electrodeposition of metals and alloys. The main advantages of DC over PC and PRC method are: (i) simple and economically affordable process and (ii) the sufficient technological knowledge.

5.2. PC electrodeposition

In the PC electrodeposition the current in a periodic manner reaches zero (Fig. 4). In this case, negatively charged layer is formed on the cathode surface. The thickness of this layer increases to a
particular extent and then remains constant. This layer hinders diffusion of ions. The discharging of this layer during off-time in PC electrodeposition permits diffusion of ions toward the cathode surface [7]. In addition to electroplating bath variables (temperature, composition, and pH) which are effective in any type of electrodeposition process, peak current density ($I_{\text{peak}}$), pulse On-time ($t_{\text{on}}$) and off-time ($t_{\text{off}}$) are the other effective parameters in PC electrodeposition process. These parameters are shown in Fig. 4. The pulse frequency and duty cycle are used for better evaluation of pulse variables in electrodeposition process. Pulse frequency and duty cycle are calculated according to Equations (1) and (2), respectively:

$$f = \frac{1}{t_{\text{off}} + t_{\text{on}}}$$  \hspace{1cm} (1)

$$d\% = \frac{t_{\text{on}}}{t_{\text{off}} + t_{\text{on}}} \times 100$$  \hspace{1cm} (2)

where, $f$ is the pulse frequency and $d\%$ is pulse duty cycle in each pulse. The average current density can be defined as follows:

$$I_{\text{avg}} = \frac{t_{\text{on}}}{t_{\text{off}} + t_{\text{on}}} \times I_{\text{peak}} = d\% \times I_{\text{peak}}$$  \hspace{1cm} (3)

where $I_{\text{peak}}$ is the pulse peak current density and $I_{\text{ave}}$ is the average current density in each pulse. Each of these variables can be changed independently in a wide range and thus a wide variety of coating properties can be controlled by changing any of these parameters [66].

In general, the advantages of pulse current in comparison to direct current is summarized as follows:

(1) Yielding a more compact structure: Pulse off-time in PC electrodeposition inhibits the grain growth and increases the possibility of nucleation on the cathode surface when a pulse is fully completed, the next pulse will start immediately [66]. This condition leads to an increase in the nucleation rate and a decrease in growth rate, which in turn cause the formation of a more compact structure [67].

(2) The ability to control the chemical composition and microstructure: The change in pulse parameters such as $I_{\text{peak}}$, duty cycle and frequency make it possible to control the adsorption and desorption of various species in the electrolyte [68,69]. Therefore, the microstructure, chemical composition and properties of coatings can be controlled in PC electrodeposition [70].

(3) The decrease in frequency of generated pores and cracks because of reduced oxygen and hydrogen gases on the cathode surface: The decrease of pores in coating can be attributed to two factors; (i) during electrodeposition process, the released gases on the cathodic such as oxygen and hydrogen have enough time to leave the surface of the cathode and thus the possibility of their entrainment in the coating is low. (ii) The volume of gasses released from the water electrolysis during pulse on-time compared to DC electrodeposition is very low [67]. The micrometer and nanometer sized bubbles are formed during pulse on-time in PC electrodeposition in which the joining of bubbles to form a larger bubble is impossible. Nevertheless, the possibility of joining these bubbles and formation of porosity in DC electrodeposition process is high.

(4) Increasing the content of ceramic particles in nanocomposite electrodeposition [71–73]: Once the electrodeposition process starts, a negative charge layer is formed on the cathode in the presence of ceramic particles suspended in an electrolyte. This layer acts as a barrier between ceramic charged nanoparticles and surface of the electrode. Within PC electrodeposition, this negatively charged layer is discharged during pulse off-time in pulse current electrodeposition process. In this case, diffusion of ceramic particles into the adjacent layer and finally reaching the electrode surface become easier [74].

5.3. PRC electrodeposition

The current required for reduction of ions reaches to zero by a change in polarity in the PRC electrodeposition process and thus the oxidation reaction occurs on the cathode surface. In this case, at the anodic potential of electrode dissolution rate of Ni is very low while the dissolution rate of Fe from the cathode is higher than that of Ni [75,76]. Therefore, the pulse electrodeposition process is a useful method to reduce the anomalous deposition of Fe. The higher dissolution rate of Fe in comparison to Ni during exerting anodic current can be attributed to the oxidation of absorbed H$_2$ on the surface of the substrate [77]. When cathodic current is applied to the cathode, hydrogen gas is released. Such high fraction of released hydrogen does not have enough time to leave the surface. The presence and oxidation of hydrogen gas on the surface of coating prevents the increment of pH value which in turn leads to a decrease in the extent of anomalous deposition [30]. Another effect of PRC is lowering the internal stresses in the deposits. Fig. 5 shows the internal stress of PRC electrodeposited Ni-Fe coating in comparison to DC deposited one. Clearly, the internal stress increases...
content in electrolyte around the cathode by an increase in current density is attributed to the formation of metallic hydroxides [25,57]. Nevertheless, some works revealed that the diffusion process has a dominant role on the Fe content at higher current densities. The main effect of high current density is depletion of cathode’s surface from Fe ions. Thus, the diffusion of ions from the bulk of the solution toward the cathode surface is an effective parameter [84].

6.2. Electrolyte agitation

The stirring of the solution has a significant effect on the chemical composition of alloys deposited with anomalous deposition. Fig. 7 illustrates the effect of stirring rate on the Fe content in fluoroborate bath. The figure shows that an increase in the stirring rate increased Fe content in the coating. In this case, the role of mass transfer is more important than the kinetics of reactions. The stirring rate leads to an increase the transfer rate of Fe ions in the electrolyte and thus their facilitated diffusion from the bulk of solution toward the cathode surface [86]. It should be noted that the raising the agitation rate to a certain value leads to increase in Fe content, while more increase has a slight effect on the chemical composition of the coating. Furthermore, the current efficiency decreases with rising the stirring rate as shown in Fig. 7. This behavior can be attributed to the mass transfer process and its effect on the hydrogen evolution rate. The significant decrease in current efficiency can be described with the decrease in deposition rate of metals on the cathode surface. In this process, the hydrogen evolution is the dominant reaction in cathode [82,84].

6.3. Electrolyte pH

The electroplating baths with pH values in the range of 2–3.5 are used in the electrodeposition process of Ni-Fe. The formation of hydroxides, particularly iron hydroxide, is possible at higher pH values [82]. The results of previous investigations indicate that a decrease in pH value reduces both current efficiency and Fe content in the coating. Fig. 7 shows an instance for effect of pH on the chemical composition. The increase in Fe content in the coating is attributed to the increase in pH value on the cathode surface, which consequently leads to the accelerated formation of FeOH$. According to Matlosz [29] mechanism, the covering of the surface with FeOH$ increases the possibility of an increase in Fe content in the coating. The content of protons at low pH values is very high and a high fraction of current is consumed through the reduction process of these protons which in turn decreases the current efficiency.

6.4. Pulse frequency

The adsorption and desorption of various ions in the electrolyte can be controlled by changing the PC variables such as $I_{\text{peak}}$, duty cycle, and frequency [5,87,88]. Therefore, the control of microstructure, chemical composition and properties of coatings in PC electrodeposition is possible [89]. There are several reports about the effect of frequency on the chemical composition of electrodeposited alloys. Yin et al. [79] indicated that the frequency variation has not been effective on the content of Fe. Sanaty-zadeh et al. [24] reported that the increase in frequency from 0.5 to 1000 Hz has a negligible effect on the Fe content in the coating, but further increase in frequency from 1000 to 16000 Hz increased the Fe content from 61 to 71 wt%. This behavior is explained by the increase in local concentrations of Fe ions near the cathode surface during pulse off-time. The recent research of Torabinejad et al. [19] is also showed that frequency variation is
The change in grain size is a known influence of frequency variation on the coating microstructure [70]. The pulse duration is very short in high frequencies. Therefore, the time of charging and discharging process in pulse on-time and off-time is very short. Under such a condition, the nucleation rate increases and growth rate decreases which in turn results in the formation of a compact structure [66,90]. This behavior was also observed in the previous reports [24]. In fact, when the nuclei are formed on the surface the grain growth is limited due to the repeated interruption of current (high frequencies) and thus, so many nuclei are formed on the surface which eventually leads to a decrease in grain size [5]. The influence of pulse frequency on the microstructure of Ni-Fe has received less attention in the literature. The possible effect of this parameter on the resultant properties of the coatings may be attractive for many field of science and technology.

6.5. Duty cycle

The chemical composition, grain size and texture of the coating can be affected by variation of the duty cycle. In PC electrodeposition of Ni-Fe alloy, the decrease in duty cycle increases Fe deposition. This phenomenon was confirmed in several recent studies [19,91]. The mechanism of Fe deposition in Ni-Fe coating is an anomalous process and thus the events observed can be explained accordingly. In an anomalous deposition, the deposition of Ni is an activation controlled process, while the deposition of Fe is controlled by diffusion. Since the concentration of Fe ions in the electrolyte is lower than that of Ni ions, the chemical composition of the coating is more dominated by diffusion of ions to reach the cathode surface. The presence of pulse off-time helps eliminate the concentration gradients near the cathode surface and thus the Fe ions have enough time to move toward the cathode surface [92]. The mass transfer is a continuous process in PC electrodeposition because of stirring the electrolyte, while the charge transfer occurs just at pulse on-times. At short duty cycles in the PC electrodeposition, the off-time of a cycle is much longer than that of on-time. In this case, the depletion of Fe ions adjacent the cathode surface is compensated with diffusion of Fe ions from bulk. In the presence of ions on the cathode surface, the reduction continues without restrictions and thus the content of Fe in Ni-Fe coating increases [93]. The above discussion is a summary of speculations in the literature. Thus, there is a serious need for research in this area to explore the exact mechanism of deposition at different duty cycles by taking the electrochemical aspects into consideration.

7. Properties of electrodeposited Ni-Fe

7.1. Microstructure

The XRD patterns of Ni-Fe coatings with different Fe content is depicted in Fig. 8. As shown, the characteristic peaks of FCC phase are clear and increasing Fe to 43 wt% affects the intensity of (1 1 1) and (2 0 0). In comparison, increasing the Fe to 58 wt% in the deposited coating leads to the appearance of a new peak at (1 1 0) which is the characteristic peak of BCC phase. This observation determined the approximate range of phase stability in electrodeposited Ni-Fe coatings. This patterns illustrates that Ni$_{1-x}$Fe$_x$ alloy at x < 58% is FCC phase, while at 58% < x < 65% mixed state of FCC and BCC is observed. Finally, at x > 65% the only phase is BCC [86].

The deposition of Ni-Fe alloys results in a solid solution alloy. The lattice strains are generated in the coating structure due to the difference in atomic radius of Fe and Ni atoms. An increase in Fe content causes lattice distortion and thus lattice defects such as vacancies and dislocations are developed in the coating structure. When the number of dislocations reaches to a certain value, the low angle boundaries are formed which leads to grain refinement of coating structure. The effect of Fe content on the grain size of the coating is shown in Fig. 9. When Fe content in Ni-Fe coating is lower than 25 wt%, the grain size decreases with a decrease in the Fe content of the coating. However, the variation of grain size with Fe
content is negligible in Fe contents of 25–40 wt%. This is in a good agreement with those of the previous works, which they reported a similar behavior for variation of grain size with Fe content [35,94–96]. Furthermore, the grain size of Ni-Fe alloy usually is in the nanoregime although grain size may be varied by variation of electrodeposition parameters.

7.2. Mechanical properties

Ebrahimi et al. [97] evaluated the microhardness and flow stress of electrodeplated Ni-Fe coating. They reported that the optimum mechanical properties obtained in Fe contents of 20 wt%. The results indicated that the increase in Fe content to 20 wt% leads to the enhanced hardness and flow stress, but the presence of more amounts of Fe leads to a decrease in hardness and flow stress values. In contrast, Sanaty-Zadeh et al. [24] observed that the variation of microhardness is negligible when the Fe content is in the range of 20–40 wt%, while more contents of Fe and thus formation of a metallic phase with BCC structure leads to a significant increase in microhardness. Fig. 10 presents the engineering stress-strain curves of Ni-Fe alloys with different grain sizes determined by TEM observations. The first point indicates a significant increase of strength in the nanostructured alloy in comparison to the microcrystalline alloy [98]. There is a more accessed fact in the mechanical behavior of alloys and demonstrated by Hall-Petch relationship [99]. The second point shown in Fig. 10 indicates the enhanced strength of Ni-6%Fe in comparison with pure electrodeposited Ni. This increment is the result of the hardening effect of the substitutional solid solution. The other point of tensile plots is the higher strength of Ni-15%Fe than the Ni-15%Fe alloy that is attributed to the grain size of former alloy and its stronger strain hardening [98]. When strain hardening in the above alloys exhausted, the plastic instability occurs as a consequent. Instability of plastic deformation can be attributed to various mechanisms such as necking, microcracks, and shear bands. These researches claimed as there are no signs of microcracks and shear bands in the microstructure of deformed specimens, the possible mechanism of instability is necking [100], which is also confirmed by other research works [21]. Fig. 11 displays a series of multiple load-unload tensions of electrodeposited Ni-Fe samples. The specimen was unloaded when the stress was close to the maximum during the transient regime. This figure shows that during each reloading, higher stresses are observed, clearly exceeding the stresses obtained for the continuous tensile test. This phenomenon is named as yield point phenomenon [101]. Yield points are often ascribed to a lack of mobile dislocations [102]; however, the main reason for this observation is unclear in literature for Ni-Fe alloy.

7.3. Magnetic properties

The chemical composition of the alloy, electroplating bath, applied potential, and the addition of additive agents are the parameters which can control the magnetic properties of an electrodeposited Ni-Fe coating [103,104]. The effect of these parameters on the magnetic properties of the coating was investigated in the previous studies. The coercivity, magnetic flux density, saturation magnetization, magnetic remanence, permeability, anisotropy, and squareness are the magnetic properties which have been investigated [105–107]. The coercivity and magnetic flux density are the most attractive properties investigated by researchers. A decrease in coercivity and an increase in magnetic flux density and also saturation magnetization causes to promote the magnetic properties of the coating [108–111]. Therefore, many investigations have been done to decrease the coercivity and increase the magnetic flux density and saturation magnetization. The concentration of Fe in Ni-Fe coating is an effective parameter on the magnetic properties of coatings, so that the alloy coating provides better magnetic properties when the Fe content of the coating is almost 19–24 wt% [112]. In this regard, Permalloy is the most important alloy which is widely used in the electrodeposition process of Ni-Fe coatings [113]. It is stated that an increase in cathode potential for Ni-Fe coatings with the same thickness leads to a decrease in the percentage of Fe and an increase in the percentage of Ni in the coating.
Thus, the coercivity increases and magnetization decreases [114]. A similar behavior with an increase in thickness was observed in the case of coatings with the same cathodic potential of deposition [115]. It has been suggested that the type of applied current is effective on the grain size and subsequently the magnetic properties. The coercivity reduction in coating electroplated with PRC is almost 37% more than that of electroplated with DC. This behavior is explained with the smaller grain size of coatings electroplated with PRC [77]. As shown in Fig. 12, an increase in Fe content causes an increase in magnetic saturation and a decrease in coercivity. This is ascribed to the grain size of deposit that is decreased with increasing Fe content [112].

The presence of sodium saccharin which as a strain reducer agent in electrolyte leads to a decrease in the grain size, which in turn decreases the coercivity and subsequently enhances the magnetic properties of the coating [22] (see Fig. 13). The annealing process is also effective on the magnetic properties so that the lattice strain and defects decrease with increase in temperature, which in turn decreases the coercivity since coercivity is highly controlled by the number of dislocations and grain boundaries [46,116]. Therefore, an increase in annealing temperature increases saturation magnetization and magnetic flux density.

The use of a magnetic field in electrodeposition process is effective on magnetic permeability [117,118]. The presence of a magnetic field parallel or perpendicular to the substrate surface in an electrodeposition system leads to the increased permeability. In this case, the permeability reaches a maximum value when a magnetic field is parallel to the substrate surface. Fig. 14 indicates the effect of magnetic field on the coercivity. As shown in Fig. 14, the coercivity can be affected by a magnetic field, while it is independent of the direction of the magnetic field [118]. The presence of a magnetic field is also effective on the composition of the coating. An increase in magnetic flux density leads to a subsequent increase in Fe content. The magnetic properties of a coating can be influenced by the increase in Fe content, which results in saturated magnetization state [119].

### 7.4. Electrocatalytic properties

Finding an appropriate, cost effective, and eco-friendly replacement for fossil fuels is necessary. The electrical energies generated by fuel cells are proposed as a popular source of energies. It seems that the use of fuel cells is a good choice to solve the problem of energy and environment pollutions because it provides a high efficiency without contamination and also uses hydrogen as a fuel (hydrogen gas can be achieved from renewable and nonrenewable resources) [120,121]. Many studies are conducted in order to produce the hydrogen in acidic and alkaline solutions. Different materials are used as a catalyzer to produce hydrogen. For instance, water electrolysis reaction in alkaline solutions occurs within two stages as follows: Hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). In order to increase efficiency of the electrolysis cell, these reactions should occur at lower values of overpotential. The
overpotential of oxygen evolution reaction is considered as the main factor for energy loss in water electrolysis reaction [122,123]. Ni is a good choice to use in electrolysis reaction, because of its appropriate chemical stability. Furthermore, Ni can be used as a catalyzer for anodic and cathodic reactions. Preparation of an alloy coating with Ni and Fe elements improves the electrocatalytic behavior of Ni [124–126]. The results show that activity of Ni-Fe anodes for oxygen evolution reaction is controlled by the chemical composition of electrodes and the morphology of coating [125]. The entrance of Fe into the electrodes (as Fe oxide or Fe hydroxide) changes the electrical properties of electrodes so that these variations enhances the activity of OER [127]. Ullal and coworkers [128] investigated various Ni-Fe coatings deposited with different current densities. They reported that coating with 35 wt% Ni provides a high efficiency for OER and HER. According to this report, the surface conditions which improve the HER have a negative effect on the OER. Ni-Fe alloy has been also used as an electrocatalyst in an air-hydrazine fuel cell. The main problem with an air-hydrazine fuel cell is the use of expensive noble metals as a catalyzer; though having many benefits [129]. Multiwall carbon nanotube (MWCNT) filled with Ni-Fe alloy are used for oxidation of hydrazine [130]. This alloy is embedded in nanotubes using the electrodeposition process in the presence of methylbenzene. Fig. 15 displays the cyclic voltammograms of MWCNT-based alloys with in comparison to graphene based alloys. As observed the catalytic activity of MWCNT-based Ni-Fe is higher than the graphene-based one, and the reason of this phenomenon is not clear up to now. Thorough dispersion of Ni-Fe alloy on the carbon cathodes led to the high catalytic activity of MWCNT- and graphene-based Ni-Fe alloy. The significant result of this graph is that Ni is the active catalyst, while iron has a synergistic role in the oxidation of hydrazine hydrate [131].

7.5. Corrosion behavior

A widely used method for measuring the corrosion resistance is polarization curve of alloys. Addition of Fe as an active element rather than Ni reduces the corrosion resistance. According to Starosta et al. [132], the corrosion rate has a proportional relation while the corrosion potential is inversely proportional to iron content. For instance, the difference between corrosion potentials for nickel and Ni–19% Fe coatings were small but it rose to over 330 mV for Ni–29% Fe and Ni–41% Fe. Torabinejad et al. [133], taking this fact into consideration, deposited functionally graded coating. By using the continuous alteration of duty cycle and $I_{\text{peak}}$ in eight steps from 88% duty cycle to 11% duty cycle, the content of Fe from 37 wt% in the interface of coating-substrate was reduced to 15 wt% in the outer layer of coating. This variation in chemical composition is displayed in Fig. 16 that is ascribed to $I_{\text{peak}}$. Therefore, content of active element in the top layer of coating is lower than that of the beneath layers, leading to the improved corrosion resistance. To improve the corrosion resistance of Ni-Fe alloys, the addition of neutral ceramic particles to the matrix is proposed. In this respect, Starosta [132] added the micrometric particles of $\text{Al}_2\text{O}_3$ into the Ni-Fe matrix, which deteriorated the corrosion resistance of coatings. Such a behavior may be attributed to the large size of particles embodied in the matrix. Fig. 17 shows the influence of SiC nanoparticles on the corrosion behavior of Ni-Fe alloy. It is obvious that the corrosion potential shifted to the positive value and the corrosion current reduced to a lower value indicating the better corrosion resistance of Ni-Fe-SiC coating [134]. The main mechanisms effective in improving the corrosion resistance will be explained in the next sections.

7.6. Wear behavior

Limited studies have been performed on wear properties of Ni-Fe. These studies found that Fe addition reduces the wear resistance in comparison to Ni coating. Also, the wear resistance of the composite Ni-Fe-$\text{Al}_2\text{O}_3$ coating is higher than the Ni-Fe coating. To improve the wear resistance of Ni-Fe, several methods have been applied in the recent years; the addition of hard ceramic particles such as $\text{Al}_2\text{O}_3$ and employing the PC electrodeposition parameters is one of these methods. The low duty cycle leads to the high fraction of embedded ceramic particles. Hence, the deposited Ni-Fe composite coatings at low duty cycle may have a higher wear resistance. This fact has used also to deposit functionally graded and multilayer coatings for wear-resistant applications [91,133]. Continuous variation of duty cycle during the PC electrodeposition can result in the high fraction of ceramic particles in the top layers rather than the layers adjacent to the substrate. Fig. 18 shows the variation of hardness across the functionally graded composite coating. It is obvious that the hardness of the surface layer is greater than the beneath layers, leading to improved wear resistance of the functionally graded coating. Although there are few studies on the wear behavior of Ni-Fe coatings, researchers have claimed that using multilayer coatings can improve their wear resistance [19,135]. These studies are still in progress.
8. Thermal treatment of electrodeposited Ni-Fe

The applications of Ni-Fe coatings are greatly influenced due to the presence of internal stresses in the coating structure. An increase in Fe content in electrodeposited Ni-Fe alloys causes a consequent increase in internal stresses. The presence of stress in Ni-Fe coating decreases the fatigue life time and stimulates the stress corrosion cracking [136]. The results of previous studies indicate that an increase in current density and a resulted decrease in Fe content results in a decrease in internal stresses in Ni-Fe coating. The increase in Fe content and distortion in the coating structure leads to the development of some defects such as vacancies, dislocations, voids, and twins. This fact together with a nonhomogeneous dispersion of Fe in different areas of the coating can lead to an increase in internal stresses. In order to decrease internal stresses in the coating, two different ways are available: (1) the use of stress relieving additives such as saccharine and/or (2) annealing treatment of coating. The effect of saccharin additive has been investigated in several studies, and a ductility reduction was observed after annealing process in the view of the mechanical behavior of Ni-Fe coating. Mechanical properties of the electrodeposited coatings were investigated by several researchers using tension and compression tests and the obtained results compared with coatings annealed at different temperatures. Fig. 19 is an instance which indicates the mechanical properties of electrodeposited Ni-20%Fe coating after annealing treatment. The mechanical properties of coatings show the annealed coatings were embrittled. In order to decrease the internal stresses of coating, saccharin is used in the electroplating bath. The microstructure studies by Buchheit [92] indicate that high quantity of sulfur is added to the coating in the presence of saccharin in an electroplating bath, which diffuses into grain boundaries by annealing treatment. The solubility of sulfur in Ni is very low and thus sulfur diffuses toward grain boundaries with an increase in temperature. In this case, precipitation of thin layer of sulfur in grain boundaries leads to an increase in the coating brittleness. The increase in annealing temperature to 300 °C promotes the mechanical properties. The grain size and also precipitation of sulfur in grain boundaries are increased with temperature at temperatures above 300 °C; thus, Fe sulfides and Ni sulfides are formed. The effect of annealing treatment on the mechanical properties of Ni-23%Fe coating which was investigated by Li et al. [137], is shown in Fig. 19(b). As seen in the figure, an annealing treatment at 250 °C...
leads to a decrease in ductility and an increase in coating strength. It is known that the plastic deformation of metals is controlled with activities of dislocations and grain boundaries [138]. In the case of large grain size metals, the movement of dislocations plays a dominant role in plastic deformation. The production and dispersion of dislocation initiate from grain boundaries and then intergranular glide occurs. The grain growth of coatings annealed at 250 °C is negligible while relaxation of grain boundaries in this temperature leads to the ordering of grain boundaries. Therefore, the dislocation dispersion from grain boundaries hindered and strength increases. The presence of dislocation and dividing them into the partial dislocations facilitates generation of the Lomer-Cottrell locks which act as a barrier against the other dislocations, leading to the enhanced strain hardening. The decrease in dislocation density in the grain boundaries of the annealed coating indicates the reduced Lomer-Cottrell locks. This behavior leads to a decrease in the rate of strain hardening which can be another reason for the reducing ductility [34,98,100,138].

The changes in the microstructure of Ni-Fe coating after annealing process depend on the chemical composition of the coating and electroplating bath additives. The addition of Fe element into the Ni nanocrystalline coating enhances thermal stability of the coating. Fig. 20 represents the effect of heat treatment on the grain size of Ni-Fe coatings. According to previous studies, the lattice strain and hardness of Ni-21% Fe coating decrease significantly through heat treatment at 100 °C; although the heat treatment process is not effective on the grain size. The relaxation of grain boundaries is the most common event at 100 °C; although the heat treatment of dislocation initiate from grain boundaries and then intergranular glide occurs. The grain growth is controlled by lattice diffusion mechanism [138]. According to Fig. 20, the effect of temperature on the grain size can be divided into two distinct stages. The grain size variations with temperature are negligible at temperature below 327 °C, while above that a fast grain growth occurs. According to previous investigations [98,139], the grain growth in this range of temperature is abnormal. In this case, some of the grains with a better orientation than the neighbors are grown and surround the other grains. Therefore, the difference in grain sizes increases in this region and thus a bimodal structure is formed [139].

9. Ni-Fe composite coating

The Ni-Fe composite coating produced by electrodeposition process has been rarely investigated. The presence of second phase particles in the composite coating can affect the corrosion and tribological properties of the coating. The hard (rigid) particles improve the tribological properties and hardness of composite layer by dispersion hardening mechanism. The presence of a hard ceramic phase in a metallic matrix leads to the increased hardness of composite because of the Orowan and Hall-Petch effects. The rigid particles can act as a barrier against grain boundary mobility and thus prevent grain growth (Hall-Petch effect). The increase in the number of rigid particles leads to a subsequent rise in the number of locked dislocations and thus, according to Orowan effect, the required stress for movement of dislocations will be increased [142]. However, the interfacial intersections in the presence of particles with smaller grain size lead to the decreased mobility of grain boundaries due to the increase in surface area of particles [143]. The ceramic particles can improve the corrosion resistance of coating with various mechanisms. These particles can act as a barrier against the corrosive agents and prevent diffusion of them into the coating and subsequently leads to the reduced number of defects potentially created by corrosion attacks in the coating [144]. However, the embedding of nanoparticles in the coating decreases the defects and intergranular discontinuity and thus a high quality smooth coating can be created [145]. It was also stated with Praveen et al. [146] that the embedded particles on the surface decrease the exposed area against corrosion attacks and accordingly, the corrosion resistance of the coating can be increased.

In the case of composite coating with Ni-Fe matrix, the effect of Al2O3, SiC, Si3N4, ZrO2, and In2O on properties of the coating was investigated. Table 1 indicates the condition of electroplating used in these studies. The effect of these particles on the properties of coating can be described as follows:

9.1. Effect of Al2O3 particles

Starosta et al. [132] reported that a fine grain composite coating with good coherency can be achieved with the addition of Al2O3 micro particles. The amount of ceramic particles embedded in coating increases with the increase in the content of Fe. Also, it is found a decrease in content of ceramic particles from 50 to 250 g/dm³ in the electrodeposition bath led to a decrease in contents of ceramic particles embedded in the coating. The embedded ceramic particles increases the roughness of coating. The hardness of the coating increases with Fe contents while the size and content of ceramic particles have a slight effect on hardness. An increase in Fe content of the coating causes an increase in corrosion current; thus, the maximum corrosion attacks occur in Fe-reached areas. This behavior may be due to the formation of a Ni-Fe Galvanic cells. The functionally graded coatings have been produced in recent studies [91]. The constant variation in duty cycle results in a gradual increase in alumina content from interface toward the surface. The maximum content of particles is in the outer layer at the minimum duty cycle.

9.2. Effect of SiC

The presence of SiC nanoparticles in Ni-Fe matrix leads to an improvement in hardness and corrosion resistance. The texture of the coating can be affected by the presence of second phase particles. In this regard, the addition of nanoparticles prevents the formation of preferential texture and thus a structure with a more random texture is achieved. A major part of the composite coating structure are composed of (200) fiber texture. Some (111) and (311) fiber streaks are created by the addition of particles which increase the possibility of forming a random microstructure [78].
particles can help grain re
dispersing reinforcing particles and electrodeposition parameters such as the current and chemical composition of electroplating bath are some other parameters effective on hardness value. The grain size for this nanocomposite was between 50 and 60 nm [47].

9.4. Effect of Si3N4 particles

The effect of the ratio of Si3N4 particles to saccharine in the electroplating bath has been investigated. In general, the presence of saccharin in Ni-Fe coating can lead to grain refinement. An increase in Si3N4 to saccharine ratio leads to a decrease in grain size and an increase in hardness of the coating. The use of Si3N4 ceramic particles can help grain refinement so that the presence of these particles prevents grain growth [20]. Furthermore, the presence of Si3N4 particles can increase the surface roughness of the coating [147,148]. Increasing the current density enhanced the embedment of these particles into the Ni-Fe matrix as well as the microhardness. Presence of Si3N4 particles shifted the reduction potential of Ni-Fe to the less negative potential by 287 mV. This ascribed to the availability of more active sites on the surface offered by conducting Si3N4 particles [48].

9.5. Effect of In2O3 nanoparticles

Indium oxide particles have a good electrical conductance, because of their small band gap energy and a high number of carriers in comparison to other ceramic particles. In addition, these particles are widely used considering their high chemical stability at high temperatures, excellent transparency, and luminescence. The use of indium oxide promotes the corrosion resistance, hardness, magnetic properties, and electrical conductance. The current density is not effective on the content of embedded nanoparticles in this coating [46].

10. Addition of other elements to Ni-Fe coating

10.1. Ni-Fe-W

The W metal cannot deposit alone with electrodeposition technique and requires a metal from Fe group for this purpose [149,150]. The presence of an oxide layer as an intermediate phase for deposition of alloy has been introduced as the main mechanism to produce an alloy coating of W and Fe group metals. The W ions are adsorbed on the hydroxyl species of Ni. Therefore, the occurrence of parallel reactions leads to the formation of a heteropolytungstate film on the surface. Some microcrack can be generated on the surface due to the presence of high stresses in the presence of W alone in Ni-W coating. Despite the fact that Fe-W coatings have a good adhesion to the substrate, their appearance and surface roughness is not favorable. To overcome this problem, Fe, Ni, and W alloys are used with together [151]. Incorporation of W in the composition of Ni-Fe alloy leads to the increased hardness of the coating. However, the presence of Fe and a decrease in stresses can lead to a significant decrease in the number of microcracks. An increase in W content improves the strength and hardness, since W in the lattice which acts as a barrier against dislocations movement [152,153]. The temperature rise has a significant effect on the structure and mechanical properties of the coating. The temperature increase to 500 °C during heat treatment can lead to an increase in hardness while by exceeding this temperature the hardness value is decreased [150].

10.2. Ni-Fe-Cr

Various efforts have been made to enhance the corrosion resistance of Ni-Fe coating. The addition of alloy elements such as chromium is one of the methods to increase the corrosion resistance. To apply trivalent chromium, Cr(III), which has fewer risks compared to Cr(VI), the chloride bath is used in the electrodeposition process. FeCl2, NiCl2, and CrCl3 as well as some other additives, are used in chloride electroplating baths [154]. The effect of current density and PC electrodeposition parameters on the deposition of alloying elements in Ni-Fe-Cr system has been investigated [154,155]. The content of Cr in these coatings often is in the range of 2–14 wt% and depends on the electrodeposition condition. The increase in current density led to a decrease in the deposition of Fe and Ni, while the deposition of Cr increased. This behavior is attributed to the fact that the potential of Cr element is lower (more negative) than that of Ni and Fe. The lower potential (more overpotential) for Cr can stimulate the reduction of Cr at more negative potentials. Therefore, the increased current density, which leads to higher overpotential, provides the condition for deposition of Cr on the substrate [154]. The increase in pulse frequency leads to a decrease in the deposition of Cr and an increase in deposition of Ni in PC electrodeposition process. In comparison, the Fe content does not change significantly with a variation of frequency. A decrease in duty cycle leads to an increase in the Cr content in the chemical composition of the coating. The reduction

9.3. Effect of ZrO2 particles

Ni-Fe-ZrO2 nanocomposite has been produced using sulphamate bath in ethylene glycol solution. According to obtained results, the content of particles in the composite is not the only effective parameter on the composite hardness; however, the maximum contents of particles embedded in the composite coating reached 36%. The hardness value for Ni-Fe coating was between 570 and 750 HV while the hardness value obtained for nanocomposite coating was between 590 and 842 HV. The microstructure, nature, and dispersion of reinforcing particles and electrodeposition parameters such as the current and chemical composition of electroplating bath are some other parameters effective on hardness value. The grain size for this nanocomposite was between 50 and 60 nm [47].
reaction of trivalent Cr occurs in two steps. At the initial step, the reduction of Cr$^{3+}$ to Cr$^{2+}$ occurs and then next reduction reaction converts Cr$^{2+}$ to Cr. At lower duty cycles, which the pulse $t_{on}$ is long, Cr$^{2+}$ ions have sufficient time to exit from cathode surface which, in turn, leads to a decrease in Cr content in the chemical composition of the coating. The results of studies indicated that the corrosion resistance of three component coatings produced by PC is higher than that produced by DC [155]. Furthermore, the use of heat treatment process immediately after coating resulted in a significant decrease in microcracks [154]. In the more recent work, using the pulse duty cycle in an alternative manner between two values of 20% and 90% resulted in a multilayer Ni-Fe-Cr coating. This work showed that at high duty cycles the content of deposited Cr in the coating is higher than the one deposited at a low duty cycle of 20% [156].

10.3. Ni-Fe-P

The control of Fe in Ni-Fe coating produced by electrodeposition process is difficult due to anomalous deposition. In addition, the properties of Ni-P coating is weakened because of the fast grain growth at temperatures above 350 °C [44]. Some studies indicate that the control of Fe content in the coating is possible by use of phosphorus element in the electroplating bath. The use of phosphorus and the presence of Fe in the chemical composition of the coating facilitates the control of grain growth [45]. Furthermore, the presence of phosphorus in the composition of the coating can lead to the formation of an amorphous structure. The use of phosphorus leads to the enhanced ductility, corrosion resistance, and magnetic properties of the coating, although it increases the stresses of coating structure. To reduce the residual stresses in the coating the sulphamate baths can be used. One of the most important limitations to applying this type of bath is the formation of impurities in coating structure [157].

10.4. Ni-Fe-Mo

The incorporation of Mo into the chemical composition of Ni-Fe was carried out by the addition of molybdate into sulphamate and/or chloride baths. This ternary alloy is used for electrocatalytic applications and HER [158]. The results show that this alloy provides a good stability and catalytic activity in KOH 30%. Zn and Mo were also used simultaneously in the chemical composition of Ni-Fe coating. Zn element can be dissolved by the use of leaching treatment. In this case, a structure with a high surface area is created. The high activity of produced structure provides a favorable HER condition [159]. Permalloy is widely used for applications that need soft magnetic properties. The electrical resistance is also one of the most important physical features for magnetic applications. The oxidation resistance and special resistance of this alloy can be promoted by addition of Mo and Cr elements [94]. The electrical resistance is also an important characteristic of soft magnetic films which can increase the performance of these films. The electrical resistance of Permalloy can be built up from 180 to 240 $\Omega$ cm by the adding small amounts of Mo. The presence of Mo and Cr in the chemical composition of coating leads to a decrease in magnetoresistance of Permalloy. This behavior can be attributed to the structural variations such as a change in grain size and chemical composition. The addition of above-mentioned elements can cause a decrease in grain size, which in turn leads to a decrease in magnetoresistance [160].

10.5. Ni-Fe-C

Electroplated Ni-Fe-C coating is used for hydrogen evolution reaction because of its high catalytic activity and a good stability [161]. The appropriate activity of this coating is attributed to the natural activity of carbon, which is entered into Ni-Fe coating. The Lysine is used in sulfate based solution for embedding carbon in Ni-Fe coating. Song et al. [162] reported that the maximum content of carbon in the coating can reach 1.59%. The overpotential value for a coating with a carbon content of 1.59% is very low and thus this coating is very convenient for HER. The catalytic behavior of the coating can be influenced by the content of carbon and grain size. A decrease in grain size causes an increase in density of grain boundaries which act as preferred places for HER, leading to the reduced values of overpotential.

11. Applications

Nowadays, the main use of Ni-Fe is related to its magnetic properties. The magnetic properties of the coating can be improved by a decrease in coercivity and an increase in saturated current density and saturated magnetization. Some of the industrial applications of Ni-Fe deposits are shown in Fig. 21. The Ni-Fe alloy deposits are used in the electronic industry for memory, recording and storage devices in computers, null-balance transformer for residual current devices with medium response sensitivity, measurement transducers, pulse transformers, thyristor protective chokes, transducer cores, relay parts, stator laminations for stepping motors in quartz watches, shielding for low temperature applications (e.g. liquid helium or nitrogen), storage chokes, flux conductors and pole pieces in magnetic valves, printer, electro valves, magnetic heads for tape recorders [51,52,58,160,163–167]. The above mentioned applications have used extensively in practical applications, however there are some ongoing applications that is expected to be expanded in near future. These cases are briefly demonstrated in the following.

Ni-Fe powders are widely used as functional filler for electromagnetic wave absorbent composites. Presently, Ni-Fe powder with a disk-shaped morphology is produced using mechanical alloying [168]. The high density of Ni-Fe powders is a drawback for fabrication of light-weight magnetic absorbent composites. To overcome this drawback, the core-shell particles are used as a substrate in the electrodeposition of Ni-Fe alloy. For this purpose, Diatomite particle, which is a kind of silica stone, is used in the electrodeposition process. At first, a copper coating is applied on the surface of these particles using the electroless technique to increase their electrical conductivity and subsequently a Ni-Fe coating is produced by an electrodeposition process. Therefore, a particle with low density is produced which provide good magnetic properties and can be used as a magnetic absorbent functional filler [169].

NiFe$_2$O$_4$ spinel is used in microwave devices, storage of large volumes of data in the magnetic form, solid oxide fuel cell, and neutral anodes for the electrolysis process of aluminum. Ni-Fe coatings produced by electrodeposition process have been considered recently for fabrication of NiFe$_2$O$_4$ spinel [35]. Electrodeposition process is a cost effective process which is ideal for coating the components with complex geometry. In order to produce the NiFe$_2$O$_4$ spinel, the thermal oxidation process for Ni-Fe coatings is performed at high temperatures. The heat treatment process in the presence of oxygen or air can lead to a change in microstructure which is dependent on the properties of the coating produced by an electrodeposition process.

12. Future scope and conclusion

This article summarized different aspects of Ni-Fe electrodeposition and its properties. The process, effective parameters and
related properties were reviewed. The effects of alloying elements to Ni-Fe electrodeposits and reinforcements are briefly discussed and eventually applications of Ni-Fe alloy were mentioned.

Based on the mentioned assessments in previous sections, although the magnetic and electrical properties of electrodeposited Ni-Fe alloy has attracted attentions, corrosion and wear resistance of the Ni-Fe coating is not still appropriate. It is obvious that using the coating in various industries need an improvement of corrosion and wear resistance. For instance, this alloy has used in electro-valves, relay parts and printers as a coating or electroformed material. In these situations, resistance to wear and corrosion is critical for this coating. In the case of wear and corrosion behavior of Ni-Fe coating in various conditions, not only few studies have been considered but also for improvement of these properties little efforts have dedicated. Increasing the wear and corrosion resistance can be done by different methods such as addition of other alloying elements, addition of ceramic particles, and manipulation of electrodeposition parameters. Addition of other elements and ceramic particles to the Ni-Fe matrix have considered in previous studies, however a deep understanding of subject is not yet achieved. These studies are not enough for judgment about the performance of above methods. Accordingly, it is expected that more attentions will devote to these subjects in future studies. Moreover, the effect of alloying elements and embedding particles on the magnetic properties of Ni-Fe coatings, as a main character of this kind of alloys, are neglected in previous reports. Superior resistance to wear and corrosion may also be achieved by manipulation of pulsed current parameters. In this regard, multilayer and graded metallic Ni-Fe coatings have been the subject of investigations in recent years due to their proper electrical, magnetic, optical and mechanical properties and appropriate corrosion resistance [170–172]. The developed multilayer coatings fabricated through capability of PC electrodeposition parameters. It seems that development of multilayer and graded Ni-Fe coatings in the future as well as investigation of their magnetic and electrocatalytic properties of these coatings become the popular issues for researchers. In addition, electrochemical aspects of PC electrodeposition is more important in future. Incorporation of alloying elements into the Ni-Fe deposits may be interesting as they may improve the corrosion or wear resistance. Maintenance of magnetic properties is the most important subject in this field and the dedicated works seem not to be sufficient up to now.

Electrodeposited Ni-Fe coatings could have bright future for electrocatalytic applications. Combination of electrodeposition and other methods for production of a system with more exposed area for HER or OER may be useful. In this regard, electrodeposits of Ni-Fe on CNT and MWCNT and hierarchically structured coatings [173] were fabricated and probably will be used in future.

References


