



# Role of Diamond Nanoparticles in Ni Based Protective Coatings

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## Abstract

Protective coatings are important for mitigation of the corrosion and erosive wear of equipment components and infrastructure in oil and gas industry. Ni-based metal-matrix nanocomposite (MMnC) coatings incorporated with diamond nanoparticles offer an interesting alternative to hard chromium and conventional Ni coatings. It is expected that components manufactured from inexpensive base materials coated with MMnCs should have longer service life, which translates into lower operating costs. In the present work, two different Ni-based MMnCs filled with nanodiamond particles were developed through Ni-P electroless and Ni-B electroplating deposition. The role of co-deposited diamond nanoparticles in these Ni-based MMnCs has been assessed by following the relationship between hardness and corrosion potential and microstructure and particle size of the coatings. The results presented in this paper demonstrate that Ni-based MMnC coatings outperform conventional electroless Ni-P and electroplated Ni-B coatings and validate their ability to provide simultaneous corrosion and erosion protection for oil and gas tools and components.

## Introduction

Maintenance and repair expenses in the oil and gas industry caused by wear, erosion and corrosion are very large. To a great extent, corrosion phenomena experienced in oil and gas systems are based on aqueous corrosion caused by soluble corrosive gases, which include carbon dioxide, hydrogen sulfide and oxygen. Corrosion is additionally accompanied by abrasive wear, resulting from interaction between moving parts or erosive wear caused by interaction with particulate-loaded flowing fluids. Erosive wear can be mitigated with the use of hard and tough surface coatings [1]. Generally, chromium coatings have been utilized for this purpose in the industry. However, the increasing pressure to eliminate hard chromium in oil and gas applications due to environmental concerns related to hexavalent chromium has fueled the need for substitutes with comparable economics and performance. Nickel (Ni) presents a viable alternative coating material that has been widely used in industrial applications over the past five decades because of its unique characteristics that improve resistance to corrosion, abrasion and wear. Performance of Ni-based coatings can be further advanced with the development of MMnCs.

The composite coatings described here are formed by simultaneous deposition of the nanoparticles particles and nickel on the growth surface with the envelopment of the former by the depositing Ni ions. In the case of composite coatings, the particle content, size, and in some cases the orientation affect the ultimate properties of the coatings [2]. MMnCs are reinforced with the particles added into the metal matrix that results in remarkable

improvement of mechanical properties. Several different types of particles, such as oxides ( $Al_2O_3$ ,  $Y_2O_3$ ), nitrides ( $Si_3N_4$ , AlN), carbides (TiC, SiC), hydrides ( $TiH_2$ ) and borides ( $TiB_2$ ), have been employed as reinforcement additives [3] with carborundum and alumina becoming the most common ceramic reinforcements for MMnCs. Earlier efforts on preparing Ni-diamond composite coatings with different plating conditions and bath compositions have shown the benefits of composite coatings over monolithic metallic coatings [4-7]. Furthermore, we have shown that the Ni-P and Ni-B coatings with the added particle provide an overall improvement towards erosion and corrosion resistance [8-10].

In general, the electroplated and the electroless deposited Ni-P and Ni-B coatings are amorphous and may contain only a very small nanocrystalline domain ranging from 2 to 20nm. As deposited, these coatings are hard and relatively brittle. Corrosion resistance of Ni-P is superior to Ni-B. Following the deposition, a heat treatment at temperatures between 250 °C and 400 °C precipitates  $Ni_3P$  or  $Ni_3B$  crystals out of the matrix. This heat treatment improves the mechanical properties and corrosion resistance of the coatings [11]. These coatings are typically produced with the P or B concentrations varying from 2 to 14wt.%, where the exact content determines their properties. Electroless deposition is usually performed at 80 to 90 °C and at high pH conditions. The typical fabrication of these coatings uses an electroless process. Conventional electroplating can provide an alternative route for simpler geometries. Electroplating is typically conducted at lower

temperatures, around 50 °C, and for Ni-B coatings traditionally uses boric acid, boron hydrides or carboranes as boron sources. Recently, a number of publications have suggested the use of trimethylamine or dimethylamine borane [12,13]. The absence of strong reducing agents in electroplating bath prevents the self-catalytic precipitation of Ni particles from solution [14] and makes this process inherently more stable than electroless deposition. Previously, we stated that with use of non-traditional boron source, which enables higher B-contents in the matrix, superior hardness and resistance to corrosion can be achieved [9]. In this paper we describe the impact that boron, phosphorus and nanodiamond, incorporated in the matrix, have on growth, microstructure, corrosion and mechanical properties of this new class of metal matrix nanocomposite coatings.

### Experimental Section

Ni-P and Ni-P-diamond composite coatings were produced by electroless deposition on tool-grade 4140 steel coupons and then heat treated at 400 °C for 1 hour in air. Electroless Ni-P coatings were prepared with the concentration of phosphorus as high as approximately 10wt.%. The high-P monolithic and nanocomposite films were prepared in a mechanically stirred electroless bath at a pH of 9 and at 85 °C. During the deposition of nanocomposite coatings, diamond particles with an average particle size of 100 nm were added to the bath and mechanically stirred throughout the process. Coatings were prepared by using a bath solution with 2.5wt.% diamond concentration. Prior to deposition, the 4140 tool steel coupons were polished down to 600 meshes and washed in a caustic soap at room temperature, followed by rinse in ethanol and short (10sec) activation in 10% HCl solution. A final rinse in de-ionized water was conducted immediately prior to the start of the coating.

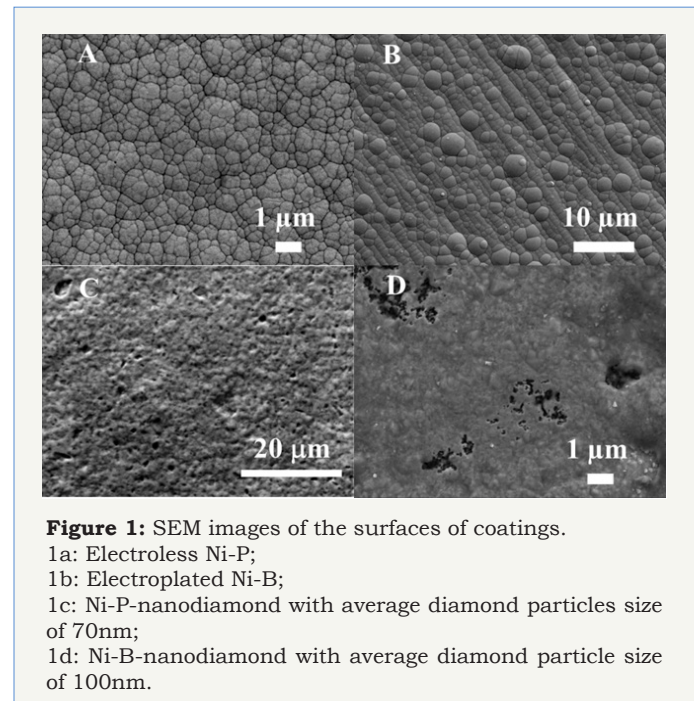
Electroplating was carried out in a conventional Watts bath modified with the addition of 1wt.% trimethylamine borane as the source of boron. Depositions were carried out at 0.1 A/dm<sup>2</sup> current density for 1 hour at 50°C. The pH of the solution was adjusted to a value of 3.5 using 30% HCl. In the electrolyte bath other additives used to modify the film microstructure were sodium dodecyl sulfonate (SDS) and saccharine. Ni-B-nanodiamond composite coatings with the average particle size of 100nm added to the Watts bath prior to the insertion of the cathode. The bath solution was mechanically stirred, and the weight content of the nanoparticles in the bath remained unchanged during the deposition.

The morphology of the coatings was characterized by scanning electron microscope (SEM) (model JSM-7800). Microhardness measurements were conducted with a Knoop microindenter at a load of 50g. The values reported in this paper are the averages of five measurements.

Cyclic potentiodynamic polarization measurements were performed to determine relative susceptibility to localized corrosion in 3.5% NaCl water solution (chloride environment) at room temperature according to ASTM (G 61-86). This is the standard test used to find the localized corrosion susceptibility of

iron-, nickel- or cobalt-based alloys; its application was extended to evaluate the performance of the protective coatings.

### Results and Discussion



**Figure 1:** SEM images of the surfaces of coatings.

1a: Electroless Ni-P;

1b: Electroplated Ni-B;

1c: Ni-P-nanodiamond with average diamond particles size of 70nm;

1d: Ni-B-nanodiamond with average diamond particle size of 100nm.

Figure 1a & 1b shows the SEM images of electroless Ni-P and electroplated Ni-B coatings having the cauliflower-like structure, which is typical of films produced under conditions of limited atomic mobility. Incorporation of the nanoparticles changes the morphology of the coating, leading to significantly finer domes, as shown in Figure 1c & 1d. Ashassi-Sorkhabi & Es'haghi [15] have postulated that incorporation of nanoparticles during deposition of composite coatings disrupts the boundaries of the Ni-P/Ni-B clusters, breaking down the otherwise “columnar” structure, resulting in a morphology with finer dome size. In both cases the coatings studied here were 50μm thick. The phosphorous and boron concentration determined by EDS was approximately 10wt.% for P in Ni-P coatings and 8wt.% boron in Ni-B coatings.

The effect of hard particles on the erosive wear of composite materials is often described by the following relationship (1):

$$J \propto \frac{AW^3}{\epsilon}$$

Where J is the erosive wear rate, W is the flow velocity, A is the particle shape and  $\epsilon$  is the erosion resistance that is directly related to the ratio of the hardness of the impinging particle to the hardness of the substrate. According to Equation (1) the erosive wear is inversely related to the hardness of the eroded material. Several authors assumed that the hardness of a composite material can be described by the direct rule of mixtures, i.e., the weighted average of the hardness of the different phases [16], although this is not proven to hold in all cases. The presence of the dispersed phase in electroless or electroplated coatings affects the microstructure and the hardness of the matrix phase in Ni-based coatings [8-10].

Moreover, the adhesion between the particles and the matrix plays an important role in determining the hardness as well as other mechanical properties of the composite material.

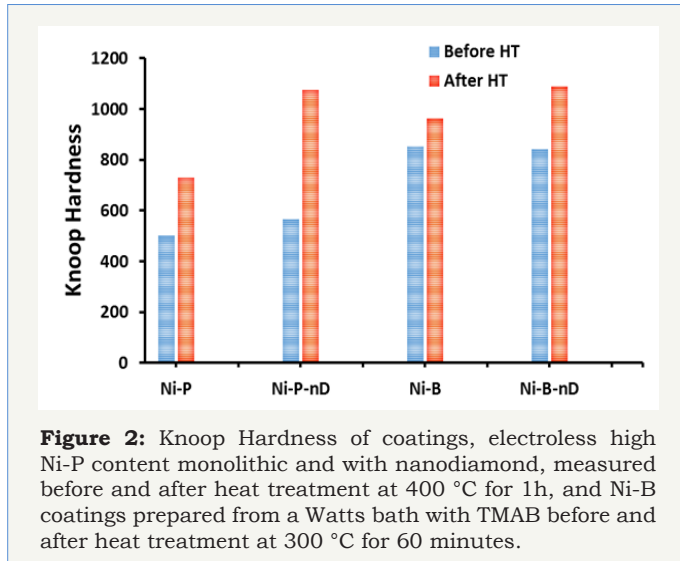
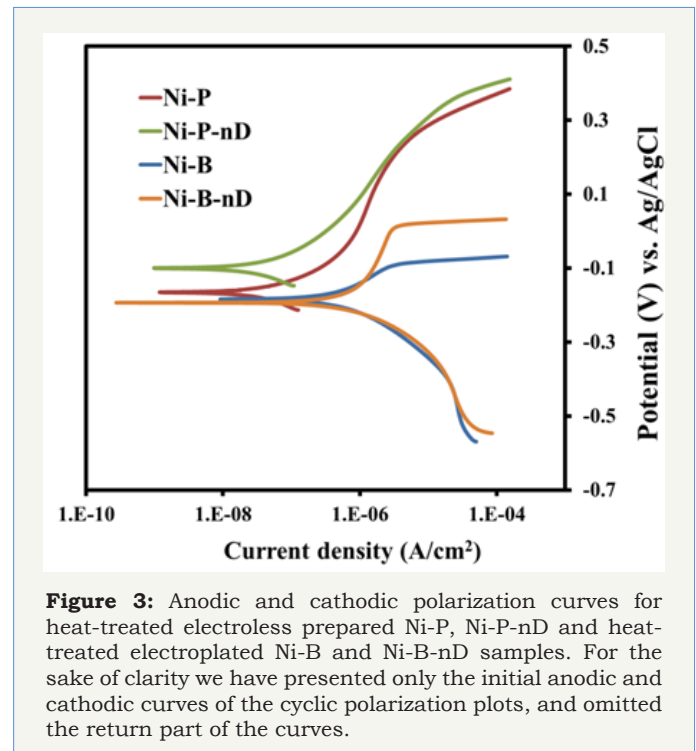


Figure 2 shows the hardness values of electroless Ni-P and Ni-P with nanodiamond coatings compared with the electroplated Ni-B and Ni-B with nanodiamond coatings. Hardness of the Ni-P and Ni-B coatings increases with the heat treatment. Heat treatment facilitates a precipitation-hardening in the Ni (B or P) coatings making them to become harder than the as deposited coatings. The increase in hardness following the heat treatment in the case of Ni-B coatings is attributed to Ni<sub>3</sub>B precipitation strengthening, while in the case of Ni-P coatings it is due to Ni<sub>3</sub>P precipitation strengthening. The hardness of as-deposited Ni-P and Ni-B coatings and after-heat treatment increases with the diamond content (Figure 2). The benefit of heat treatment on hardness and wear resistance of the composite coatings is related to an increase in the matrix-particle adhesion strength. We have proven that earlier in our publications [8] through observing the scratch marks behavior with load and speeds for coatings before and after heat treatments. We observed that the preferential crack propagation along the diamond-Ni interface is obvious in the case of the as-deposited coating. Under similar loads, crack propagation is much less pronounced in the heat-treated coatings, which contributes into increasing their hardness and wear resistance.

A concern in replacing monolithic materials with composites is the potential negative impact of the second phase on corrosion. A second phase affects the corrosion resistance because it is electrically different from the base material (the matrix) and it introduces the interphase boundaries that may favor the diffusion of anions or cations and accelerate the dissolution of the matrix. When the dispersed phase is a dielectric ceramic, as is the case of the nanodiamond used here, localized galvanic effects are not active; however, the metal-ceramic interface may still lead to a preferential path for the diffusion of aggressive ions.

The corrosion behavior of the Ni-P/Ni-B MMnC coatings prepared has been assessed by cyclic polarization in 3.5% NaCl

solutions. The anodic and cathodic polarization curves are shown in Figure 3. Corrosion potential  $E_{Corr}$  obtained from the polarization curves in Figure 3 shows no detrimental impact on the corrosion resistance resulting from incorporating the nanodiamond.



The corrosion potential of the nanocrystalline high-P coatings increases with the increasing diamond content, particularly after heat treatment. Incorporation of nano-crystalline diamond is more disruptive, improving the corrosion resistance.

The corrosion potential of the prepared films decreases in the following order:

$$E_{Corr}^{Ni-P-nD} > E_{Corr}^{Ni-P} > E_{Corr}^{Ni-B} > E_{Corr}^{Ni-B-nD}$$

This nobility order correlates well with the texture of the deposited films rather than with the interphase boundary area.

Nanodiamond strongly influences the growth texture, the final microstructure of the coatings, and, as shown in Figure 3, affects the corrosion potential in Ni-P nanocomposite coatings. The impact of nanodiamond on the corrosion potential of the Ni-B coatings is not nearly as strong as in the case of Ni-P. In a recent publication [17], we demonstrated that the improvement of the corrosion resistance of Ni-P due to the incorporation of the nanodiamond was related to the change of the dissolution mechanism from intergranular to uniform. This effect does not seem to be operative in the case of the Ni-B coatings.

## Summary

We have demonstrated that diamond particles play important role in the Ni-based protective coatings. They are especially critical for increasing the hardness of the coatings and versatile in preparing the coatings with different dopants such as boron and phosphorus



to increase the hardness. It was shown that these coatings can be prepared by different deposition processes, such as electroplating and electroless. Nanoparticles disrupt the columnar growth of Ni-P, leading to improved corrosion resistance. The impact of those particles on the corrosion resistance of Ni-B coatings is practically in-existent.

### Acknowledgement

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