



A Review on Hardness and Anti Corrosion Behavior of Steel Substrate By Electroless Coating of Ni-P and Ni-P-B₄C

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ABSTRACT

Metallic materials are very important component for many engineering works. Nowadays it is seen that these metallic materials get affected very easily by various environmental species such as chloride, sulfur, moisture present in our surrounding etc and loose its strength and durability. Corrosion is one of the major problems associated to metallic materials which reduce its strength. For enhancement of metallic properties such as corrosion, hardness etc., electroless plating method of metallic substrate is considered as an effective approach to overcome from these types of problems. This paper gives a review of the various types of research which has been done in the field of deposition of Ni-P and Ni-P-B₄C on metallic or non-metallic substrate by electroless method to improve the engineering properties. The main focus of this review paper is to give a brief understanding about variation in the behavior of corrosion resistance and hardness of substrate after coating it by such types of nano particles. Boron carbide (B₄C) is a material which having some unique properties such as high hardness, better chemical resistance, higher melting point, neutral absorption and low density (2.52g/cm³). Due to these properties researchers attract towards B₄C and do many researches in this field. This review paper gives an idea about that.

Keywords: Electroless plating, Metallic substrate, Boron carbide (B₄C), Corrosion, hardness

1.INTRODUCTION

Metallic material such as steel is one of the most important engineering materials which are used in major construction projects. But corrosion is a major issue associated with the metallic materials which affect the strength and durability of structures. When metallic materials are come in contact with several environmental species then it start to come in its natural state and due to this corrosion may happened. The corrosion problem of steel can be addressed by coating its surface which would act as a barrier to prevent contact between corrosive materials and chemical compounds which is present in environment. However surface properties of metallic substrate may be an important aspect which decided its durability and applicability. Surface properties of metallic substrate can be described by its corrosion resistance behavior, surface hardness, wear and erosion resistance and antibacterial activity. Hence some physical or chemical modification is done on the surface of metallic substrate to get superior performance of steel structure or any other structure in which steel is used as a major component. Due to its excellent performance after coating it has been widely used in various important project works to attain a specific benchmark. Now a day there are many methods available to improve the exterior coating phenomenon some of them are heat treatment, surface hardening, surface coating etc. however for achieving better appearance, good physical and chemical properties and advanced functionalities against corrosion action or any other problems associated with metallic body, the surface coating has been considered as an important method with large acceptance in engineering works. Addition of micro or nano sized secondary particles on metallic materials (either in alloy or pure form), ceramic material, polymeric material and composite coating materials may result in enhancement the engineering properties such as strength and durability. Various methods available for purpose of deposition of nano materials on metallic or non-metallic substrate, but one of them which attract researchers is electroless coating process. This technique is base on the deposition of metal, alloy or a composite in by autocatalytic reduction of metallic ion from the salt solution containing a reducing agent happens on an activated surface. Now a day this method is most famous and most frequently used for coating of different types of substrate. In this method of deposition, the operation is take place by without any external source of electric current and that's why it is called electroless deposition process.

This paper reviews the articles related to enhancing the surface properties like corrosion resistance and hardness by incorporating nano-particles (B₄C) in the electroless Ni-P bath. After diamond and cubical boron nitride, B₄C is most hardest material having Vickers hardness value 2900 to 3900 kg/mm² and has very high melting point these properties is due to the highly covalent bond in its structure. The basic geometry of B₄C is, it contain

twelve atom which is in the form of icosahedral cluster bounded by direct covalent bond and these cluster of atom is located at the corner of a rhombohedral unit cell [1-2]. B₄C having low density (2.52 g/cm³), neutral absorption properties, and good chemical resistance, these unique properties make it important material in different research areas. Due to its excellent abrasion resistance properties B₄C is used in different important works such as making hot-pressed sand-blasting nozzles, ceramic tooling dies, dressing diamond tools etc. Because of its light weight and high hardness B₄C plays an important role in defence sector. If armor material and B₄C are used in combined form than the new material form by its combination is very effective to protect the military personnel and vehicles from ballistic attack. B₄C is also used as an absorbent for neutron radiation emitted from nuclear power plants in the form of control rod, shielding, and shut down pellets [3]. B₄C having lot of attractive properties, so due to these properties achieving high density component of it has been a challenging work. Even under typical compaction pressure it is difficult to deform B₄C particle because it is very hard. This hardness is due to its irregular particles arrangement. The surface particles of B₄C must be well smooth and regular in shape for easiest movement of particles with respect to each other and well arranged under the compaction condition. Since the particles are not smooth and also not arranged in regular manner so its re-arrangement and particle movement under compaction condition are difficult. B₄C having high melting point (2450°C) due to this it is difficult to sinter and due to high covalent bond, B₄C has low boron and carbon mobility. For achieving near theoretical density of B₄C is a very tough process. It is very difficult to achieve density higher than 75 to 80% for pure B₄C. Even at higher temperature (2300°C) theoretical density is not achieved. Hot isostatic pressing, pressureless sintering and hot pressing are most famous current technique which is very frequently used for produced B₄C component. Due to large number of special quality sometimes B₄C is less efficient in processing and cost increases. Some special types of additives such as TiB₂ [4, 5], TiO₂ [6] etc. have been added into B₄C matrix to achieving the density near to its theoretical density. However it was seen by many experimental works that due to the formation of second phase may degrade the mechanical performance. Hence based on mechanical and physical properties of B₄C, it has been studied mostly as a structural material. In current research field area the novel properties of B₄C in the functional material is going to be under developing and discovering stage. Whenever a thin layer incorporation of B₄C on the metallic substrate it should give better facilities on rearrangement of B₄C particles at the time of compaction and during sintering its species diffused. Due to these superior properties the substrate shows better corrosion resistance and good hardness.

Nickel coating on substrate is also shows some unique properties such as excellent wear and corrosion resistance, good lubricity and ductility, fantastic magnetic and electrical properties. Due to those extra-ordinary properties of nickel it is used extensively in coating. If electroless Ni-P is incorporated on metallic substrate with B₄C nano-particle then, it will show excellent surface properties of metallic substrate such as hardness and corrosion behavior. In this review paper a brief idea of performance of surface phenomenon of metallic or non-metallic substrate after incorporation of Ni-P coating and Ni-P-B₄C coating is well studied. Incorporation of these nano particles is done with the help of electroless plating method and the properties which are most focused are corrosion behavior and hardness performance of substrate.

2.LITERATURE REVIEW

Jin-Yih Kao(2021)-The study was carried out for understanding variation on the wear resistance, hardness, surface morphology, structural surface phenomenon of the electroless Ni-P coated substrate by using combination of different parameter of coated bath. The different combinations of bath parameters are such as the temperature of bath (60, 80 and 95°C), duration of deposition (10, 20 and 30 min) and pH value of solution (6, 7 and 8). It was seen by experimental results that at bath temperature 95°C, pH value of 8, and deposition time of 30 min showed minimum wear for the optimum combination coating parameters. Further, they investigated the structural changes of the coatings by method of X-ray diffraction (XRD) and also the elemental composition and surface morphology of coating surface was investigated by scanning electron microscope (SEM) and energy dispersive spectrometer (EDS). These properties were investigated before and after annealing treatment (100 ~ 700°C) in a vacuum ambient. The Ni-P films were subjected to annealing temperature at 400°C for 1 hour, leading to re-crystallization of the Ni matrix and the precipitation of Ni₃P. The hardness will increase with increasing tempering temperature to a peak of 960 HV at 400°C and so decreases monotonously [7].

K. Abdi-Alghanab,(2020)- worked on to found out the corrosion protection performance of the AM60B magnesium alloy substrate by deposition of LDH/Ni-P composite coating on it. He found that the LDH layer showed an excellent performance against the corrosion resistance when a layer of Ni-P coated LDH was immersed in 3.5 wt. % NaCl for 6 hr duration. Thus it is concluded that at the end of the immersion of substrate its corrosion resistance value is found to be about 93 kΩ cm². Since the chloride ions were trapped by the LDH layers, hence an excellent corrosion protection layer of the Ni-P coating was attributed. The value of surface roughness was found to be about Ra=199.7 nm which is very low, but the micro-hardness of the base alloy was promoted after the Ni-P plating [8].

S Vijay et. al. (2020) used two different types of metal substrate blends 601AC and 201AC for the comparison of experimental results. Mechanical Alloying technique (MA), a special technique which is used for the purpose of blending the metal powder. In this study B₄C which is a nano particle was used with Nickel coating and without Nickel coating as particulate. The average size of particles of B₄C which was selected for this experimental work was 20µm and 50µm. From the various experimental work's results clearly showed that number of layers influences the hardness and compressive strength of coated layer. It was found that the average specimen hardness increased from 55HV for two layered FGM and to 73HV for three layered FGM. Whereas the compressive strength was also shown an increment such as increase from 613MPa for three layered specimen without Ni coated B₄C to 732MPa for three layered specimen with Ni coating. Best possible combination of all parameters is observed from the experiment is particle size of 20µm, sintering temperature of 570°C, and B₄C particulate with Nickel coating. Whereas for the compressive strength 201AC matrix shows superior values as compared to 601AC for the best possible combination of all the other variables [9].

Xiou- Jia Liuet et. Al. (2019) – they investigated the microstructure and corrosion resistance behavior of magnesium alloy (AZ91D, 25×15×10 mm) substrate after deposition with Ni-P gradient coating/stannate conversion film. They made an observation on the behavior of corrosion and microstructure of coated substrate and found that the corrosion resistance of AZ91D alloy substrate was significantly improved when the stannate

conversion film and the Ni-P gradient coating were done on it by electroless coating method. They also found that with increasing P content the corrosion resistance was gradually enhanced, and the corrosion resistance of Ni-P gradient coating was better than stannate conversion film. In this coating approach of the electroless Ni-P coating substrate structure of its surface transitioned such as crystalline → microcrystalline → amorphous, on the basis of variation in P content such that increased from 3.31 to 12.58 wt% [10].

Omar Chaar et al. (2019) – they evaluated structural changes of steel substrate by deposited Ni-P on AISI 1012 steel substrate by electroless coating process. As a result, scanning electron microscopy (SEM) used for investigation of surface and cross-section morphology of composite, EDS analysis system used for determined volumetric percentage of co-deposited particles, potentiodynamic polarization was used to find out corrosion resistance of various EN coatings and current density, and mechanical properties were evaluated using wear and nano-indentation tests. The results showed that Alumina oxide (Al_2O_3) can give the best compromise between surface smoothness and deposition rate, Titanium oxide (TiO_2) can reach the highest levels of volumetric incorporation whereas Carbon can improve further lubrication effect on wear action, finally hardness and corrosion behavior had the best results with the existence of Alumina oxide (Al_2O_3) [11].

Beilei Ma et al. (2018) – worked on AZ31B alloy substrate which is coated with Ni-P coatings electroless plating method. It was observed by different-different experimental work that corrosion resistance was being improved with the coating/substrate interface. It had been found that by forming a phosphate layer on the surface of substrate phosphate process effectively tune the interface and hence remarkably reducing the surface roughness. When associated degree tempering treatment, the coatings which was deposited on the AZ31B alloy substrate with the phosphate layer had a high density and a remarkably improved corrosion resistance. [12]

Guangying Sheng, (2016) – They mainly studied that the changes of coating morphology after pretreatment in different alkaline plating baths and the properties of the electroless nickel plating after different time plating in the acidic chemical plating bath on aluminium alloy and observed that With the increment in electroless plating time, the thickness of the coating increased and the porosity gets decreased, it shows a better corrosion resistance when the porosity is zero and the coating thickness is 25 μm . Due to an instability in bath, the roughness of the coating decreased as time became smaller and larger. With an increase in the time of electroless plating, the micro-hardness of the coatings increased. The highest hardness of the coating observed by experiment was 624.2HV0.2. [13]

Lin Naiming et. Al. (2015) this investigation is done to investigate the best coating method which help to enhance the life period of P110 oil casing tube steel. During operation this pipe was easily get affected by corrosion and decrease the life so a coating of Ni-P was applied on it by electroless method to achieve a good corrosion resistance and better surface performance and thus increase the lifetime of P110 oil casing tube steel. It was found here that coated steel had better corrosion resistant, better wear resistant, had excellent friction reduction property and significantly enhanced the surface hardness. [14]

Ying Wang et. al (2015) In this research article two type of electroless coating Ni-P and Ni-P- B_4C composite coatings were investigated and studied the micro-hardness and wear resistance behaviors of coating. The investigation was done by deposition of B_4C nano-particles and electroless Ni-P alloy on the carbon steel substrate by electroless plating method and then applied a heat treatment process at the temperature of 200, 400 and 600 °C respectively for 1 hr. The experimental work was mainly done for made a brief observation of the cross-section, morphology and microstructure of carbon substrate after the composite coatings. Focus of experiment was on evaluation of micro-hardness and tri-biological behavior of substrate which was composite coated by nano particle.

The better wear resistance of Ni-P- B_4C composite achieved as compare to Ni-P coating as shown in experimental results. This Ni-P- B_4C composite coatings shows better micro-hardness and higher wear resistance when it was treated with heat treatment of 400 °C. The highest hardness was 1200 HV found by results and the minimum wear weight loss was 0.12 mg and the lowest friction coefficient was 0.2054. [15]

Mohsen Rezagholizadeh et. al. (2015) - In this study, electroless Ni-P/Ni-P- B_4C duplex composite coating used which was coated on a substrate of Ck45 steel substrate, and found that the morphology of created coatings was cauliflower shape. Furthermore, created coatings were very uniform and have good connection to the substrate. Moreover, B_4C nanoparticles have been evenly distributed in the electroless coating matrix. Heat treatment at 400°C for 1 hour leads to nanocrystalline structure and therefore, an increase strength and abrasion resistance of coating because of structure changing and creating Ni_3B hard phase. Maximum abrasion resistance was related to composite duplex coating that was heat operated. Existence of Ni-P electroless layer and B_4C particles distribution lead to an improvement in the corrosion resistance of Ni-P/Ni-P- B_4C coating. due to addition of B_4C nano particles lead to filling grooves and holes and therefore, this leads to a decrease in corrosion susceptible regions and an increase in corrosion resistance of coating. [16]

Araghi et. al. (2014) – In this study, main focus was the microhardness, wear and corrosion resistance of electroless deposited Ni-W-P- B_4C , Ni-P- B_4C , Ni-W-P and Ni-P coatings on AZ91D magnesium alloy were investigated. They found that the hardness of the Ni-W-P- B_4C and Ni-P- B_4C composite coatings was more than that of the Ni-P and Ni-W-P coatings. The Ni-W-P- B_4C and Ni-P- B_4C composite coatings have a better wear resistance in comparison to the Ni-W-P and Ni-P coatings shown by Pin on disk wear test results. The worn surfaces exhibited a change in the wear mechanism from adhesive for the Ni-P coating to abrasive for the Ni-W-P and Ni-W-P- B_4C coatings and combination of adhesive and abrasive for the Ni-P- B_4C composite coating. Corrosion performance of substrate was determined by Tafel test; it was shown by Tafel test, the Ni-W-P coatings exhibited the best corrosion resistance while the Ni-W-P- B_4C and Ni-P- B_4C composite coatings showed slightly less corrosion performance than the Ni-W-P and Ni-P coatings respectively. [17]

Araghi et. al. (2012) – In this work, electroless deposition of quaternary Ni-W-P- B_4C composite coatings on AZ91D magnesium alloy substrate was investigated. The coatings characteristics such as microstructure, crystallite size, morphology, microhardness and corrosion resistance behavior studied and compared with Ni-P and Ni-P- B_4C composite coatings, prepared with the same method. They found the hardness of the Ni-W-P- B_4C composite coatings was around 1290 MPa which was more than that of the Ni-P and Ni-P- B_4C coatings (about 700 and 1200 MPa, respectively). On the basis of polarization test results, the Ni-W-P- B_4C composite coating exhibits less and more corrosion rates with respect to the Ni-P- B_4C and the Ni-P coatings, respectively. The Ni-W-P- B_4C coating has a combination of amorphous and nanocrystalline structures shown by X-ray diffraction (XRD) analysis

results for the Ni-W-P-B₄C coating. Also WilliamsoneHall analysis on the X-ray patterns revealed that the Ni-W-P-B₄C coating has an average crystallite size of 1.5 nm.[18]

Xu Xiu-qing et. Al. (2012)-observed the corrosion behaviour of electroless Ni-P coating in Cl⁻/H₂S environment similar to the corrosion problem of refining equipments in petroleum industry especially the heat-exchangers by coating it on a substrate of 20# carbon steel and compared it with 316L stainless steel. The experimental results in this paper show that this kind of Ni-P coating owns the excellent corrosion resistance in Cl⁻/H₂S environment, which is superior to that of 316L stainless. So the amorphous state Ni-P coating was found to be comfortably suitable for the protective layer of refinery heat exchanger.[19]

A Araghi et. al. (2010)- found that the Ni-P-B₄C composite coating posses a cauliflower type structure as Ni-P coating, as well as good homogeneity and high density and also has a combination of amorphous and nanocrystalline structure same as Ni-P coating. The microhardness obtained for the Ni-P-B₄C composite coatings was 1200 MPa, which is more than that of what obtained for the Ni-P coating (about 700 MPa). On the basis of the polarization tests results, it can be said that both types of the coatings used in the present study were more resistant to corrosion than that of the AZ91D magnesium alloy and also corrosion resistance was decreased from the Ni-P coating to the Ni-P-B₄C coating. Due to the creating micro cracks in the coated Ni-P-B₄C microstructure corrosion resistance decreases. The Ni-P-B₄C composite coating on AZ91D magnesium alloy, having higher coefficient of friction, improves the wear resistance significantly, which is because of the presence of B₄C particles in the composite coating.[20]

A. Farzanehet al.(2010)-Here Corrosion performance of the electroless Ni-P coatings had been prepared in different conditions and optimized by the Taguchi method. It was found that Annealing temperature, surfactant concentration and substrate finishing procedure had significant influences on the corrosion resistance of the electroless Ni-P coatings. Corrosion tests resulted in higher corrosion resistance of coated mild steel in all conditions. The optimal condition to achieve the minimum corrosion rate was obtained as:- the surfactant concentration = 1.5g L⁻¹, pH = 5.5, emery paper number = 2,000 and annealing temperature = 200 °C.[21]

Y. H. Wuet al. (2009)- experimented the Corrosion characteristics of electroless Ni-P coating in sulfur-bearing solution and found that the electroless Ni-P coated A3 steel had a better corrosion resistance than 316L stainless steel against Cl⁻ corrosion in sulfur-bearing solution.[22]

M. Ebrahimian-Hosseinabadi et. al.(2005) found that after heat treatment at 400°C for 1 hr heat of electroless Ni-P coatings and electroless Ni-P-B₄C composite coatings results in an increase in the coating hardness, with a maximum hardness being achieved. The reason behind the increase in hardness was due to the formation of Ni₃P and Ni₅P₂ hard phases from the amorphous phase. The increase in the thickness of the electroless Ni-P coating and electroless Ni-P-B₄C composite coating results in an increase of the coating hardness. Also incorporation of B₄C particles within the electroless Ni-P matrix provides an increase of hardness of the coating. The wear resistance of electroless Ni-P-B₄C composite coatings under 15, 30 and 60 N loads was improved 60 to 90% with increasing B₄C percent up to 25 vol.%. Further increasing of B₄C particles from 25 to 33 vol.% results in a 15 to 100% decreased of wear resistance. In electroless Ni-P-B₄C composite coatings, the Boron Carbide particles are origins for developing and growth of cracks. More cracks had developed and reached together with increase of B₄C particles from 25 to 33 vol.%. Dynamic friction coefficient also increased by addition of B₄C particles in electroless Ni-P. The friction coefficient of electroless Ni-P-B₄C composite coating with 25 vol.% of B₄C was approximately doubled with increasing the loads from 15 to 60 N.[23]

Singh et. Al (2005) did experiment to investigate the corrosion resistance behaviour of Ni-P coated steel rebars substrate which is exposed in chloride-contaminated media simulated concrete pore solution (SPS) and compared it with the bare rebars. It was observed by different experiment that a superior corrosion resistance behaviour shown by rebar substrate at at pH value of 4 when it was deposited by electroless nickel phosphorus coating in SPS+1 M Cl⁻-solution. The corrosion resistance behavior was increased at pH value equal to 4 as compare to at lower and higher pH values. Medium phosphorous containing electroless nickel (MEPEN) coating (8% P) imparts a very high degree of corrosion protection than the higher phosphorous containing coating (16%). Also found that heat treatment of Medium phosphorous containing electroless nickel (MEPEN) at 600 °C in air has deteriorating effect on its corrosion resistance.[24]

S.M. Monir Vaghefi et. al. (2002) They worked on composite coating substrate and there were farious investigation was done. Electroless coating of substrate by Ni-P and Ni-P-B₄C composite deposition done separately were studied and a comparison between factors which were responsible for variation in this electroless process was done. In this study they worked on various concentration of B₄C such as 1, 2, 4 and 8 g/l. These various concentration of B₄C used in bath in such a way that these concentration produced different volume percentage of Ni-P-B₄C electroless coatings such as 12, 18, 25, 33 44 vol.% of B₄C produced. Various experimental works were done on the coated substrate to find out a brief study of variation in its thickness properties, heat treatment process, and deposition rate of coating phenomenon. For investigation of these properties of coating, the technique which used was optical microscopy test, Scanning electron microscopy (SEM), micro-hardening test, and EDAX. Experimental results clearly indicate that hardness was increased due to an increase in the percentage of the particles in the coating,. Heat treatment of the electroless composite coatings with 33 vol.% of B₄C at 400°C for 1 h in an increased the hardness by 1400 HV.[25]

B.-H. Chen et.al (2002) electroless deposition of Ni-P was used for deposition process with the incorporation of nine types of different surfactants. The effect and properties of substrate was examined after incorporation of nanoparticles on substrate. It was seen that the deposition rate increased up to 25% as compare to that of the surfactant free bath by an extra addition of a small quantity of surfactants into the plating bath. Also the experimental works were done for determining the corrosion rate of Ni-P deposited substrate in an acidic environment. found to be described well by a power function of the amount of the dissolved Ni-P alloys, equivalently the concentration of the nickel ions present in the corrosive solution. The corresponding power indices are between 0.3 and 0.4, which indicates that the corrosion process is controlled neither diffusionally nor interfacially.[26]

3.CONCLUSION

The main focus of this review article is to provide a brief idea about the performance of metallic substrate after incorporation of Ni-P and Ni-P-B₄C on steel substrate by electroless plating method. The various test perform on the coated substrate and found that the Ni-P composite coating and Ni-P-B₄C

coating were successfully and very uniformly incorporated on the substrate. It was seen that a remarkable increase in corrosion resistance and hardness value achieve because of presence of B₄C nanoparticles in the electroless bath coating. Also wear resistance was improved. Basically the heat treatment at 400°C for 1 hour may responsible for enhancement of wear and hardness performance. The reason behind the improvement of Corrosion resistance of substrate when incorporation B₄C particles was done , because of reduction of porosity of Ni-P coating and its increasing coherence as well as the development of the surface with a high chemical resistance mechanism against corrosive environment. resulted in the improvement of the corrosion resistance of Ni-P-B₄C composite coatings

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