



ELECTROLESS Ni-B AND Ni-B-Si₃N₄ COMPOSITE COATINGS - THEIR ROLE IN SURFACE ENGINEERING

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ABSTRACT

Electroless Ni-B coatings were prepared from a borohydride bath. The structural aspects of electroless Ni-B coatings were studied and the hardness and wear resistance were evaluated. The incorporation of silicon nitride particles in the Ni-B matrix by electroless deposition route was studied. The incorporation level of particles in the coating, among other factors was found to be a function of concentration of particles in the bath. The influence of the incorporation of the silicon nitride particles on the hardness and wear resistance of the electroless Ni-B coating in both the as-plated and heat-treated conditions was studied.

Keywords: electroless deposition, composite coating, wear resistance.

1.INTRODUCTION

The recognition that the vast majority of engineering components can degrade or fail catastrophically in service through surface related phenomena such as wear, corrosion and fatigue, led in the early 1980s to the development of the interdisciplinary subject of surface engineering.¹ Surface engineering can be defined as the design of a substrate and surface together as a system to produce a cost-effective performance enhancement of which neither is capable on its own. Among the various surface modification processes like physical vapor deposition, chemical vapor deposition, thermal spraying, electrodeposition and electroless deposition etc., electro- and electroless deposited coatings are widely accepted owing to their cost-effectiveness, higher production rate and ease of operation. Since the discovery of electroless plating by Brenner and Riddell, hundreds of papers describing the process and the resulting deposits have been published. Among the various types of electroless plating, electroless nickel has gained immense popularity due to its ability to provide a hard, wear and corrosion resistant surface.²⁻⁴ Borohydride is the most powerful reducing agent available for commercial electroless nickel plating. Successful codeposition of particles within an electroless metal matrix has led to the development of a new class of composite materials, which offer improved wear resistance. Much research has been directed towards the optimization of the deposition process in relation to the main coatings properties such as uniform deposition of particles, microhardness, corrosion and wear resistance.⁵ Silicon nitride (Si₃N₄) is a very strong, hard material, which retains its room temperature strength upto about 1200°C and has excellent dimensional stability and oxidation resistance.⁶ The present investigation is to study the preparation of Ni-B and Ni-B-Si₃N₄ composite coating coatings by electroless deposition route and to evaluate the effect of particle incorporation on the properties of electroless Ni-B coatings and to justify their role in surface engineering.

2.EXPERIMENTAL DETAILS

Mild steel substrates were surface ground, degreased with acetone, electrolytically cleaned in an alkaline solution and washed thoroughly with de-ionized water. A nickel strike using Watt's nickel bath was given to substrates prior to their immersion in electroless plating bath. The chemical composition of the plating bath employed and its operating conditions are given in Table 1. The boron and thallium content of the deposit were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES), whereas the nickel content was determined gravimetrically after precipitating nickel as Ni-DMG complex. The silicon nitride particle content in the deposit was estimated gravimetrically, after dissolving the Ni-B-Si₃N₄ composite film deposited on a thin copper substrate in 1:1 nitric acid.

The structure of electroless Ni-B deposits, in as-plated and heat-treated (450 °C for 1 h) conditions was assessed by X- ray diffraction (XRD). The coating hardness was measured on the surface using a Leitz microhardness tester with a Vickers diamond indenter using a 100-g load (0.98 N). The lap time for each indentation was 15 s and the values reported represent the average and standard deviation of a minimum of five measurements.

The wear resistance of as-plated and heat-treated (350 and 450 °C for 1 h) electroless Ni-B and Ni-B-Si₃N₄ composite coatings was evaluated under dry sliding conditions using a pin-on-disc apparatus (DUCOM, India). In this method, the pin and disc are arranged in such a way that the rotating disc served as the counterface material while the stationary pin served as the test specimen. Steel discs (composition conforming to EN 31 specification) of 100 mm diameter and 5 mm thickness were chosen as counterface materials to slide against the test specimens. The applied normal loads were 20, 30 and 40 N. The sliding speed was kept constant at 0.5-m/s. for all tests by adjusting the diameter of the wear track and the rotational speed of the disc. The specific wear rate was calculated by the expression: $w_s = w/(l.L)$, where w is the wear mass, L is the normal load and ' l ' is the sliding distance. Immediately after the end of each test, the wear track on the pins was examined using a scanning electron microscope.

3.RESULTS AND DISCUSSION

The thickness of the electroless Ni-B coating increases with increase in plating time. However, the extent of increase in thickness is not linear throughout the entire duration of plating and it saturates after some time. This is due to the accumulation of oxidation product of borohydride in the plating bath. The Ni-B deposit prepared using the bath composition and operating conditions given in Table 1 contains 93.2% nickel, 6.5 wt% B, 2wt% Si₃N₄ particles and 0.3-wt% thallium. The incorporation of thallium along with nickel and boron is due to the use of thallium acetate as the stabilizer in the plating bath, which is also confirmed by other researchers.⁷⁻¹⁰ The scanning electron micrograph of electroless Ni-B coating (Fig.1) exhibits a typical 'cauliflower' like structure that makes the deposit naturally lubricious.^{9, 10}

The level of incorporation of the silicon nitride particles in the Ni-B coating increased with its increase in concentration in the bath up to 10 g/L, beyond which saturation was observed, inspite of a continuous increase in their concentration up to 25 g/l. Similar observation has been reported by several researchers^{11,12}. In general, the incorporation of second phase particles in electroless composite coatings depends on two factors.¹³

- (i) Particle impingement on the electrode surface; and
- (ii) Holding time of the particle on the electrode surface.

The impingement of the particle on the electrode is determined by the flux of the particle at the interface. The particle flux at the interface in turn is determined by the concentration, size and

density of the particle. The holding time is a function of mode of agitation and speed, and particle shape.¹⁴ In the case of Ni-B-Si₃N₄ composite coatings, though the particle flux can be increased by increasing the concentration of silicon nitride particles in the bath, the holding time is less because of the heavy hydrogen evolution on the surface of the substrate. Sodium borohydride is a very powerful reducing agent and it can provide up to 8 electrons for the reduction of some metals. Heavy hydrogen evolution on the surface of the substrate tends to push away the particles, which are in contact with the substrate. So, an incorporation level of approximately 2 wt.% can be obtained in the case of Ni-B-Si₃N₄ composite coating using the borohydride bath.

X-ray diffraction pattern of the electroless Ni-B coating in the as-plated condition exhibits a single broad peak indicative of the amorphous nature of the coating (Fig.2). In electroless deposition process, the extent of segregation of metalloid alloy in the coating determines its crystallinity. Since the required boron segregation (6.5 wt%) is relatively large, nucleation of nickel phase is prevented and this has resulted in amorphous structure. Watanabe et al¹⁵, Srivastava et al¹⁶ and Evan and Schlesinger¹⁷ also observed the amorphous nature of electroless Ni-B in the same composition range. Heat-treatment results in the transformation of the amorphous phase to crystalline nickel and nickel boride phases.¹⁸ XRD patterns of electroless Ni-B coatings, heat-treated at 450 °C for 1 h, confirm the formation of crystalline nickel and Ni₃B and Ni₂B phases (Fig. 3). The microhardness (HV₁₀₀) of electroless Ni-B and Ni-B-Si₃N₄ composite coatings is determined in both as-plated and heat-treated conditions. The microhardness for as-plated Ni-B and Ni-B-Si₃N₄ composite coatings is in the order of 570 and 700 (HV₁₀₀) respectively. The Ni-B and Ni-B-Si₃N₄ composite coatings heat-treated at 450°C for 1h, exhibit microhardness values in the range of 908 and 1070 (HV₁₀₀) respectively. The increase in hardness in the case of electroless Ni-B coatings is due to the precipitation of nickel borides, Ni₃B and Ni₂B. The higher hardness of the composite coatings is based on the addition of the particles dispersed uniformly in the matrix, and the composite coatings have a double strengthening effect from the dispersion strengthening of hard phase and precipitation strengthening of Ni-B alloy.¹⁹

The specific wear rate of electroless Ni-B coatings, both in as plated and heat-treated conditions, obtained at different applied loads, are given in Table2. The specific wear rate increases with increase in applied load from 20 to 40 N and this trend is common for as-plated and heat-treated Ni-B coatings. At all applied loads, the specific wear rate is less for heat-treated electroless Ni-B deposits compared to that obtained for as-plated ones. This is due to the formation of hard nickel boride phases following heat-treatment, which presents a virtually incompatible surface for the counterface material, as there exists very little solubility between iron and these hard phases, leading to a decrease in specific wear rate. The average friction coefficient, μ_{av} of electroless Ni-B coatings in as-plated and heat-treated conditions, is given in Table3. The coefficient of friction is less for heat-treated electroless Ni-B deposits compared to that obtained for as-plated ones.

The mechanism of wear of electroless Ni-B coating depends on the attractive force that operates between the atoms of nickel from the coating and iron from the counter disk. Scanning electron micrographs of electroless Ni-B coatings subjected to pin-on-disc wear test, clearly indicate the presence of torn patches and, in some places even detachment of the coating, in their as-plated condition. (Fig 4) This type of morphological feature, commonly called as ‘prows’ is reported for adhesive wear failure of electroless Ni-P coatings, by several researchers.^{20,21} The transferred patches from the electroless Ni-B coatings and the wear debris are also observed on the surface of the counter disc, which clearly indicates an adhesion between the electroless Ni-B coated mild steel pins and the counter disc had occurred.

The specific wear rate of electroless Ni-B-Si₃N₄ coatings, both in as plated and heat-treated conditions, obtained at different applied loads, are given in Table 4. The wear resistance of Ni-B-Si₃N₄ coating is better than that of Ni-B coating. Several researchers report similar improvement in wear resistance due to incorporation of particles²²⁻²⁴. The wear volume of the composite coating is lower when heat-treated at higher temperatures, which is related to the microstructural change of Ni-B alloy matrix and the dispersed effect of Si₃N₄ particles.^{22, 23} The average friction coefficient, μ_{av} of electroless Ni-B-Si₃N₄ composite coatings in as-plated and heat-treated conditions, is given in Table 5. The friction coefficient of Ni-B-Si₃N₄ composite coatings is relatively high owing to its high surface roughness and high mechanical interlocking forces under similar loading and temperature conditions.²³ Because the hardness of Ni-B-Si₃N₄ coating is greater than that of Ni-B, grooves in the former are finer and shallower. (Fig 5) The particles distributed uniformly in the matrix actually act as supporting points and play an anti-wear effect, resulting in an increase of wear resistance of the composite coatings.²³

4. CONCLUSIONS

Electroless Ni-B coatings of the present study are amorphous in the as-plated condition. Heat treatment results in the transformation of the amorphous phase to crystalline nickel and nickel boride phases. The level of incorporation of silicon nitride particles in the Ni-B coating increases initially and saturates with further increase in the concentration of particles in the bath. The lower level of incorporation is attributed to the heavy hydrogen evolution, the characteristic of the borohydride bath, which pushes the particles away from the substrate. The Ni-B-Si₃N₄ composite coatings have higher hardness due to the double strengthening effect from the dispersion strengthening of the hard phase and precipitation strengthening of Ni-B alloy. The Ni-B-Si₃N₄ composite coatings are found to be better in restricting wear than Ni-B coatings, though their coefficient of friction is higher.

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TABLES

Table 1: Bath composition and operating conditions

Bath composition	
Nickel chloride hexahydrate	30g/l
Ethylene diamine (98%)	90g/l
Sodium hydroxide	90g/l
Thallium acetate	16mg/l
Sodium borohydride	0.8g/l
Sodium lauryl sulphate	0.1g/l
Silicon nitride	0-25g/l
Operating conditions	
Agitation	Mechanical (600 rpm)
pH	14
Temperature	95 ±1°C

Table 2 Specific wear rate of electroless Ni-B coatings in their as-plated and heat-treated conditions obtained at different applied loads after a sliding distance of 1800 m

Applied Load (N)	Specific wear rate* ($\text{kg.N}^{-1}.\text{m}^{-1} \times 10^{-10}$)	
	As-plated	Heat treated at 350°C/1 hour
20	0.52	0.39
30	1.36	0.68
40	2.46	1.72

*Average of two determinations.

Table 3 Coefficient of friction of electroless Ni-B coatings in their as-plated and heat-treated conditions obtained at different applied loads after a sliding distance of 1800 m

Applied Load (N)	Average Coefficient of Friction (μ_{av})	
	As-plated	Heat treated at 350°C/1 hour
20	0.742	0.710
30	0.770	0.732
40	0.784	0.749

*Average of two determinations.

Table 4 Specific wear rate of electroless Ni-B-Si₃N₄ composite coatings in their as-plated and heat-treated conditions obtained at different applied loads after a sliding distance of 1800 m

Applied Load (N)	Specific wear rate* ($\text{kg.N}^{-1}.\text{m}^{-1} \times 10^{-10}$)	
	As-plated	Heat treated at 350°C/1 hour
20	0.32	0.15
30	1.08	0.42
40	2.14	1.35

*Average of two determinations.

Table 5 Coefficient of friction of electroless Ni-B-Si₃N₄ composite coatings in their as-plated and heat-treated conditions obtained at different applied loads after a sliding distance of 1800 m

Applied Load (N)	Average Coefficient of Friction (μ_{av})	
	As-plated	Heat treated at 350°C/1 hour
20	0.846	0.821
30	0.865	0.832
40	0.883	0.854

*Average of two determinations.

FIGURES

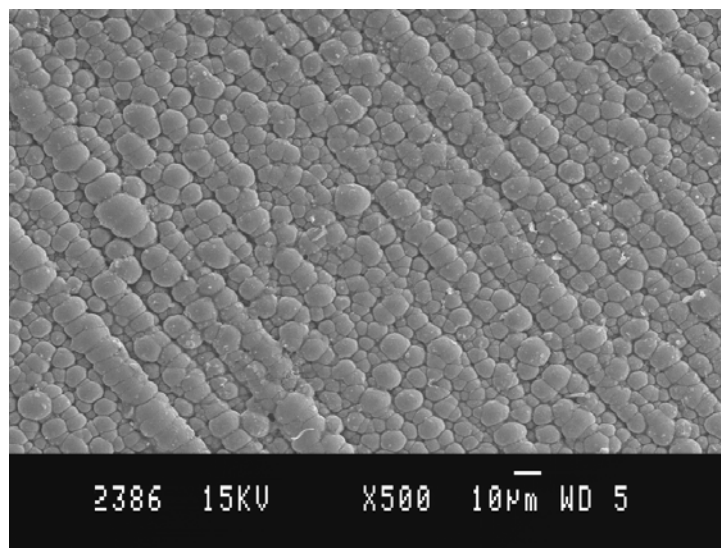


Fig. 1 Surface morphology of electroless Ni-B coating

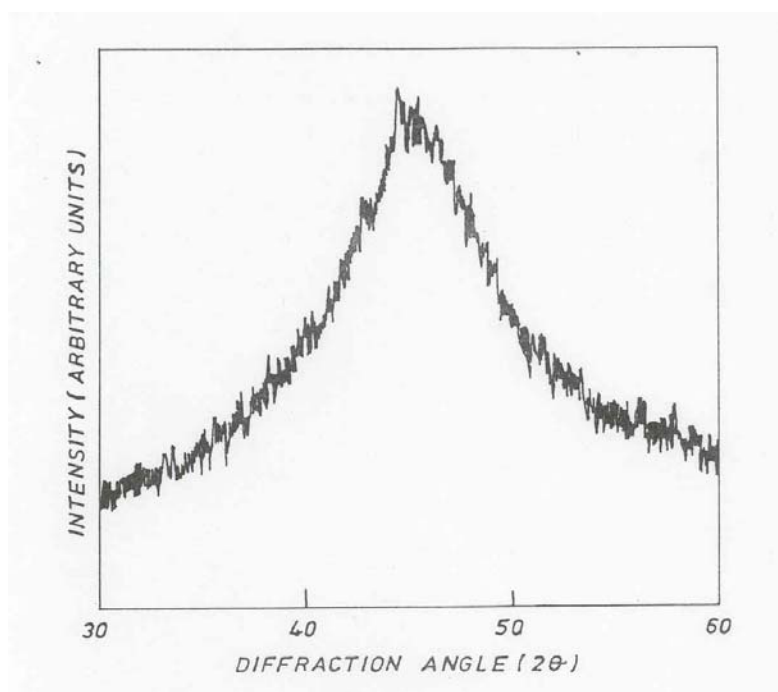


Fig. 2 X-ray diffraction pattern of electroless Ni-B coating in its as-plated condition

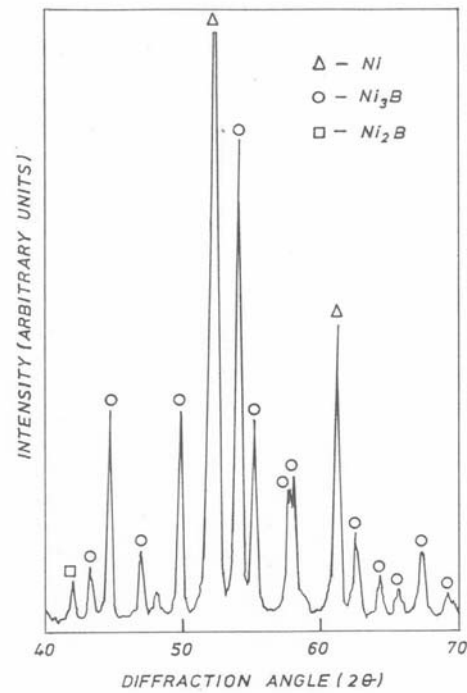


Fig. 3 X-ray diffraction pattern of electroless Ni-B coating heat-treated at 350°C for 1 hour

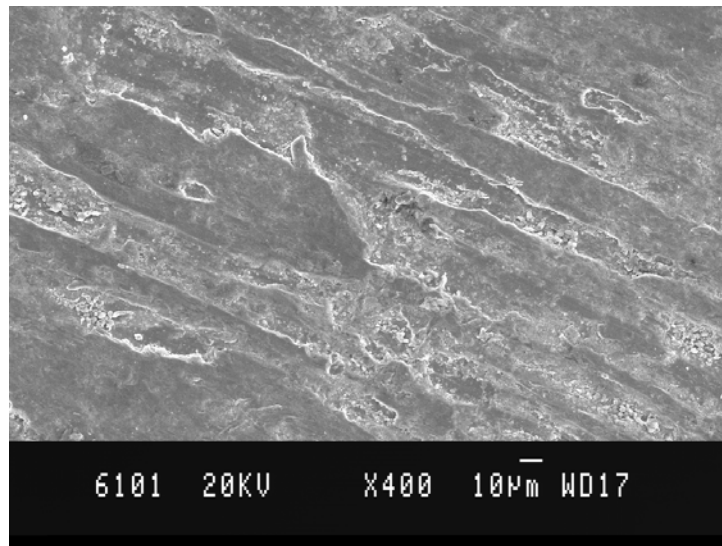


Fig. 4 Wear track pattern of electroless Ni-B coating at an applied load of 40N after a sliding distance of 1800m

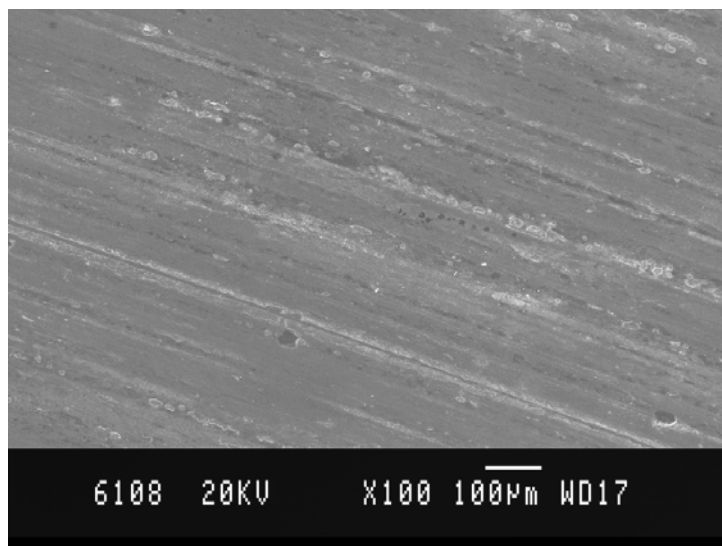


Fig. 5 Wear track pattern of electroless Ni-B-Si₃N₄ composite coating at an applied load of 40N after a sliding distance of 1800 m