Characteristics of Ni-BN Electrocomposites

By G.N.K. Ramesh Bapu

Nickel-boron nitride (Ni-BN) electrocomposites were produced by conventional electrodeposition methods, using a Watts nickel electrolyte containing BN particles in suspension. The effects of particle concentration in the bath, current density, pH and temperature on vol percent incorporation of BN particles in the composites were investigated. Microhardness, wear resistance and corrosion behavior of the composites was also examined and compared with those of BN-free nickel deposits. It was found that the vol percent incorporation of BN particles in the composite increased with increasing BN content in the bath and with increasing current density. An optimum BN incorporation (28.8 vol percent) was possible by operating the bath containing 30 g/L of BN particles in suspension at 5 A/dm^2, at pH 3.0 and 50 °C. The hardness and wear resistance of the composite were found to be 3 to 4 times greater than those of BN-free nickel deposits. The results of corrosion studies reveal that the composite confers on steel improved protection against corrosion in a NaCl medium.

In electrolytic plating of composites, the dispersed particles are maintained in suspension in the plating bath so that they may be incorporated in the deposit.[1] For a number of applications, electrocomposites are found to be superior to other coatings, such as those resulting from flame spraying, hard chromium plating, nitriding, etc.[2] Industrial applications of coatings of composites are of special interest to the mechanical, engineering, aeronautical, marine, mining, agriculture and nuclear fields. As high-temperature oxidation and corrosion-resistant coatings, they are employed in combustion chambers, flame tubes and other jet engine components.[3] In this investigation, the possibility of incorporating fine boron nitride (BN) particles in a nickel matrix was studied systematically with a Watts nickel bath. Boron nitride closely resembles carbon in structure. This, together with certain of its physical characteristics, makes BN interesting from both fundamental and application points of view. Considering its high chemical and thermal stability, it is valuable as a crucible material, heat sink and mounting material in (vacuum) tube and transistor circuits, replacing the toxic and less readily worked beryllia.[4] To examine BN-containing nickel deposits for wider industrial use, experiments on the effects of particle concentration in suspension, current density, bath pH and temperature on the vol percent of BN content of the composite were examined. Microhardness, wear resistance and corrosion behavior of the Ni-BN composite coatings were also investigated and compared with those of BN-free nickel deposits.

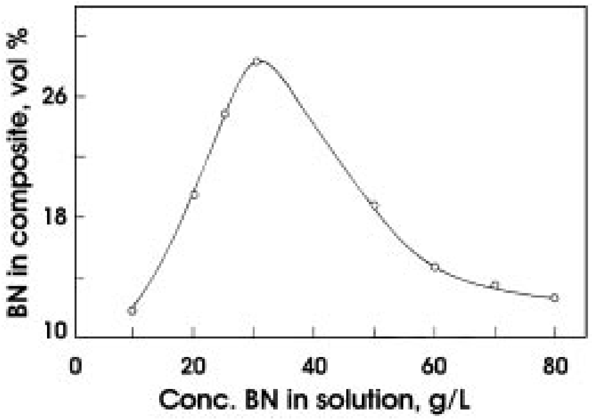

Fig. 1—Effect of BN concentration in solution on incorporation of BN in the composite.

Experimental Procedure

Electrodeposition of Ni-BN Composites

Electrodeposition of nickel was performed in a solution consisting of 240 g/L nickel sulfate, 40 g/L nickel chloride, 30 g/L boric acid and 0.1 g/L sodium lauryl sulfate. The experimental set-up has been described elsewhere.[5] By means of a mechanically controlled glass stirrer, the BN powder (size 6–8 µm) was kept in suspension uniformly in the bath for 8 hr.

Codeposition was carried out in a 1-L glass beaker. Two nickel pieces, 5 mm thick, served as anodes. Stainless steel specimens 7.5 x 5 x 0.1 cm were the cathodes, from which the coatings could be easily stripped off for analysis. The extent of BN incorporation in nickel was studied with respect to particle concentration ranging from 10 to 80 g/L, current density ranging from 2 to 10 A/dm^2, bath pH from 2 to 5 and bath temperature 30 to 70 °C.

The plated stainless steel samples were weighed (W_1) within 0.1 mg, then stripped in 50 mL of 20-percent, warm nitric acid. The resulting solutions were made up to 100 mL in standard volumetric flasks. After stripping, the stainless steel substrates were again weighed (W_2), with the difference ($W_1 - W_2$) yielding the mass of the plated composite. The nickel contents of the composite were determined by atomic absorption spectrometry. The BN contents of the composites could be deduced from the differences between the values of the mass of the composite and the nickel therein. The vol percent contents of BN were evaluated as follows:

Vol of Ni in the composite, V_1 = mass of Ni/density of Ni
Vol of BN in the composite, V_2 = mass of BN/density of BN
Total volume, $V = V_1 + V_2$
Vol percentage content of BN = $V_2/V \times 100$

Triplicate analyses were performed in each case and the average values reported.

Characterization of Ni-BN Composites

Microhardness

The Vickers microhardness of the as-plated composites was determined by an indentation technique at 50 gf load with a diamond pyramid indenter and the hardness calculated, using the relation:

Vickers hardness (kgf/mm^2) = 1854 x load (gf)/d^2, where d is the indentation diagonal (mm).

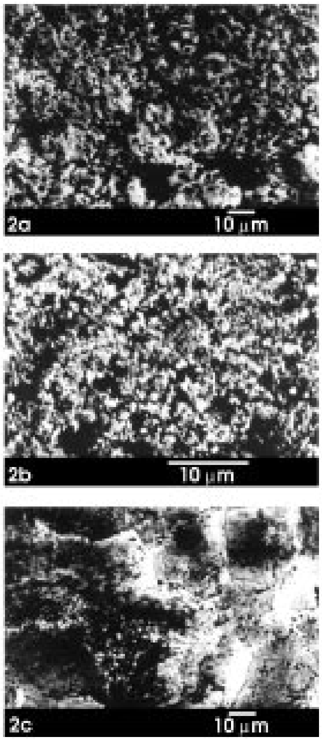

Fig. 2—SEM photograph of Ni-BN composite at various BN concentrations: (a) 10 g/L; (b) 30 g/L; (c) 80 g/L.

Wear Resistance

The abrasion wear resistance of the as-plated composites was determined with a Taber abraser, using a CS-10 wheel at 1000 gf load.[6] The test sample (10 x 10 x 0.1 cm) of mild steel was weighed before and after abrasion, following each cycle, which consisted of 1000 revolutions. The Taber wear index (TWI), which is the weight loss in mg/cycle of abrasion, was calculated.

Corrosion Behavior

For polarization studies, a three-electrode cell assembly was used and the Ni-BN composites were deposited on 2.5 x 2.5 cm mild steel substrates. The specimen was masked with lacquer to expose a one-cm^2 area that served as a working electrode. A saturated calomel electrode (SCE) was used as a reference and a platinum foil (2.5 x 2.5 cm^2) was the counter electrode.

In the galvanostatic polarization method, a constant current regulator ranging between 1 µA and 500 mA was used and the potential of the working electrode was tracked, using a digital multimeter. The specimens were immersed in 5-percent NaCl solution and allowed to attain a steady potential value (open-circuit potential, OCP). The galvanostatic polarization was carried out from -200 to +200 mV to the OCP and the potential (E) between the working electrode and the SCE was measured at different polarizing currents (i). From the resulting E vs. log i polarization curves, the corrosion potential (E_{corr}) and corrosion current densities (i_{corr}) of the specimens were obtained using the Tafel extrapolation method.[7]

Structure of the Deposits

The structure and distribution of BN particles in the composite were examined by scanning electron microscopy.

Table 1
Taber Wear Index of Ni-BN Composites

Coating	Cycle I	Cycle II	Cycle III
	Load: 1 kg, CS-10 Calibrase Wheel		
1. Mild steel	5.7	4.9	4.8
2. Ni-BN, 11.8 vol %	5.0	4.5	3.6
3. Ni-BN, 19.6 vol %	4.5	3.9	3.4
4. Ni-BN, 28.8 vol %	3.5	2.5	2.4

Results and Discussion

Effects of BN Concentration in Suspension On the Vol percentage in the Composite

In general, the extent of incorporation of the finely suspended particles depends on effective collision at the cathode surface. Figure 1 shows the vol percentage incorporation of BN obtained at 10 to 80 g/L of BN particles in suspension at 5 A/dm^2. As can be seen, particle incorporation increases sharply with suspension concentration and attains an optimum value at 30 g/L. This limiting concentration may correspond to steady-state equilibrium, whereby the number of codepositing particles equals the number approaching the cathode surface. It was found that with further additions, the particles appeared to agglomerate in the bath and a decreasing trend was observed, resulting in rough and nodular deposits. The decreasing trend beyond 30 g/L BN suspension may result from insufficient stirring.[8]

The topography of the Ni-BN composites with varying BN incorporation is shown in Fig. 2. At 10 g/L particle concentration (Fig. 2a), coverage of the BN particles at fewer sites was seen, where spreading increased with further addition of BN. Complete coverage of the nickel matrix was obtained at 30 g/L of BN suspension (Fig. 2b). The agglomerated deposit was revealed clearly at 80 g/L of BN suspension (Fig. 2c), as observed during codeposition.

Effect of Current Density On BN Content of Composite

The effect of varying the current density from 2 to 10 A/dm^2 for 30 g/L of BN in suspension at 50 °C and at pH 3.0 is shown in Fig. 3. Over the range of BN inclusions, maximum incorporation of 28.8 vol percent could be seen at 5 A/dm^2, above which the extent of codeposition decreased significantly to about 23 vol percent at 10 A/dm^2. This trend is inconsistent with other types of metal particle composites,[9] where the metal is being deposited under conditions of charge transfer

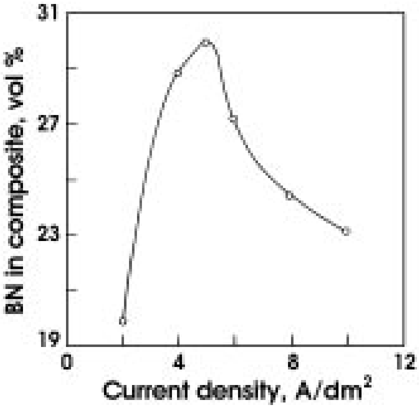

Fig. 3—Effect of current density on incorporation of BN in the composite.

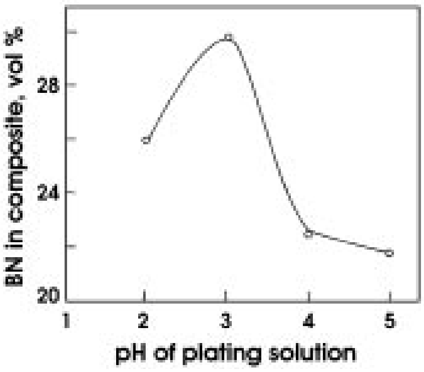

Fig. 4—Effect of pH on incorporation of BN in the composite.

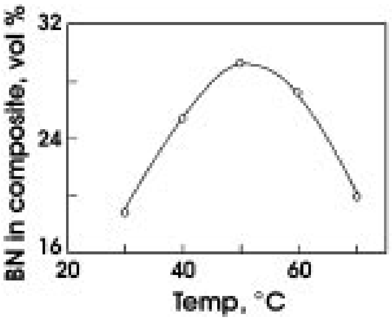

Fig. 5—Effect of temperature on incorporation of BN in the composite.

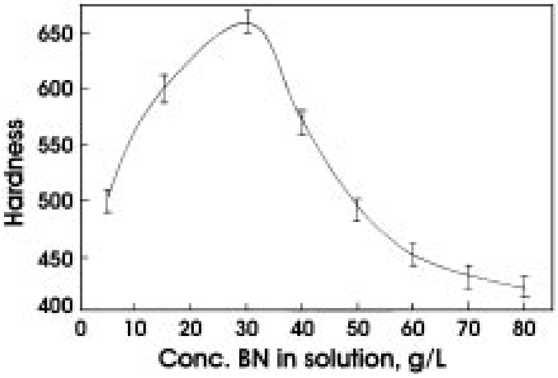

Fig. 6—Effect of BN incorporation on microhardness.

overpotential control. Above 5 A/dm^2, as the reduction of nickel ions is controlled by concentration overpotential, the amount of codeposited BN particles gradually decreases. The dependency of codeposition on charge-transfer overpotential control indicates that the rate of codeposition is determined by the formation of a real contact between the nickel ions adsorbed on BN particles and the cathode surface.[10]

Effects of pH & Temperature on Vol percent Content of Composite

The influence of pH on BN incorporation is shown in Fig. 4. A smooth, uniform and semibright deposit, containing 29.8 vol percent BN was obtained at pH 3 for a BN suspension of 30 g/L at 5 A/dm^2 and 50 °C. Increasing the pH from 3 to 5 markedly lowered incorporation of BN (22 vol percent) in the composite. The decreasing trend with increasing pH may be a result of a decrease in the efficiency of nickel deposition and an increase in viscosity of the solution.[8]

It was found that the temperature of the plating bath noticeably influenced the extent of codeposition (Fig. 5). BN incorporation increased from 18.4 to 29.3 vol percent when the temperature was increased from 30 to 50 °C. Above this value, a decreasing trend was observed, probably resulting from decrease in the current efficiency of nickel deposition.

Microhardness

The variation in microhardness of the Ni-BN composite vs. the BN concentration in the bath is shown in Fig. 6. With incorporation of BN in the deposit, the hardness increases to about 3 to 4 times more than that of electrodeposited nickel (VHN$_{50}$ 160). The greater hardness produced is not entirely a result of the dispersion hardening effect of the BN particle, but also a result of the fine-grained structure of the deposit. During hardness measurements, the dispersed particles in the fine-grained matrix may obstruct the easy movement of dislocations and resist plastic flow.[11] This resistance to deformation is shown by an increased hardness value for Ni-BN composite in the as-plated condition. The decreasing trend in hardness beyond 30 g/L BN additions results from the agglomerated deposit, as observed during codeposition.

Table 2
Corrosion Data from Galvanostatic Polarization

Sample	**Electrolyte**			
	5% NaCl, pH 3		**5% NaCl, pH 6.5**	
	E_{corr} vs. SCE mV + 10 mV	**i_{corr} μA/cm^2**	**E_{corr} vs. SCE mV + 10 mV**	**i_{corr} μA/cm^2**
Mild steel	-660	24	-580	40
Ni-BN, 11.8 vol %	-488	4	-488	14
Ni-BN, 19.6 vol %	-546	8	-538	24
Ni-BN, 28.8 vol %	-548	8	-538	26

Wear Resistance

The Taber wear index of Ni-BN deposits for three successive cycles is shown in Table 1. Incorporation of BN was found to improve significantly the wear resistance of nickel coatings. Hardness and grain structure of the deposit may affect wear properties of coatings, among various other factors, such as mating surfaces and coefficient of friction. For nickel deposits, the principal mechanism of material removal by the abrasive particles was plowing to produce grooves.[12] Because of the load-bearing capacity of the Ni-BN composite, abrasion of the composite was less than that seen on the nickel surface. This can be understood from the improved wear index values.

For a given vol percent incorporation of BN in the deposit, the wear index measured in consecutive cycles has decreased, relative to the previous cycle, and tended to attain a steady value after a few cycles of abrasion. The observed initially greater value may be a result of abrasion on the rough surface of the composite, produced by the protruding particles yet to be engulfed by the metallic matrix.

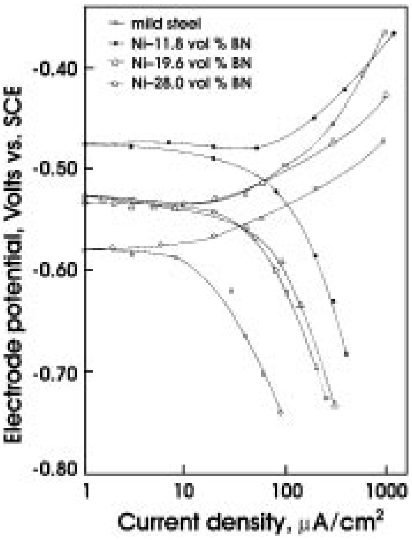

Fig. 7—Galvanostatic polarization curves for corrosion of Ni-BN composites in pH 6.5 NaCl solution.

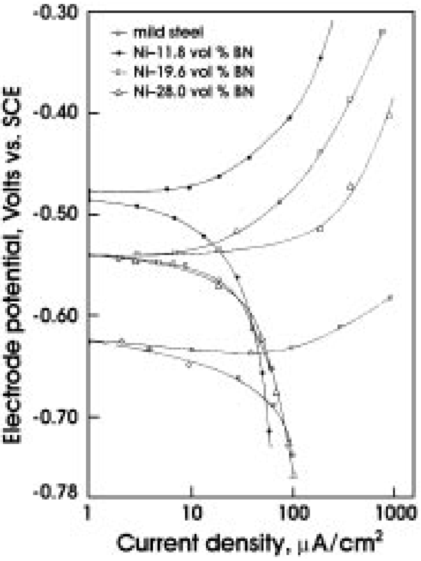

Fig. 8—Galvanostatic polarization curves for corrosion of Ni-BN composites in pH 3 NaCl solution.

Corrosion Resistance

Figures 7 and 8 show the galvanostatic polarization curves for mild steel and Ni-BN composites with 11.8, 19.6 and 28.8 vol percent incorporation of BN in 5-percent NaCl solutions of pH 3 and 6.5. The linear segments of the polarization curves were extrapolated to OCP to obtain the corrosion current density (i_{corr}). The corrosion data are summarized in Table 2.

Compared to mild steel, the corrosion potentials for Ni-BN composites are shifted more toward anodic potentials in NaCl solutions of pH 3 and 6.5 (Table 2). This behavior is as expected because of the presence of the corrosion-resistant nickel matrix on steel.

The corrosion currents are significantly decreased in comparison with mild steel; consequently, the composites offer improved protection to steel against corrosion in 5-percent NaCl solutions. More incorporation of BN, however, is found to lower the corrosion resistance, compared to 11.8 vol percent BN composite. Additional BN incorporation accelerates the corrosion process, as the metal particle boundary acts as an anodic area for active dissolution.[13] Accordingly, a larger corrosion current is observed for Ni-BN composites with more than 11.8 vol percent BN.

Findings

1. Ni-BN (28.8 vol percent) composite was obtained by operating the bath at 5 A/dm^2 at pH 3 and 50 °C for a BN particle suspension of 30 g/L.
2. The vol percent incorporation of BN in the composite increased with increasing BN content in the bath and increasing current density.
3. The hardness and wear resistance of the composite were found to be three to four times greater than those of electrodeposited nickel.
4. The Ni-BN composites offer improved protection against corrosion of steel in 5-percent NaCl solutions of pH 3 and 6.5.

Editor's Note: *Manuscript received, January 1995.*

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