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Review

Synthesis, Characterization and Applications of Electroless Ni-B Coatings-A review

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Electroless nickel coating process has experienced remarkable modifications since its invention by Branner and Riddell in 1946. This process has proven to be very useful for applying uniform, hard, wear resistant coatings on many kinds of substrates including metals, alloys and even non-metallic materials such as plastics. Ni-B coatings have high hardness (higher than tool steels) and high wear resistance (better than hard chromium coatings) but inferior corrosion resistant properties (Ni-P coatings).The successful development of Ni-P composite coatings through electroless coating process and attractive properties of Ni-B coatings have remarkably motivated the research community to develop cost effective and high performance Ni-B coatings to fulfill the challenging requirements of chemical, oil, automobile, petrochemical, electronic, aerospace and textile industries. Since reasonable advancements have been made in the field of electroless Ni-B coatings, it warrants, reviewing their development, physicochemical properties, and deposition mechanism to have deep insight of the earlier work and to design new processing techniques to cope up their existed limitations. In this article, a comprehensive review on electroless Ni-B coatings has been under taken with an emphasize on the coating bath compositions (nickel source, reducing agent, complexing agent, bath stabilizers etc),characterization techniques (structural, chemical and mechanical), factors affecting deposit properties and post coating treatments (heat treatment etc). Finally, some examples of the industrial applications of Ni-B coatings have also been discussed to have an idea about the diversity of their utility.

Keywords: Electroless coatings, hardness, wear resistance, corrosion behaviour, amorphous structure, crystalline structure

1. INTRODUCTION

Material degradation due to wear and corrosion has a significant influence on the performance of industrial plants. The component failure due to corrosion and wear in industrial plants usually leads to wastage of resources, energy, manpower and time. The material damage due to high wear and corrosion also raise safety concerns and if not addressed properly may result in even severe accidents [1].

The properties of materials determine their specific use and conformance of the desired set of properties guarantees their safe and efficient use. The mechanical properties (strength, hardness, wear and scratch resistance etc) of the bulk materials can be improved by many processes such as heat treatment (annealing, normalizing, hardening) and thermomechanical treatments etc [2-12]. Mostly, the surface of the materials experiences high mechanical forces and corrosive medium attack. In such circumstances, it is quite logical and feasible to alter the surface properties such as has hardness, wear, surface morphology and anticorrosion etc without taking into account the bulk properties of the material [13-15]. It has been well reported that modification of surface properties can be brought about by many processes such as carburizing [16-18] nitriding [19-23] carbonitriding [24-27],flame hardening[28], laser hardening[29-30], induction hardening [31-35] internal oxidation[36-37],chemical vapour deposition[38-42] and physical vapour deposition[43-49] etc.

Recently, coating process making use of aqueous solutions (electroplating and electroless plating) have gained significant consideration because of their salient benefits such as ease of the coating process, low cost, high deposition rate, formation of uniform coating layer and promising final properties such as high hardness, amazing wear resistance and decent anticorrosion properties [50-53]. Among aqueous solution metal deposition processes, electroless nickel coating process is more popular and has experienced remarkable modifications since its invention by Branner and Riddell in 1946. This process possess some distinct collection of properties such as uniform thickness, high hardness, good wear and abrasion resistance, excellent corrosion resistance, good solderability, amorphous and/or microcrystalline deposit, low coefficient of friction, high reflectivity, low resistivity and good magnetic properties etc. Electroless nickel deposition has become commercially important for modifying the surface properties of a large number of materials such as steel, aluminum, copper etc and non-conducting materials like plastics [54].

The autocatalytic nature of electroless coating process has been well reported. The electroless coating bath is mainly comprised of an appropriate source of metallic ions, efficient reducing agent, suitable complexing agent, and promising stabilizer. During this process, the substrate material (the material to be coated having high active surface) usually generates a potential when it is immersed into the electroless coating bath. The initiation of this potential in the coating bath enables both positive and negative ions to move towards the surface of substrate material. At the substrate surface, the transported ions discharge their energy and thus enable to attach to the surface of the substrate to form a layer of coating. Electroless coatings are finding their applications in many areas like MEMS, electromagnetic interference (EMI), powder metallurgy, reactor membranes, heat exchangers and reduction of bacterial adhesion. The thickness uniformity is an outstanding advantage of electroless coating process when compared with the electrodeposition process [55-66].

Considering the apparent benefits of boron and promising advantages of electroless coating process, improvement of surface properties by depositing Ni-B coating through electroless coating process can be regarded as a reasonable choice. After its maturity, scalability and repeatability in 1989, the Ni-B electroless coating process was adopted as a mass production process. Since then the electroless Ni-B coating process is gaining remarkable attention to improve the surface properties of a large variety of substrates [67-68]. Electroless Ni–B coating process produces uniform coatings containing appreciable amount of nickel boride which induces substantial improvement in wear and abrasion properties [69-73]. A large variety of substrate materials can be employed including carbon steels, stainless steels, iron, aluminium and aluminium alloys, glasses, plastics, etc. The outstanding benefits of electroless Ni-B coatings include their high hardness (higher than tool steels), excessive wear resistance (superior as compared to hard chromium coatings) and promising corrosion resistant properties (Ni-P coatings). Instead of above mentioned advantages, low cost, uniform thickness, high wear resistance, good lubricity, promising ductility and corrosion resistance, marvelous solderability, high electrical properties, small porosity, high bonding, good conductivity, outstanding electromagnetic properties are added merits of electroless Ni-B coatings [74]. In addition, Ni–B coating process is also found to have better deposition efficiency as compared to nickel-phosphate (Ni-P) coating process due to use of more effective reducing agent (sodium borohydride) in the coating bath. Finally, the high basicity associated with electroless Ni–B coating bath solution (usually pH>13) is an inherent and outstanding advantage for coating of reactive materials including Mg alloys. Generally, electroless Ni–B coating process is believed to be better as compared to Ni-P plating and is becoming much attractive for many industries [60, 72, 73, 75, 76, 77]. However, borohydride baths are suffering from low stability in acidic or neutral medium. The borohydride ions are readily hydrolyze and spontaneously yields nickel boride in the presence of nickel ions. Therefore, a close control, of pH is very important (pH ≤13) [69, 72].

The crystal structure and the properties of electroless Ni-B coatings are dependent on their composition, process parameters and thermal history. A sufficient number of reports have been published focusing on structure-property relationship and process parameters [69, 71, 72, 78-84]. In as deposited state, Ni-B coatings are usually nanocrystalline or amorphous. As the concentration of boron increases the grain refinement and transition from crystalline to amorphous behavior is more pronounced. In general, coatings having boron contents ≥ 4 wt.% generally show amorphous behavior. The structure and properties of these coatings are greatly influenced by the heat treatment process which can result in crystallization and grain growth of the deposit [78, 82].

Since reasonable advancements have been made in the field of electroless Ni-B coatings, it warrants, reviewing their development, properties (mechanical, electrochemical) and deposition mechanism to have deep insight of the earlier work and to design new processing techniques to cope up their existed limitations. In this article, a comprehensive review on elecroless Ni-B coatings has been conducted with an emphasize on the coating bath constituents (nickel source, reducing agent, complexing agent, bath stabilizers etc), characterization techniques (structural, chemical and mechanical), factors affecting deposit properties and post coating treatments (heat treatment etc).

Finally, some examples of the industrial applications of Ni-B coatings have also been discussed to have an idea about the diversity of their utility.

2. THE COMPONENTS OF ELECTROLESS NICKEL BATH AND THEIR FUNCTIONS

The electroless Ni-B coating bath is comprised a source of metallic ions, suitable reducing agent, an appropriate complexing agent, adequate stabilizer and some other components. The components of electroless nickel bath usually comprised of Nickel ion (source of nickel), reducing agent (source of electrons), complexing agent (solution stabilizer), accelerators (activate the reaction), Buffers (control pH of the solution for long time), pH regulators (control pH of the solution for short time), stabilizers (prevent the breakdown of solution) and wetting agent (improve the wettability of the substrate)[55, 60, 80, 89-91].

2.1 Nickel source

In principle, any salt containing nickel can be used as a nickel source to synthesize Ni-B coatings. However, most of the studies have been conducted using nickel chloride hexa hydrate ($NiCl_2.6H_2O$) as a source of nickel [37, 60, 67, 71, 80, 89, 92, 93]. Nickel sulphate hexa hydrtae ($NiSO_4.6H_2O$) has also been reported for some electroless Ni-B baths [69, 76, 93, 94] and electroplated Ni-B baths [79, 95, 96].

2.2 Reducing agent

Many kinds of reducing agents can be employed for electroless Ni-B coating process [60]. However, mostly dimethylamine borane (DMAB) and sodium borohydride have been reported as reducing agents for electroless Ni–B coatings.

2.2.1 Dimethylamine borane (DMAB)

Recently, dimethylamine borane (DMAB) has proven to be an attractive reducing agent for Ni-B electroless coating bath [69, 71, 06, 90, 93, 97]. It is a white solid granule with strong amine odor. It has flash point of 65 ˚C with bulk density as 300-350 g/l. It is soluble in water, CH_3OH and Toluene but not soluble in hexane. DMAB has also been used to deposit copper on to electroless nickel, palladium activated plastic, copper substrates and tin/palladium activated epoxy. DMAB coating baths offer significant advantages such as high bath stability, lower operating temperatures, better corrosion resistance, lower electrical resistance and higher purity in the plated deposit. Despite its beneficial effects it is a hazardous and must be dealt with necessary precautions.

2.2.2 Sodium borohydride

The strong reducing ability of borohydride makes it an attractive reducing agent for electroless nickel coatings. Sodium borohydride ($NaBH_4$) has superior reduction efficiency when compared with

DMAB and sodium hypophosphite. The high efficiency Sodium borohydride is because of its inherent ability to provide more number of electrons (up to eight electrons) as compared to sodium hypophosphite (two electrons) during the metal reduction process for the same chemical reaction. In addition, borohydride coating baths are also more economical as compared to DMAB. The only drawback is that borohydride ions can easily hydrolyze when exposed to acidic or neutral media and instantaneously yield nickel boride in the coating bath in presence of nickel ions. This necessitates a strict control of pH to avoid immediate decomposition of the coating bath and to avoid any extra expense. A close control of pH of the coating bath between 12 and 14 ensures the suppression of the formation of nickel boride and guarantees the deposition of nickel on the substrate surface. That is why borohydride reducing agents are typically used in alkaline medium [98].

It is reported that electroless coatings developed using sodium borohydride demonstrate enhanced properties as compared to those coatings reduced with other boron compounds or with sodium hypophosphite. The primary benefits of borohydride-reduced electroless nickel coatings include their high hardness and improved wear properties in as their as synthesized state [55, 67, 68, 69, 70, 77, 78, 81, 87]. The electroless Ni-B coating synthesis reactions can be represented by the following chemical equations [60]:

$2Ni^{+2} + BH_4^{-1} + 4OH^- \rightarrow 2Ni + BO_2^- + 2H_2O + 2H_2$ ……………………………….(1)

$BH_4^{-1} + 2H_2O \rightarrow 2B + 2OH^- + 5H_2$…………………………………………………..(2)

Reaction (1) is considered responsible for reduction of nickel ions while reaction (2) ensures boron contents in the developed coatings.

2.3 Complexing agent

The main objectives of the addition of complexing agents in the electroless coating baths can be summarized as below:

1. Hinder the rapid reduction of pH of the solution.
2. Inhibit the precipitation of constituents of the coating bath such as nickel salts.
3. Facilitate the formation of metastable complex compounds to minimize the amount of free nickel ions in the coating bath.

Additionally, it has also been reported that the complexing agent has a significant influence on the reaction mechanism and the rate of formation of coatings. Normally, at initial stages the rate of formation of coatings increases with increasing amount of complexing agent and thereafter it starts to decrease [55]. In order to find out the most suitable complexing agent for borohydride bath, Gorbunova [99] et al used various complexing agents. The result of their study indicates that ethylenediamine (EDA) is the most appropriate complexing agent. Now a day, EDA is a popular complexing agent used for the development of electroless Ni-B coatings and its optimum concentration is found to be 90 g/l [60, 67, 70, 71, 72, 85, 89, 99, 100]. Normally, both organic (acetate, succinate, propionate, citrate, etc) and inorganic compounds (pyrophosphate, ammonium ion etc) are employed as complexing agents [55].

2.4 Surfactants

Generally, the surfactants are used to improve the wetting action that reduces the surface tension of the coating bath solution. The adequate use of surfactants in the coating bath facilitates smooth spreading of coating material and reduces the interfacial tension between the molecules of associated solution or a solution and the surface of a solid. Typically, in the electroless nickel bath, addition of proper amount of surfactant improves the coating deposition rate [55]. Although, the use of surfactants has been reasonably reported for Ni-P coating baths [101-105], however, their use in electroless Ni-B bath is not much popular [106-110].

2.5 Stabilizers

In spite of the use of the most effective complexing agent, the solution shows insufficient stability and forms precipitates of metal powder in the solution. In order to circumvent or decrease the undesirable metal powder precipitation, some substances are used introduced into the plating solution which are commonly known as stabilizers [99]. Delaunois et al [106] reported that for a controlled reduction reaction in the electroless Ni-B bath the use of appropriate stabilizers is essential. In the electroless coating bath the reduction reaction can be controlled by a careful choice of the stabilizers which eventually control the deposition rate and ensures formation of coating layer only at the substrate. During their action, the stabilizers are adsorbed on the surface of many particles present in the solution and thus preclude nickel reduction on them [106]. There are number of different stabilizers are available having promising performance. The proper choice of the stabilizer is quite important. Some reports indicate that lead nitrate and mercapto benzothiazole are quite effective to stabilize the electroless coating baths. However, these are suffering from poor deposition rate. Thallium compounds such as thalium nitrate are attractive stabilizers to attain good bath stabilization with high deposition rates [91].

3. ELECTROLESS Ni-B COATING SYSTEMS AND THEIR PROPERTIES

Owing to promising properties of boron, it has been used to develop various coatings with improved properties [68, 71, 80, 90, 106]. Among various electroless coatings processes, electroless Ni-B coating is a developing and vital area of research [83]. The following types of electroless Ni-B coatings have been developed and their structural, chemical, mechanical, magnetic and electrochemical (corrosion) properties have been studied.

3.1 Binary electroless Ni-B coatings

Many reports have been published addressing the formation, characterization and applications of Ni-B coatings [60, 72, 73, 76-80, 85, 87]. The electroless Ni-B coatings can be broadly classified into two classes on the basis of reducing agent used.

3.1.1 DMAB reduced electroless binary Ni-B coatings

DMAB has been employed as a reducing agent for the synthesis of electroless Ni-B coatings since long. Saito et al. [76] employed DMAB to develop electroless Ni-B, Co-B and Ni-Co-B coatings. After synthesis of these coatings, the effect of different coating parameters were investigated. They have studied the effect of concentration of DMAB on deposition rate and boron content on Ni-B and Co-B coatings. It is reported that the boron contents of the coating increases with the increase in DMAB concentration [76].

Hamid et al. [90] investigated the effect of deposition temperature and heat treatment on crystal structure, micro hardness, deposition rate and corrosion behavior of Ni-B coatings using DMAB as reducing agent. Their XRD patterns clearly discloses that electroless Ni–B coatings deposited at 60 and 80 ˚C are amorphous in as-deposited state and experience phase transformation when subjected to the process of heat-treatment. It is revealed that micro hardness can be remarkably improved with heat treatment process. The influence of heat treatment on micro hardness has also been reported by them. It is reported that hardness increases with the increase in temperature. This improvement in hardness is ascribed to the nucleation of crystalline phases like Ni_3B.

The influence of deposition temperature and immersion time on plating rate indicates that the deposition rate decreases with the increase in deposition time and increases with deposition temperature. Electroless Ni-B coatings show decent anti-corrosion properties. The corrosion study of electroless Ni-B coatings deposited on copper and steel substrates indicates that corrosion resistance of steel and copper when coated with Ni–B is higher than the uncoated substrates. It is also reported that in as deposited state the corrosion resistance of Ni–B coatings synthesized at 60 ˚C is higher than the coatings prepared at 80 ˚C. This improvement in corrosion resistance can be presumably regarded as the effect of reduction in grain size because Ni-B coatings synthesized at 60 ˚C have smaller grain size as compared the coatings developed at 80 ˚C. The small particle size of Ni–B coatings hinders the corrosion to take place at the surface. Moreover, while studying the effect of heat treatment temperature on corrosion behavior, the lowest corrosion rates have been noticed for the Ni–B coatings heat treated at 400 ˚C (either for steel or copper coated samples) and an improvement of about 9.5 times is noticed as compared to substrates. This improvement in corrosion behavior can be attributed to the complete nucleation of crystalline Ni_3B into the Ni-B matrix. These findings indicate that Ni–B coatings decreases the vulnerability of substrates against chloride ions attack by forming a protective layer on its surface. Contrary to above observations, heat treatment of Ni-B coatings at 250 ˚C has resulted in slight increase in the corrosion rate as compared to their as deposited state and the substrates (steel or copper).This change in corrosion behavior can be ascribed to the partial transformation of amorphous structure to microcrystalline [90].

Rios et al. [93] studied the effect of annealing time on particle size and surface morphology of electroless Ni-B coatings. The Ni-B coatings were annealed at 450 ˚C for various intervals of time. They concluded that the coating grain size increases with increasing annealing time [93].

3.1.2 Sodium borohydride reduced electroless binary Ni-B coatings

Sodium borohydride ($NaBH_4$) reduced baths are most commonly used to develop electroless Ni-B coatings due to their superior properties. The salient advantages associated with these coating baths are their ability to induce significant improvement in hardness and wear properties even in their as deposited state [71, 91]. Moreover, high corrosion resistance and formation of cauliflower structure which reduces friction are considered as their added advantages [110]. Owing to their promising properties such as high hardness, good wear and abrasion resistance, decent solderability, borohydride electroless coatings have succeeded to find their widespread applications in aerospace, automotive, chemical and electrical industries [82, 106, 127,111].

Electroless Ni-B coatings using $NaBH_4$ have been successfully deposited on many types of substrates like mild steel [67, 80, 82, 85, 89, 91], stainless steel [91], copper [91], aluminum [60, 105] etc. Electroless Ni-B coatings are grey in color after deposition.

Electroless Ni-B coatings in as deposited state are usually found to be amorphous in nature; however, these can be transformed into crystalline phase by an appropriate heat treatment process [61, 71, 80, 89, 91, 106]. It is reported that with increasing temperature the amorphous structure is transformed into crystalline resulting in the formation of crystalline phases such as Ni_2B and Ni_3B into the microstructure [91].

The structural transformations in electroless Ni-B coatings have also been confirmed with the help of differential scanning calorimetry (DSC). Studies indicate that the position and the number of exothermic peaks are very sensitive to amount of boron in the coatings. Ni-B coatings having boron contents ≤ 6 at. % does not experience any phase transformation. Whereas at 6–20 at. % boron, a single exothermic peak at 300–350 ˚C is predominant which is also sensitive to boron contents. Usually, a high amount of boron in this class (6-20 at. %) leads to the formation of this peak at low temperature. However, coatings having boron ≥20 at. % exhibit additional exothermic peaks at temperatures higher than 400 ˚C due to the crystallization of nickel, Ni_3B and nucleation of Ni_2B into the structure [91]. Finally, Ni-B coatings with boron ≥ 30 at. %, display a single broad exothermic peak at 410–415 ˚C [71, 91].

Dervos et al. [89] have reported high hardness of electroless Ni-B coatings. It is reported that the process of heat treatment has a substantial effect on mechanical properties. A remarkable improvement in hardness (1670±20) has been reported after the process of vacuum heat treatment. Similar studies can be found at many other research reports [72, 81, 82, 83, 106].

Delaunious et al. [106] reported the effect of heat treatment on the wear and hardness of electroless Ni-B coating on aluminum alloys. They evaluated the Knoop hardness of the coatings at different heat treatment temperatures and soaking times. It is reported that the hardness of the Ni–B–(Pb) coatings increases with the increasing heat treatment temperature and soaking time. This improvement in hardness can be attributed to the transformation of amorphous structure into crystalline due to the heat-treatment process [106].

Electroless Ni-B coatings usually have a typical cauliflower microstructure which can retain lubricant and thus improves the wear properties of the coatings which makes them suitable for many applications. The effect of immersion time on the formation of Ni-B coating using borohydride bath was studied. It was reported that the formation of cauliflower structure is favoured with the elapse of immersion time [67]. Narayanan et al. [71] demonstrated with the help of SAD pattern (TEM) that in as synthesized state the Ni-B coatings are amorphous, however, through proper heat treatment process these coatings can be transformed into different crystalline phases. Contreras et al. [112] studied the surface morphology of Ni-B coating with the help of atomic force microscope (AFM) and reported the existence of fine nodular structure even under annealed condition (<100 nm) confirming the ‘‘cauliflower’’ morphology of the coatings. This type of structure enhances lubricity and thus improves the wear strength due to reduction in the contact area. Riddle et al. [68] has reported remarkable wear resistance of electroless Ni-B coatings. They have shown that the wear properties of Ni-B coatings are even much better than hard chromium.

Krishnaveni et al. [72] also studied the wear properties of electroless Ni-B coatings and laid down a detailed measurement procedure. They evaluated the wear resistance of electroless Ni–B coatings both in as deposited and heat-treated (350 and 450 ˚C for 1 h) conditions under dry sliding environment using a pin-on-disc apparatus. Tests were conducted in air at 25 ˚C with a relative humidity of about 35–45% RH. It is reported that the wear rate increases with increasing applied load for both the conditions (as deposited and heat-treated). However, it is noticed that at all applied loads, the wear rate is less for heat-treated coatings as compared to as deposited state due to the nucleation of hard nickel boride phases into Ni-B matrix which has resulted in remarkable improvement in hardness [72].

The scanning electron microscopic analysis of electroless Ni–B coatings subjected to pin-on-disc wear test confirms the presence of torn patches and in some places even detachment of the coating in their as-plated condition (usually referred to as “prows”). This suggests that adhesive wear is the prominent mechanism in as deposited state. However, after the heat treatment process, the coatings exhibit a bright and smooth finish with fine grooves along the sliding direction in contrast to as-deposited state suggesting activation of other wear mechanism [72]. Some more results on wear behavior of electroless Ni-B coatings can be found somewhere else at [98].

The magnetic properties of electroless Ni-B electroless coatings can be found in the literature [99, 71]. Baskaran et al. [71] studied magnetic properties of electroless Ni-B coating in as deposited and heat treated states for various $NaBH_4$ contents. They conclude that in as deposited state, coating having more boron show relatively low saturation magnetization as compared to the coatings with less boron. This suggests that the magnetic properties of electroless Ni-B coatings are significantly influenced by their composition (higher the boron content, lesser will be the saturation magnetization). However, the process of heat treatment (400 ˚C/1 h) increases the saturation magnetization. The increase in saturation magnetization can be attributed to the crystallization of coatings due to the heat-treatment process [71].

Electroless Ni-B coatings have decent anti corrosive properties but to some extent inferior as compared to Ni-P coatings [71, 74, 89, 91, 112]. Dervos et al. [89] compared the corrosion behavior of Ni-B coatings in their as plated and vacuum heat treated condition. It is reported that Ni-B coating has a corrosion rate of 0.058 mm/year which is satisfactory but greater than Ni-P coatings (0.019 mm/year). Furthermore, it is also observed that although vacuum heat treatment at 850 ˚C, 5 min resulted in high hardness but degrades the corrosion properties (0.135 mm/year) [89]. The moderate corrosion resistance of Ni-B coatings in 3.5% NaCl solution has also been reported by Narayanan et al [91]. Electrochemical impedance spectroscopy has also been used by many researchers to study the electrochemical properties of Ni-B coatings [87, 91, 112].

3.2 Ternary alloy coatings

The properties of electroless ternary Ni-B alloy coatings have not been studied in detail. The selection of suitable alloying element is based on the final or required properties [69, 97]. We shall discuss two electroless ternary alloy Ni-B coatings.

3.2.1 Ni- B-Co ternary alloy coatings

Cobalt is considered to be the most useful element to improve magnetic properties of the coatings. Studies on electroless Ni–Co–B ternary alloy deposits are rather limited. Saito et al. [76], Yu et al. [113], Wang [97] and some other researchers [69, 114-116] have developed Ni-Co-B alloy coatings and have studied their properties. The effect of different variables on the coating deposition has been deeply studied by Narayanan et al. [69] and Saito et al. [76]. While studying the effect of DMAB concentration (0.012–0.048 M) on the deposition rate of electroless Ni–Co–B ternary alloy coatings it is reported that the coating deposition rate increases with increasing amount of DMAB. However, the destabilization of the coating bath is observed beyond 0.036 M. Similarly, the deposition rate increases with increasing pH of the coating bath from 6.0 to 8.0. This behaviour can be attributed to the enhanced oxidation of DMAB with increase in pH. However, further increase in pH value decreases the deposition rate [69]. As for coating time, it is also reported that the amount of deposit formed increases with increase in plating time throughout the entire duration of deposition confirming that the deposited Ni–Co–B alloy coatings continuously provides a catalytic surface for subsequent coating formation [69].

Thermal analysis (DSC curve) of Ni-Co-B ternary alloy coatings shows two exothermic peaks. The first exothermic peak occurs at around 292 ˚C. This existence of this peak can be ascribed to the nucleation of either nickel from the amorphous matrix or the structural relaxation of the matrix. Whereas the second exothermic peak located at about 482 ˚C can be attributed to the formation of Co_3B phase in the Ni-B matrix [69].

Wang [97] studied the effect of heat treatment on structural and magnetic properties of ternary Ni-Co-B coatings. The results indicate that these coatings are amorphous in their as deposited state. However, the crystal structure experiences phase change that leads to the nucleation of Ni_3B and Ni–Co phases when heat treated at 350 ˚C. The effect of heat treatment on the magnetic properties indicates the saturation magnetization and the residual magnetization of the coating increases with increasing heat treatment temperature (50 ˚C to 600 ˚C) [97].

The effect of heat treatment on microhardness indicates that the microhardness of the Ni-Co-B alloy coatings initially increases with increasing temperature reaching its maximum value at 350 ˚C and thereafter decreases with further increase in temperature. The initial improvement in hardness can be attributed to the nucleation of Ni_3B and Ni–Co phases into the matrix which improves the hardness. However, beyond 350 ˚C grain coarsening of the nucleated phases occurs and the hardness decreases [97].

A comparison of surface morphology of Ni-Co-B ternary alloy coatings in their as deposited and at heat treated (600 °C) states indicates that in as deposited state the coating consists of compact particles with the diameter of about 20.0 nm. The TEM diffraction pattern of coating in as plated condition confirms the amorphous nature of the coating. However, their heat treatment up to 600 °C results in significant change in shape and increase in size (50 nm). These changes are closely related to transformation of amorphous structure into crystalline [97]. A close comparative analysis of the magnetic hysteresis curves for Ni-Co-B coatings in as-deposited and under different heat treatment temperatures shows that the saturation magnetization and the residual magnetization increases as the temperature is increased from 50 °C to 600 °C [97].

The corrosion behavior of Ni–Co–B coated carbon steel, Al 6061 alloy and 304 stainless steel in 0.5M H_2SO_4 at 60 ˚C indicates that corrosion resistance of Ni–Co–B coating is higher than that of the uncoated carbon steel and 304 stainless steel. The corrosion potential (E_{corr}) of Ni-Co-B coatings is found to be more nobler as compared to the substrates [116].

3.2.2 Ni-P-B ternary alloy coatings

A limited number of reports on synthesis and characterization of ternary electroless Ni-B-P are available. Venkatakrishna et al. [110] deposited electroless Ni-B-P on copper and stainless steel substrates and studied their properties. Importantly, the plating bath consists of dual reducing agents to deposit both “P” and “B” on the surface of the substrates. It is reported that the plating rate increases with increasing amount of borohydride. This is due to the reason that borohydride is a good reducing agent and hence it enhances the rate of reaction. It is also noticed that electroless Ni-B-P coatings have cauliflower surface morphology similar to binary Ni-B coatings and the size of the nodules increases with increase in concentration of $NaBH_4$ [110]. Analysis of X-ray diffraction spectra of electroless Ni-P-B coatings in as plated condition containing different boron contents shows that (111) peak of nickel as a major peak approximately located at 40-50º (2θ). It is further found that increase in boron content broadens Ni (111) peak indicative of an amorphous behavior [110]. The response to heat treatment of electroless Ni-B-P coatings having different boron contents is also found almost similar to binary Ni-B coatings. It is reported that the hardness increases up to a certain temperature and thereafter begins to decrease. This decrease can be attributed to the phenomena of grain coarsening at high temperatures. The peak hardness of coatings is found to be a function of boron contents [110].

3.3 Duplex coatings (Ni-P/Ni-B)

In recent years, deposition of two layers having different corrosion potential (E_{corr}) has emerged as an attractive way to enhance the anti-corrosion properties of many types of substrates. Owing to the combined effects of improved corrosion resistance and decent mechanical properties, the multilayer coatings or duplex coatings are gaining considerable attention [70, 117].

Duplex coatings of Ni-P/Ni-B have been deposited on different substrates like mild steel [70], magnesium alloy (AZ91D) [117] and aluminum alloys [111] by dual coating baths and their characteristic properties such as hardness, wear and corrosion have been investigated. Wang et al. [117] deposited the Ni-P/Ni-B duplex coatings on magnesium alloy. For deposition of Ni-P coating, they used an acidic bath to have high "P" contents to improve the corrosion properties and borohydride alkaline bath to deposit Ni-B coatings to improve wear resistance. The XRD spectra of substrate, electroless Ni-P coating and duplex Ni-P/Ni-B coatings in as-plated and heat treated conditions indicates that the structure of Ni-P coating in as-deposited is amorphous. Similarly, the diffraction pattern of the as-plated electroless Ni-P/Ni-B deposits shows also a single broad peak confirming the amorphous nature of the duplex coatings in their as deposited state. However, heat treatment of Ni-P/Ni-B coatings at 350 ˚C for 2 h results in the transformation of amorphous to crystalline structure and the nucleation of nickel borides (Ni_3B) in the duplex coatings [117]. The transformation of amorphous to crystalline structure of duplex coatings upon heat treatment has also been reported by other researchers [70, 111].

A comparison of microhardness of Ni–P, Ni–B and the duplex coatings deposited on steel substrate in their as deposited and heat-treated states indicates that the microhardness is higher for coatings subjected to heat-treatment than those in as deposited state. This improvement in hardness can be attributed to the precipitation of hard particles such as nickel phosphide phase (Ni_3P) and nickel boride phase (Ni_3B) in Ni-P and Ni–B matrices respectively. The presence of Ni_3P and Ni_3B in the structure has also been confirmed by XRD. It is further noticed that the microhardness of duplex coatings is higher than that of Ni–P and Ni–B coatings of similar thickness, both in as-plated and heat-treated conditions [70,117].

Electroless Ni-P coatings in as deposited state have "cauliflower" structure. In the next step, formation of subsequent Ni-B coating on Ni-P layer induces more smooth surface morphology and good uniformity into the final coating. The presence of spherical nodules in the SEM image of the duplex coatings after heat-treatment confirms the formation of precipitates of Ni_3P and Ni_3B into the structure. The presence of some pores in the coatings has been ascribed to the hydrogen evaluation [117].

A comparison of specific wear rate of electroless Ni–P, Ni–B and the duplex coatings having the same thickness, at an applied load of 40 N in both as deposited and heat-treated (450 ˚C for 1 h) states indicates that coatings subjected to the heat-treatment process have better wear resistance than the as-plated ones due to the precipitation of hard phases (Ni_3P, Ni_3B) into the structure. Furthermore, duplex coatings have better wear resistance as compared to Ni–P and Ni–B coatings having same thickness in as deposited and heat-treated states. This can be attributed to the higher hardness of the Ni-B coating as compared with Ni-P [70]. Similar studies have also been under-taken by Vitry et al. [111] and concludes that there is significant improvement in wear behavior after heat treatment process.

The corrosion behavior of duplex coatings (Ni-P/Ni-B) deposited on magnesium alloy [117] and aluminum alloy [111] and mild steel [70] has been reported in the literature. A comparison of E_{corr}

and I_{corr} for Ni-P, Ni-B and Ni-P/Ni-B coatings indicates that duplex coatings (Ni-P/Ni-B) are more corrosion resistant and combat the corrosion phenomenon. This can be regarded as the effect of preferential corrosion of outer Ni-B layer which changes the corrosion mechanism from longitudinal pinhole to extended transverse corrosion [117]. The corrosion behavior of Ni-P/Ni-B coating deposited aluminum alloy in 0.1M NaCl solution suggests that the corrosion resistance of the duplex coating increases after heat treatment (180 ˚C, 4 hr) which may be attributed to the densification of the coating as there is no phase transformation occurred at this temperature. The more detail about the results of EIS study can be found somewhere else at [111].

The above study reveals that electroless nickel duplex coatings can fulfill the requirements of both Ni-P and Ni-B coatings. If higher hardness and wear resistance are the final desired properties, then the duplex coatings containing with an outer coating of Ni–B followed by inner Ni-P coating will be the most appropriate choice. However, if high corrosion resistance is the main objective then an outer coating of Ni-P followed by an inner Ni-B coating will be the most suitable combination[70, 111, 117].

3.4 Ni-B-X composite coatings

The addition of insoluble, hard second phase particles into electroless nickel coating baths has led to the development of unique composite coatings with amazing properties. Usually, Ni–B alloy matrix synthesized either through electrodeposition or electroless possess has high hardness and impressive wear resistance. Owing to its decent inherent properties, Ni-B is regarded as quite suitable to add insoluble and hard second phase particles into to it for the purpose of improvement of properties of binary Ni-B coatings. Studies on electrodeposited Ni-B and electroless Ni–B-based composite coatings are rather limited [94, 95, 118,119]. Since this review article is addressing the electroless Ni-B coatings, we will here mainly focus on electroless Ni-B composite coatings.

3.4.1 Ni-B-diamond composite coatings

Kaya et al. [98,118] reported a new formulation of Ni-B-diamond (Ni-B-C) coating to improve hardness and wear properties of Ni-B coatings. After successful deposition of Ni-B coating on plain carbon steel (AISI 1040), nano-sized diamond (C) particles were dispersed into Ni-B matrix through electroless coating process to form Ni-B-C coatings. In this study, five different electroless composite Ni-B coatings having different diamond contents were developed. The experimental detail can be found somewhere at [98, 118]. SEM images of Ni-B and Ni-B-C coatings after heat treatment exhibit nodular structure. This structure improves lubricious properties and thus increases the wear resistance. The SEM images also reveal agglomeration of diamonds particles and some porosity in the microstructure. A comparison of microhardness of uncoated steel substrate, Ni-B and Ni-B-C composite coating in as plated and heat treated conditions indicates that the hardness of binary Ni-B coatings is about 810 HV_{100} which is an extraordinary microhardness in as deposited state. The steel substrates coated with Ni-B binary coatings are found 2.7 times harder than without coating. It is also reported that the addition of diamond particles into Ni-B matrix does not much contribute in hardness improvement in as deposited state. However, after heat treatment, there is significant increase in hardness of Ni-B matrix containing diamond particles. It is observed that suitable amount of diamond particles and appropriate heat treatment temperature may lead to the precipitation of crystalline nickel and nickel boride which remarkably improves the hardness of the composite coating [98,118].

A comparison of the average values of coefficient of friction for steel substrate, electroless Ni-B binary and Ni-B-diamond composite coatings after heat-treated condition indicates that Ni-B and Ni-B-diamond composite coatings have high coefficient of friction and thus are not effective to minimize frictional properties. The reason of high friction coefficient is the oxide formation during the wear test and that is why the coefficient of friction increases with oxide contents. However, if we compare the wear area of electroless Ni-B coating with Ni-B composite 2-5 gr coating, it can be noticed that the composite coating has much improved performance. The above results indicate that the addition of diamond particles into the Ni-B matrix increases hardness, adhesion, reduces tribochemical oxidation and improves wear resistance [98,118].

3.4.2 Ni-B-Si_3N_4 composite coatings

Krishnaveni et al. [119] deposited electroless Ni-B and Ni-B-Si_3N_4 composite coatings on mild steel substrate using an alkaline borohydride-reduced bath. They have noticed that the amount of incorporation of Si_3N_4 particles into Ni-B matrix linearly increases with increasing concentration of Si_3N_4 in the coating bath (Si_3N_4 is 10 g/L in the coating bath).This can be regarded as the effect of accumulation of higher particle flux adjacent to the electrode surface. The level of incorporation of Si_3N_4 particles reaches a maximum of 2 wt% at 10 g/L, beyond which it decreased despite a continuous increase in its concentration up to 25 g/L. This can be regarded as the effect of agglomeration of Si_3N_4 particles and evolution of a large amount of hydrogen which forces he Si_3N_4 particles away from the substrate surface [119].

The SEM analysis of Ni-B-2 wt% Si_3N_4 composite coating reveals that Si_3N_4 particles are uniformly distributed in the Ni-B matrix and the presence of Si peaks in the corresponding EDX pattern confirms the incorporation of Si_3N_4 particles into the Ni-B matrix. The existence of boron cannot be traced out with accuracy due to its low atomic number [119].

The XRD pattern of Ni-B-2 wt% Si_3N_4 composite coating is very similar to those of binary Ni-B coating both in as deposited and heat-treated conditions. These show a single broad peak confirming amorphous structure in as deposited state and nucleation of some phases upon heat treatment. This observation indicates that the addition of Si_3N_4 particles has no significant effect on the structure, grain size of binary Ni-B matrix in as deposited and even after heat treated states [119].

A comparison of microhardness of binary and in their as deposited states shows that Ni-B-2 wt% Si_3N_4 composite coatings have $632 \pm 17 HV_{0.1}$ hardness while the binary Ni-B coatings have lower hardness 570 ± 14 $HV_{0.1}$. The higher hardness of Ni-B-Si_3N_4 composite coating can be attributed to the combined strengthening effect of solid solution hardening and dispersion hardening. An analysis of variation in hardness of Ni-B and Ni-B-Si_3N_4 composite coatings as a function of heat-treatment temperature indicates that no significant increase in hardness is noticed for both Ni-B and Ni-B-Si_3N_4

composite coating when heat treated at 200 ˚C for 1 h. However, with further increase in temperatures, a rapid increase in hardness is observed. This increase in hardness can be attributed to double strengthening effect; particle strengthening of the hard Si_3N_4 particles and precipitation strengthening due to Ni_3B and Ni_2B phases. The hardness versus heat treatment temperature curve of Ni-B-Si_3N_4 is found similar to binary Ni-B. The first maximum at 350 ˚C is due to the formation of Ni_3B phase while the second maximum observed at 450 ˚C is due to the precipitation of Ni_2B phase into the microstructure [119].

A comparison of the specific wear rate of binary Ni-B and Ni-B-Si_3N_4 composite coatings in their as deposited and heat-treated states shows that wear rate is relatively less for the composite coating. In addition, the specific wear rate is relatively less for heat treated coatings compared to the as-plated ones. The extent of decrease in specific wear rate by the addition of Si_3N_4 particles in the Ni-B matrix is 11% in as deposited state whereas for coatings heat treated at 350 ˚C and 450 ˚C for 1 h, the specific wear rates are 13% and 17%, respectively. The improvement in wear properties after heat treatment is due to particle strengthening and precipitation hardening as stated earlier [119]. A comparison of corrosion behavior (I_{corr} and E_{corr}) of binary Ni-B and Ni-B-Si_3N_4 composite coating in 3.5% NaCl suggests that the corrosion resistance of Ni-B and Ni-B-Si_3N_4 composite coatings is not appreciable in as-plated and even under heat-treated conditions [119].

4. INITIATION AND GROWTH MECHANISMS OF ELECTROLESS Ni-B COATINGS

Many mechanisms for the development of Ni-B coatings were proposed but all of those were not experimentally confirmed. Firstly, Gorbunova et al. [99] has shown through their experiments that Ni-B coating formation mechanism is based upon the catalytic decomposition of reducing agent. Later, Vitry et al. [67, 100] has published their experimental results which nicely clarifies the initiation and growth mechanism of Ni-B coatings. According to their experimental findings, the two possible mechanisms for the initiation of deposition of electroless nickel–boron coatings on steel substrate are: (i) A very thin coating of nickel is formed on the surface of the substrate due to displacement (redox) reaction with the substrate without any interference of the reducing agent. This reaction is associated with dissolution of small amount of the substrate (ii) The catalytic activity of the substrate facilitates the oxidation of the reducing agent (sodium borohydride) and the subsequent reduction of nickel salts forms a thin nickel layer on the substrate surface [100].

V. Vitry et al. [67, 100] has experimentally confirmed that oxidation of the borohydride ion by the catalytic activity of the substrate surface is the main factor for coating initiation as they could not detect any nickel present in the coating in a bath without reducing agent. The initiation of coating was studied by immersing the mild steel sample into the coating bath for different periods of time. It is found that immersion time shorter than 15 s in the coating bath has not resulted in the formation of coating. This shows that the induction period is in the order of 5–15s. After 15s, a few nodules are formed on the substrate surface favourably on the scratches and surface defects present on the substrate. After 30s, the entire substrate surface is covered with several nodules. However, it is noticed that at this stage, the deposited nickel layer is not yet continuous having nodules size in the range of

0.1 and 0.2μm. After 60 s, the nodules starts growing bigger and the nickel layer becomes almost continuous. The EDX analysis also confirms the presence of nickel on the steel substrate surface [67,100].

The size of the nodules is further increases as the immersion time is increased from 90 s to 4 min and a uniform layer is formed. The coating top morphology remains unchanged after 7 min, however, refinement of nodules size is observed after 10 min which is continued up to 30 min with an increase in thickness and improvement in uniformity of the coating. After 1 h, the inter-columnar spaces are almost completely filled out with small nodules leading to the formation of a clear typical cauliflower structure. We can thus conclude that the mechanism of initiation of electroless Ni-B coating is based on catalytic activity of the substrate surface but not a displacement reaction between nickel and iron. The different steps of the deposition process can be summarized as follows [67, 100]:

1. A short induction period during which no nodules are formed although small amount of some nickel is deposited on the substrate surface.
2. A thin continuous layer is formed on the substrate surface.
3. Nodules are formed on the substrate surface.
4. The compaction of the developed coating.
5. Nucleation/growth of phases at various spots on the substrate leading to the refinement of the columnar structure.

5. PARAMETERS CONTROLLING ELECTROLESS Ni-B COATING PROCESS

Both the experimental [60, 67, 71, 72, 90, 93, 98, 99, 106] and computational [80, 81, 83] studies have been conducted to optimize the effect of various coating parameters to improve the properties of the electroless Ni-B coatings. This section briefly summarizes the effect of different coating parameters on the properties of electroless Ni-B coatings.

5.1 Substrate surface

Electroless nickel coatings are sensitive to the surface of the substrate. Therefore, the surface roughness of the substrate has a significant influence on the morphology, hardness and wear properties of the coating [55]. The surface preparation of the substrate varies considerably with the composition of the substrate. The surface preparation techniques for mild steel [67, 91, 100], copper [71, 91], magnesium alloy [117] and aluminum alloys [78, 111] are entirely different from each other. Vitry et al. [67, 100] studied the effect of substrate roughness on the initiation and formation mechanism of electroless Ni-B coating on mild steel. They prepared the substrate surfaces using different grades SiC grinding paper to induce different roughness. A close analysis of their study reveals that after a plating time of 5s, the increase in substrate roughness facilitates the initiation of coating on the substrate. The density of nickel nodules increases with increasing roughness of the substrate. Moreover, the size of the nodules decreases with the increase in roughness and a nodule size of 50 nm is noticed on the unpolished surface. This shows that high roughness of the substrate surface facilitates the nucleation of the nickel nodules.

After an immersion of 15s, the density of nickel nodules is still decreasing with decreasing roughness. However, the size of the nodules appears homogeneous on all the samples and is size ranging to 50 nm. After 30 s, the surface of the samples is nearly completely covered by the nickel nodules having similar size as for 15 s [100]. After 60 s, all the samples are completely covered with coating. However, it is noticed that substrates with high Rp yields more homogeneous coatings. Exposing substrates longer in the coating bath results in homogenization and densification of the coating. It is pertinent to mention here that nodules are still in the same size range (50 nm), however, they tend to form aggregates which can be distinctly seen on low magnification as compared to nodules which are only visible at high magnification [100].

5.2 Nickel ion concentration

Nickel ion concentration has a significant influence on the thickness of the coating or the deposited mass. Rios et al. [93] deposited Ni-B coatings on stainless steel substrate through electroless nickel coating process using DMAB as reducing agent and ($NiSO_4.6H_2O$) as a metal source. They report that concentration of Ni^{+2} ions generally increases the thickness, deposition rate and boron content in the coating. On the other hand, Oraon et al. [81] also studied the effect of nickel source on the deposit thickness using sodium borohydride ($NaBH_4$) as a reducing agent and ($NiCl_2.6H_2O$) as a metal source. Their study indicates that there is an optimal nickel concentration after which the coating thickness starts decreasing for all immersion times.

5.3 Complexing agent

The effect of complexing agent on deposition rate and boron content of Ni-B coating was studied by Saito et al. [76]. They employed different complexing agents like sodium tartrate ($Na_2C_4H_4O_6.2H_2O$), sodium citrate ($Na_3C_6H_5O_7.2H_2O$), sodium malonate ($Na_3C_3H_2O_4.H_2O$) and succinic acid ($C_4H_4O_6$). They used DMAB as reducing agent and $NiSO_4.6H_2O$ as metal source. Their results indicate that the complexing agent has an important role on the deposition rate of N-B coating. It is reported that complexing agents having smaller stability constant to nickel ion result in higher deposition rates. The deposition rate of nickel coating decreases with increasing amount of complexing agent. The increase of Ni-B deposition rate can be explained by the buffering action of complexing agent inhibiting the pH change in the reaction layer. The acceleration effect is pronounced in the case of complexing agent having low stability constant. The deposition rate of Ni-B coating decreases by the presence of excessive complexing agent which decreases the amount of free nickel ion. The boron content of the Ni-B coating varies in the range 3 to 6 wt% as a function of complexing agent. It is further reported that the boron content decreases with increasing coating deposition rate [76]. Gorbunova et al. [99] also studied the effect of different molar ratio of ethylenediamine (EDA) and studied its effects on amount of Ni-B deposited and stability of the solutions. Their findings indicates that initially both the amount of deposit and solution stability increases with the increase in molar ratio of complexing agent (EDA). However, further increase in molar concentration of complexing agent (EDA) has a negative effect.

5.4 Reducing agent

Many reports have been published showing the effect of reducing agent on boron content [76], deposition rate [76, 81, 99], stability of the bath [99] and thickness of the deposit [60]. The coating formation rate and boron content increases with increasing concentration of reducing agent (0.025 to 0.10M). The boron contents also increases as the amount of reducing agent increases; however, it reaches to its limiting value at concentrations higher than 0.075M. Baskaran et al. [71] concludes that the deposition rate increases with the increasing concentration of $NaBH_4$ in the coating bath. Oraon et al. [81] (Fig. 49 (c)) has shown that the deposition rate increases with the increase in amount of $NaBH_4$ and reaches to a limiting value at concentration higher than 1.0 g/litr. Similarly, Gorbunova et al. [99] has shown that the plating rate increases with the increase in the amount of $NaBH_4$ in the coating bath but at the same time the stability of the bath also decreases.

5.5 Bath stabilizer

The selection of an appropriate stabilizer is very important. In spite of use of the most effective complexing agent, the solution shows insufficient stability without use of an appropriate stabilizer in suitable amount [99]. Rios et al. [93] studied the effect of concentration of stabilizer on the thickness of the coating, deposition rate and boron contents in the deposited coatings. It is reported that the thickness of Ni-B coating is less sensitive to concentration of stabilizer. The deposition rate increases with the increase in the amount of stabilizer approaching to its saturated value and thereafter deceases. It is also noticed that the boron contents decreases with the increase in concentration of stabilizer.

5.6 Bath temperature

The effect of solution bath temperature on the properties of electroless Ni-B coatings has been studied extensively. Delaunois et al. [60] studied the effect of bath temperature on deposition of electroless Ni-B coatings on aluminum alloy using borohydride coating bath. It is concluded that the thickness of the Ni-B coating increases almost linearly with the increase in the bath temperature. Gorbunova et al. [99] has also reported that deposition rate of electroless Ni-B coating increases with the increase in bath temperature. Oran et al. [81] has also shown in their study that coating deposition rate increases linearly with the increase in bath temperature for relatively smaller immersion time. However, for all other studied immersion time periods the deposition rate shows a saturation trend with the increase in bath temperature and thereafter it decreases with the increase in bath temperature.

Hamid et al. [90] also studied the effect of solution bath temperature using acidic bath (DMAB). They immersed steel and copper substrates into the coating bath at 60 ˚C and 80 ˚C temperature for different time periods. It is reported that higher coating deposition rate is achieved at high coating bath temperature (80 °C) as compared to lower temperature (60 °C) for both steel or copper substrates. It is reported as well that the deposition rate of electroless Ni–B coatings on steel substrate is higher than that on copper substrate. It is also noticed that the deposition rate does not have a linear relationship as a function of plating time and it decreases with increasing time. The decrease in the DMAB concentration with time and formation of oxidation products in electroless plating baths may be a possible reason for this phenomenon [90].

5.7 pH of the coating bath

Saito et al. [76] studied the effect of pH on Ni-B and Co-B coatings. The deposition rate and boron content of the alloys were measured as a function of pH of the solution. It is reported that the deposition rate of electroless Ni-B and Co-B coatings increases with increasing pH of the solution and the oxidation of DMAB is enhanced. However, pH of solution has negligible effect on boron contents of Ni-B coatings. In this case, a reverse relationship between the boron content and the deposition rate of Ni-B is noticed. A study on Ni-Co-B coatings by Narayanan et al.[69] indicates that pH of the bath initially increases the plating rate of coating and reaches to a saturation value (300 mg/dm^2/hr) at about pH 8 and thereafter increase in pH value rapidly decreases the plating rate.

5.8 Immersion time

Due to the auto catalytic nature of the electroless Ni-B coating process, the immersion time of the catalytic surface has significant influence on the thickness of the coating and the plating rate [60]. Delaunois et al. [60], Vitry et al. [67, 100] and Oraon et al. [81] etc have studied the effect of immersion time on the thickness of electroless Ni-B coatings. It is reported that the coating thickness increases with the increase in immersion time. Without bath replenishment (restoring the bath composition), initially, the deposition rate is constant up to 2 hrs and thereafter the deposition rate decreases rapidly at longer time. Oraon et al [81] has also observed that the coating thickness increases with increasing deposition time for all concentrations of reducing agent. Vitry et al. [67, 100] reports that initially (up to 4min), the thickness of coating increases very quickly (with a growth rate exceeding 40µm/min). Between 4 and 7min of deposition, the thickness of the coating does not increase because of the densification process. After this, a quasi linear increase in thickness is observed for up to 1 h of immersion with an average growth rate approaching to 18mm/h.

5.9 Bath Loading

During electroless Ni-B coating process bath loading is also important which influences the deposition rate of the coating. Oraon et al. [81] studied the effect of mass loading on the deposition of the Ni-B coating. They report that the more coating mass is deposited on sample having low bath loading mass for all period of immersion time.

5.10 Bath agitation

Uniform coating and good dispersion of the ceramic particles in the coating bath solution requires appropriate agitation of the solution. The effective bath agitation has been achieved by many ways like dynamic agitation, air injection or ultrasonic vibration. In addition, surfactants are also often used in conjunction with bath agitation to keep the powder particles in suspension. Normal agitation of bath is usually insufficient to keep the nano or micro particles suspended in the solution due to large surface areas. The high surface energy of second phase particles usually results in particle agglomeration in the final composite coatings and thus inferior properties. Combinations of the different agitation techniques may also be employed to minimize the chances of particle agglomeration[61, 63, 120, 121].

5.11 Bath Replenishment

Delaunois et al. [60] have reported that with the increase in immersion time, the thickness of the coating increases. However at the same time the concentration of reducing agent ($NaBH_4$) also decreases which reduces the deposition rate. Bath replenishment with reducing agent ($NaBH_4$), stabilizer (thalium nitrate) after certain time period (30 min) enables to maintain relatively constant deposition rate (25µ m/h) with the elapse of immersion time. It is further reported that bath replenishment results in thick coating. This high constant deposition rate is very useful for the industry to coat large objects with thick and uniform coatings [60].

6. POST DEPOSIT TREATMENTS

The properties of synthesized electroless coatings can be further improved/modified by post deposit treatments. The most usual reported post deposit treatment is the heat treatment process (annealing). However, some special surface treatments like nitriding are also found in the literature. This section briefly describes the effect of heat treatment and nitriding on mechanical and corrosion behavior of electroless Ni-B coatings.

6.1 Heat treatment

Heat treatment is a process in which metals and their alloys are thermally acted upon so as to change their structures and properties in the desired direction. This process is considered to be the most eminent and fundamental process to modify the properties of many materials including electroless Ni-B coatings. A promising number of reports are available addressing the effect of heat treatment temperature on structure, mechanical, magnetic and electrochemical properties of electroless Ni-B coatings [60, 70, 71, 72, 76, 78, 81, 83, 89, 90, 91,93,96,99,106, 107, 110, 111]. Electroless Ni–B coatings undergo phase transformation upon heat-treatment. Baskaran et al.[71] conducted DSC study of electroless Ni–B coatings containing different amount of $NaBH_4$ in the temperature range from 50 to 510 ˚C at heating rate of 10 ˚C/min. They report that number and position of exothermic peaks are sensitive to the composition of the coatings. It is well known that the phase transformation of electroless Ni–B coatings is a function of the boron content. Ni-B electroless coating with 4.3% (wt.%) exhibit three exothermic peaks at 305, 405 and 425 ˚C while coating with 6.4% boron content show two exothermic peaks at 300 and 420 ˚C[71].

The formation of exothermic peaks in DSC study is due to the formation of some crystalline phases which has also been confirmed through XRD. Ni-B electroless coatings are usually amorphous in their as synthesized condition. However, these are transformed to crystalline structure when subjected to proper heat treatment process [60, 71, 123, 91, 106]. The XRD spectra reveal that the sample annealed at 300 ˚C is composed of a broad peak and some sharp peaks confirming the presence of mixture of amorphous and crystalline phases. However, XRD spectra of samples annealed at 350 and 450 ˚C confirm the existence of three phases, Ni, Ni_2B, and Ni_3B. A comparison of DSC and XRD results confirms that the exothermic peak present in the sample heart treated at about 300 ˚C for 1 h is due to the formation of Ni_3B phase. However, the other exothermic peaks observed at 405 and 425 ˚C can be ascribed to the precipitation of either Ni_7B_3 phase or Ni_2B phase respectively [71, 93]. Similar observations have also been made by many other researchers [76, 99, 106].

Narayanan et al. [91] studied the effect of heat treatment temperature on structure and morphology of electroless Ni-B coating. A comparison of TEM images of electroless Ni-B coatings in as plated condition and under annealed conditions (325 ˚C and 450 ˚C) confirms the amorphous nature of the deposit in as plated condition. However, bright field images and SAD patterns confirm the transformation of amorphous crystal structure to crystalline and increase in grain size with increasing annealing temperature. It is also noticed that the annealing of Ni-B coatings above 450 ˚C results in crystalline nickel and conversion of Ni_2B phase to the more stable Ni_3B phase [91].

The properties of electroless Ni–B coatings are highly influenced by the heat treatment process. It is reported that at low heat treatment temperature (200 ˚C) there is no appreciable improvement in the hardness of the coatings. However, with further increase in temperatures, there is rapid increase in hardness. In fact, heat treatment temperature versus hardness curve clearly shows two maxima located at 350 ˚C and 450 ˚C. However, a decline in hardness value is observed with further increase in temperature (> 450 ˚C). The increase in hardness of Ni-B coatings is mainly attributed to the precipitation of nickel borides (Ni_3B and Ni_2B). The decline in hardness at temperatures above 450 ˚C can be presumably regarded as the effect of grain coarsening of nucleated phases [72]. Gorbunova et al. [99] have also reported a the same trend of change in hardness of electroless Ni–B coatings with heat treatment temperature.

A comparison of specific wear rate of electroless Ni–B coatings under different loads and heat treated conditions indicates that wear rate of coatings (as plated and heat treated) increases with increasing applied load. It can be further reported that wear rate of heat treated coatings is relatively smaller as compared to the as plated coatings. The improvement in wear behavior after heat treatment process can be attributed to the nucleation of hard nickel boride phases into the Ni-B matrix [72].

A comparison of corrosion potential (E_{corr}) and corrosion current density (i_{corr}) of electroless Ni-B coatings, both in as-plated and heat-treated (450˚ C/1 h) conditions in 3.5% NaCl clearly indicates that coatings in their as deposited states show higher corrosion resistance as compared to the heat treated condition. This confirms that the amorphous structure of coatings improves the corrosion resistance while crystalline structure induced due to the heat treatment process lowers the corrosion resistance. The decrease in corrosion resistance because of crystalline structure can be attributed to the increase in the number of grain boundaries which are considered as the active sites for corrosion attack. It can be further noticed that the corrosion resistance of electroless Ni-B coating is relatively inferior to that of high phosphorous electroless nickel coatings. The high corrosion resistance of Ni-P coatings as compared to Ni-B coatings can be ascribed to the formation of more stable and amorphous passive layer [91].

6.2 Nitriding treatment

Nitriding is an appropriate heat treatment process employed to modify the properties of a variety of metals and alloys. During this process nascent nitrogen is diffused into the structure of metals/alloys. Vitry et al.[82] deposited the electroless nickel–boron coatings on mild steel substrate and then subjected these coated samples to the nitriding treatment to study the effect of nitriding on the structure, mechanical (hardness and wear) and electrochemical properties. A comparison of SEM micrograph of the coatings before nitriding treatment, after vacuum nitriding and after ammonia nitriding reveals the formation of typical columnar morphology of Ni–B coatings. It is also noticed that nitriding treatment makes the coating structure slightly dense. Furthermore, the ammonia nitriding coatings exhibit a compact inner coating followed by a porous outer layer (white layer) representative of typical dual structure.

A comparison of the hardness of Ni-B coatings when subjected to different classic heat treatment, vacuum nitriding and ammonia nitriding indicates that the Vickers Hardness of Ni-B coatings after classical heat treatment process (400 ˚C, 1 hr) is around 1250 HV_{100}. However, there is significant increase in the hardness after vacuum nitriding (1600 HV_{100}) due to diffusion of nitrogen into Ni-B matrix. As a comparison amona nitriding imparts the most increase in hardness [82].

A comparison of potentiodynamic polarization graphs of steel substrate, electroless Ni-B coatings and nitrided Ni-B coatings indicates that the deposition of Ni–B coating on the steel substrate improves its corrosion resistance as the value of E_{corr} is less negative and the corrosion rate I_{corr} is lower on the coated sample than on plain steel (substrate). This study also reveals that heat treatment of Ni-B coatings further improves the corrosion resistance in contrast to the results of Narayanan et al. [72]. The improvement in anticorrosion properties after heat treatment process can be attributed to improvement in cathodic polarization current because of relatively high over potential value for the cathodic reaction. The corrosion behavior of nitrided Ni-B coatings also indicates that anticorrosion properties of coatings can be further improved by nitrding due to diffusion of nitrogen into the Ni-B matrix [82].

7. APPLICATIONS OF ELECTROLESS Ni-B COATINGS

Electroless nickel coatings are quite attractive because of their promising properties such as uniform thickness, excellent corrosion resistance, good wear and abrasion resistance, good solderability, high hardness, low coefficient of friction, high reflectivity, low resistivity and good magnetic properties. These coatings are well suited to develop coatings on nonconductive materials such as plastics. Electroless nickel coatings has gained considerable commercial importance to improve the surface properties of a large variety of metals which includes steel, aluminum, copper, magnesium alloys, plastics and many others [54, 60]. Electroless nickel coatings have succeeded to find their applications in many industries like petroleum, chemical, plastic, optics, aerospace, nuclear, electronics, computer, automotive, electronics, textile, paper, food and printing [83, 89].

As a comparison electroless nickel–boron coatings are not popular as electroless Ni and Ni-P coatings. However, the properties of electroless Ni-B coatings are quite promising and in some respect superior to Ni-P coatings such as high hardness (around 750 HV_{100} in the as-deposited state), good wear resistance. The hardness of Ni-B coatings is higher than too steels and wear resistance is better than hard chromium coatings. Electroless Ni-B coatings have uniform thickness and excellent solderability. At the same time their typical cauliflower has ability to retain lubricant and thus significantly improves the wear properties. The ability of electroless Ni-B coatings to undergo structural changes upon heat treatment process enabling them to improve further their properties is their amazing characteristic. Electroless Ni-B coatings have also moderate anticorrosion properties. Above all, deposition of uniform and relatively thick electroless Ni-B coating through bath replenishment is an added advantage which can be of great value for mass production in industries. Owing to the above characteristics and properties, electroless nickel–boron coatings are attractive for many industries such as food, petroleum, petrochemical, chemical, plastics injection, optics, aerospace, fire arms, automotive and electronics industries [60, 67,70, 71,80, 82, 85, 90, 100, 110].

8. CONCLUSION

This review article precisely describes the important developments made so far in the field of electroless Ni-B coatings. Electroless Ni-B coatings have attractive properties such as uniform thickness, decent corrosion resistance, good wear and abrasion resistance, good solderability, high hardness, low coefficient of friction, high reflectivity, low resistivity and good magnetic properties. Furthermore, their inherent properties can be further improved either by the addition of alloying elements, second phase particles or by the process of heat treatment and nitriding which make them suitable for surface modification of a large number of materials like steel, aluminum, copper, magnesium alloys, plastics etc. Owing to their promising mechanical properties (hardness, wear), magnetic and decent electrochemical properties (anticorrosion), the electroless Ni-B coatings are considered attractive for food, petroleum, petrochemical, chemical, plastics injection, optics, aerospace, fire arms, automotive and electronics industries.

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