ELECTRODEPOSITED COBALT-BORON NITRIDE COMPOSITES

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Electrodeposited composite coatings enhance one or more of the properties of the substrate or confer an entirely new property. The use of metals like copper, nickel, cobalt, etc., as matrix makes possible the use of composites at elevated temperatures. In this investigation cobalt-boron nitride (Co-BN) composites were produced by conventional electrodeposition methods using a cobalt sulfate bath containing boron nitride (BN) particles in suspension. The effects of BN particle concentration in the bath, current density, pH and temperature on volume percent (Vol. %) incorporation of BN particles in the composites were investigated and the optimum conditions were found. Corrosion behaviour of the Co-BN composite was studied in 5% NaCl and 1 M HCl solutions by galvanostatic polarization method and the results were compared with those of cobalt deposits. From the resulting polarization curves, the corrosion potential and the corrosion current were obtained. Surface topography of Co and Co-BN composite was also studied.

Keywords: Electro composites, Co-BN, Galvanostatic polarization, 5% NaCl, 1 M HCl.

INTRODUCTION

Electrodeposited composite coatings enhance one or more of the properties of the substrate or confer an entirely new property. The coatings are used in preference to bulk material because of economic or technological considerations. The use of metals like copper, nickel, cobalt etc., as matrix makes possible the use of composites at elevated temperatures [1-2]. In order to obtain improved properties such as high strength and stiffness with light weight, excellent oxidation and heat resistance at high temperature and good resistance to wear and anti-frictional characteristics, a considerable effort has been expended in recent years on production of commercially useful metal matrix composites by incorporating inert solid particles like borides, carbides, nitrides, oxides, polymers, sulfides etc. using electrodeposition and electroless deposition methods. For a number of applications, electrocomposites are found to be superior than other coating systems such as flame spraying, hard chromium plating and nitriding. Industrial applications of these coatings are mainly located in the field of mechanical, engineering, aeronautical, marine, mining, agriculture and nuclear sectors.

In this investigation, cobalt-boron nitride (Co-BN) composites were produced by conventional electrodeposition method [3] using a cobalt sulfate bath containing boron nitride particles in suspension. The effects of BN particle concentration in the bath, current density, pH and temperature on volume percent incorporation of BN particles in the composites were investigated and the optimum conditions were found. Corrosion behaviour of the Co-BN composite was studied in 5% sodium chloride (NaCl) and 1 M hydrochloric acid (HCl) solutions by galvanostatic polarization technique and the results were compared with those of cobalt deposits.

Surface topography of electrodeposited Co and Co-BN composite was investigated with a scanning electron microscope and the structural changes with particle incorporation were studied.

EXPERIMENTAL

Electrodeposition of Co-BN Composites

Cobalt-boron nitride electrocomposite was prepared using a solution consisting of 290 g.l^{-1} cobalt sulfate, 40 g.l^{-1} boric acid and 0.1 g.l^{-1} sodium lauryl sulfate. By means of a mechanically

controlled glass stirrer, the pre-treated boron nitride particles of average size 3 microns were kept in suspension in the plating electrolyte. The codeposition was carried out in a 1 litre glass beaker. As anodes, two 0.5 cm thick graphite sheets were used. Stainless steel specimens 7.5 x 5.0 x 0.1 cm served as cathodes, from which the coatings could be easily stripped off for analysis. The cobalt contents of the Co-BN composites were determined by analyzing the solutions using atomic absorption spectrometry with a high degree of accuracy [4]. The BN particle contents of the composites could thus be deduced from the differences between the weight of the composite and the cobalt therein. The volume percent contents of BN were then evaluated from the total volume of the composite and the volume of BN. Triplicate analyses were made in each case and the average values reported [5].

The extent of BN incorporation into cobalt matrix was studied with respect to particle concentration between 5 and 50 g.l^{-1}, current density ranging from 2 to 10 A.dm^{-2}, bath pH from 1 to 5 and a bath temperature range of 303-333 K.

Corrosion behaviour of Co-BN composites

The corrosion behaviour of Co-BN composites plated to a thickness of 7.5 and 15 microns on polished mild steel sheets were studied in 5% NaCl and 1 M HCl solutions using galvanostatic polarization technique. A three electrode cell assembly was used. The plated specimens were masked with lacquer to expose 1 cm^2 area which served as the working electrode. A platinum foil of 2.5 x 2.5 cm size was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. A constant current generator fabricated at CECRI was used as a galvanostat and the potential was measured by a HIL Digital Voltmeter. The composite was immersed in the test solution and the rest potential (OCP) was recorded after attaining a steady state. The current (I) was increased from zero in steps and the potential (E) between the working electrode and SCE was measured at steady state after 10 minutes at each current. E

Vs log I was plotted and the polarization curves were obtained. Using Tafel extrapolation technique, the corrosion potential (E_{corr}) and the corrosion current (I_{corr}) were obtained for each sample. A duplicate test was made using fresh in each case.

Structural investigations

Co and Co-BN samples of 1 cm^2 was cut and polished. The surface topography was studied using Scanning Electron Microscope at 1000X.

RESULTS AND DISCUSSION

Effect of BN particle concentration

The extent of BN incorporation into the deposit against their concentration in the suspension ranging between 5 and 50 g.l^{-1} at pH 2, 323 K and at 5 A.dm^{-2} is shown in Fig. 1. It can be seen that the BN content in the composite increased sharply and attained an optimum inclusion (25 Vol%) at 30 g.l^{-1} BN suspension. Also it was found that with further additions, the particles appeared to agglomerate in the bath and a decreasing trend was observed which suggested an insufficient stirring to maintain all the BN particles in
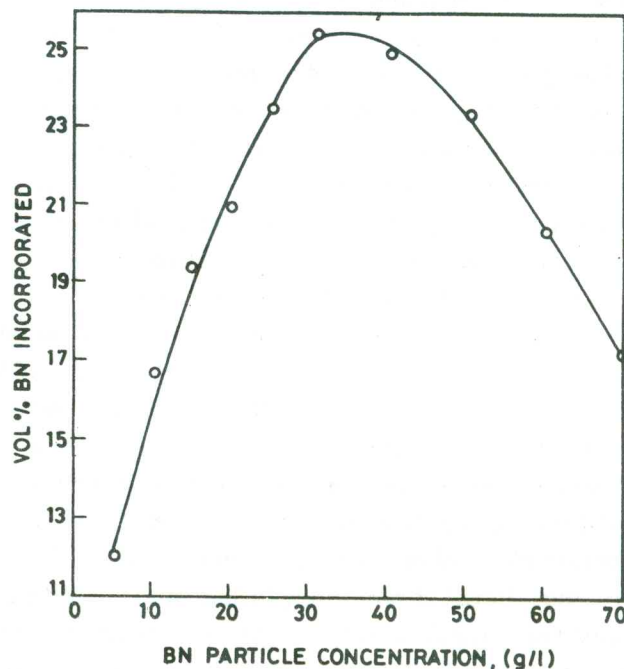

Fig 1. Effect of BN particle concentration on Vol% BN incorporated. Current density 5 A.dm^{-2}, pH 2, Temp 323 K

suspension and to the greater degree of agglomeration in the bath.

Effect of current density

Fig. 2 illustrates the effect of current density on BN incorporation into the composite. With increasing current density, the BN incorporation increased and attained 25.5 Vol% at 5 A.dm^{-2} beyond which a sharp decreasing trend was noted. This pattern was consistent with other types of metal- particle composite systems [6-7] where the metal is being deposited under conditions of charge transfer over-potential control. Probably at higher current densities, the reduction of cobalt ions may be controlled by concentration over potential which may in turn cause decreased codeposition. This dependency of codeposition on charge transfer over-potential control indicates that the rate of codeposition is determined by the formation of a real contact between the cobalt ions absorbed on BN particles and the cathode surface.

Effects of *p*H and temperature

The influence of *p*H on BN incorporation is shown in Fig. 3. A smooth, uniform and semi-bright deposit containing 25 Vol% BN was obtained at *p*H 2 for a BN suspension of 30 g.l^{-1} at
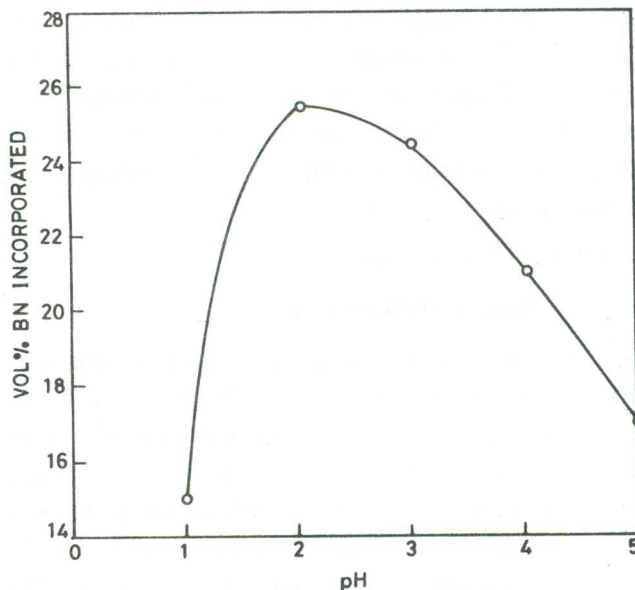

Fig 3. Effect of *p*H on Vol% BN incorporated
BN concn 30 g.l^{-1}, Current density 5 A.dm^{-2} Temp 323 K

5 A.dm^{-2} of 323 K. Increasing the *p*H had lowered the vol% BN incorporation and a brittle deposit was obtained at *p*H 4-5.

The temperature of the plating bath had shown a significant effect on codeposition (Fig. 4). BN incorporation increased from 20 to 25 vol% when the temperature was increased from 303 to 323 K.
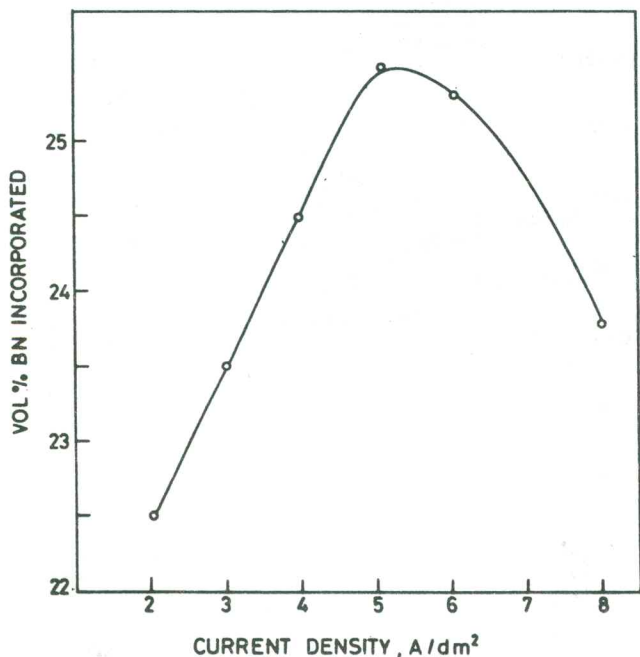

Fig 2. Effect of current density on Vol% BN incorporated
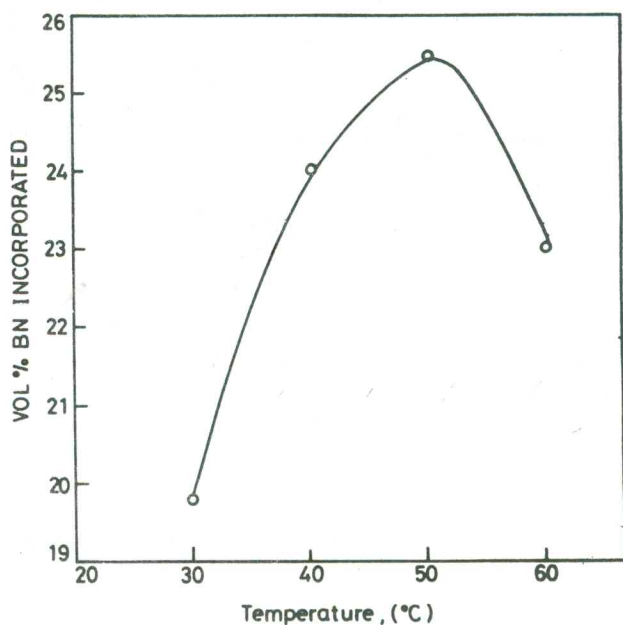BN concentration 30 g.l^{-1}, pH 2, Temp 323 K

Fig 4. Effect of temperature on Vol% BN incorporated
BN concentration 30 g.l^{-1}, Current density 5 A.dm^{-2}, pH 2.

Above this range, a decreasing trend was observed. The cathode current efficiency of the composite deposit was found to fall between 60% and 70% at higher temperature and current density which may account for the observed trend at higher temperature.

Corrosion behaviour of Co-BN composites

In 5% sodium chloride solution

Figs. 5 and 6 show the galvanostatic polarization of cobalt and cobalt-boron nitride composites over mild steel in 5% sodium chloride solution. From these curves, corrosion potential (E_{corr}) and corrosion current (I_{corr}) were calculated and these values are given in Table I. From these it can be seen that composite coatings of Co and Co-BN shift the corrosion potential anodically when compared to the corrosion potential of mild steel. The shift is more when the coating thickness is 7.5 μm. When the thickness of the deposit is increased to 15 μm, the shift in E_{corr} is less. From the table it is evident that addition of boron nitride to cobalt does not change the behaviour of

TABLE I: Corrosion data of Co-BN (25 vol%) in 5% NaCl solution by galvanostatic polarization method

Sample	Thickness (μm)	E_{corr} mV vs SCE	I_{corr} μA . cm^{-2}
Mild steel	—	-625	10
Co	7.5	-485	4
Co-BN	7.5	-515	5
Co	15.0	-560	6
Co-BN	15.0	-570	7

the deposits to a great extent. The corrosion current is less in case of the composites with 7.5 μm thickness. This also indicates that increasing coating thickness does not increase the corrosion protection to a great extent. However, these composite bring down the corrosion current from 10 μA.cm^{-2} indicating that the corrosion rate of mild steel in 5% sodium chloride can be brought down to 5% thereby protecting steel more effectively in this medium.
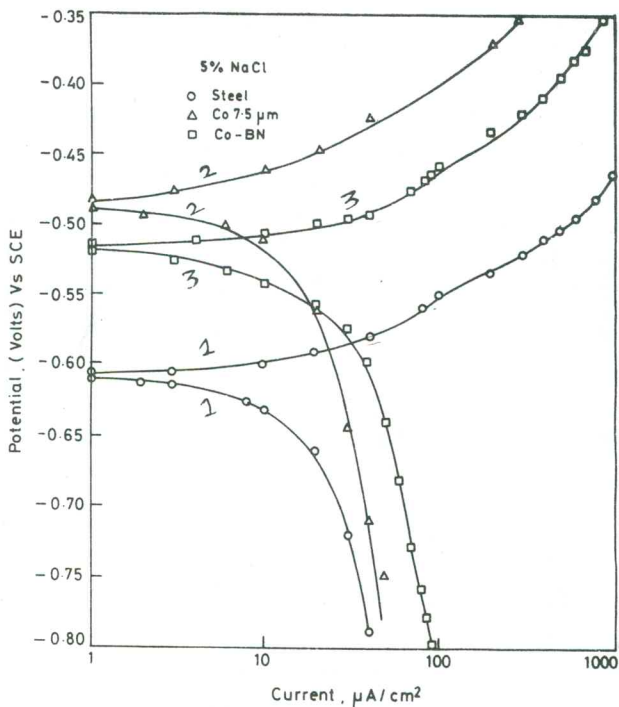

Fig 5. Galvanostatic polarization curves for corrosion of mild steel (1), Co (2) and Co-BN composite (3) in 5% NaCl solution. Deposit thickness 7.5 μm.
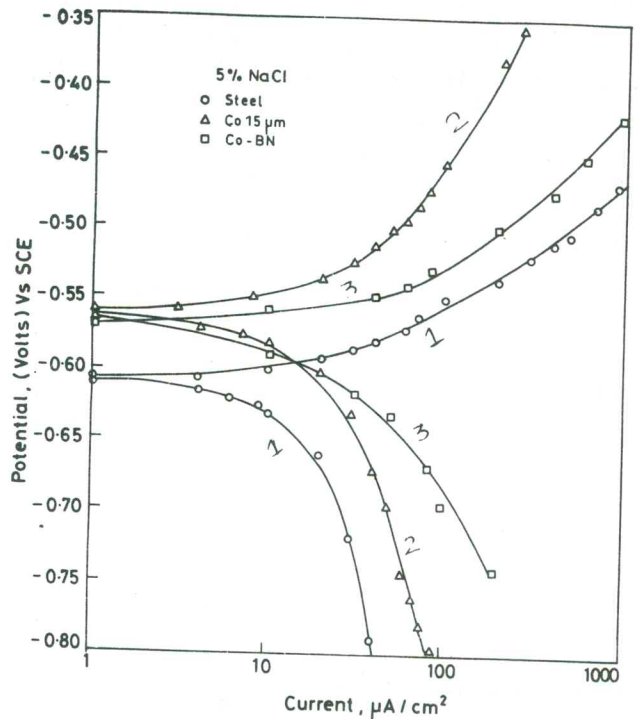

Fig 6. Galvanostatic polarization curves for corrosion of mild steel (1), Co (2) and Co-BN composite (3) in 5% NaCl solution. Deposit thickness 15 μm
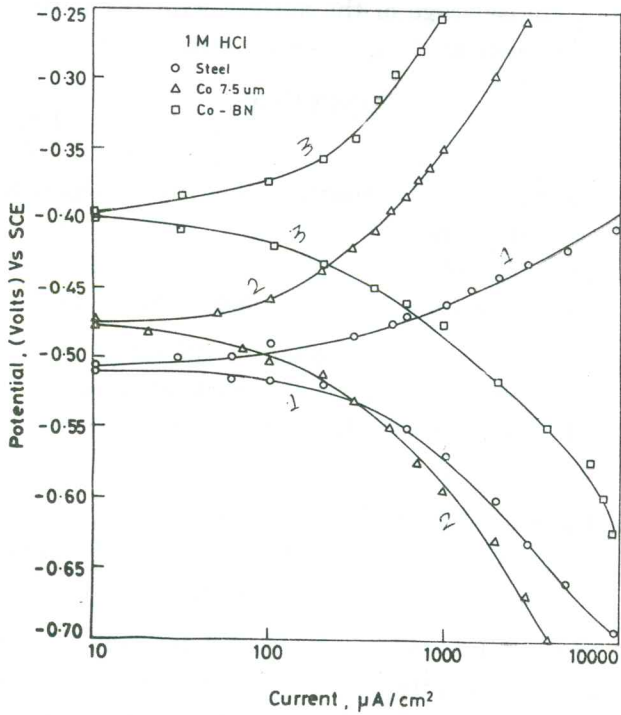
Fig 7. Galvanostatic polarization curves for corrosion of mild steel (1), Co (2) and Co-BN composite (3) in 1 M HCl solution. Deposit thickness 7.5 μm
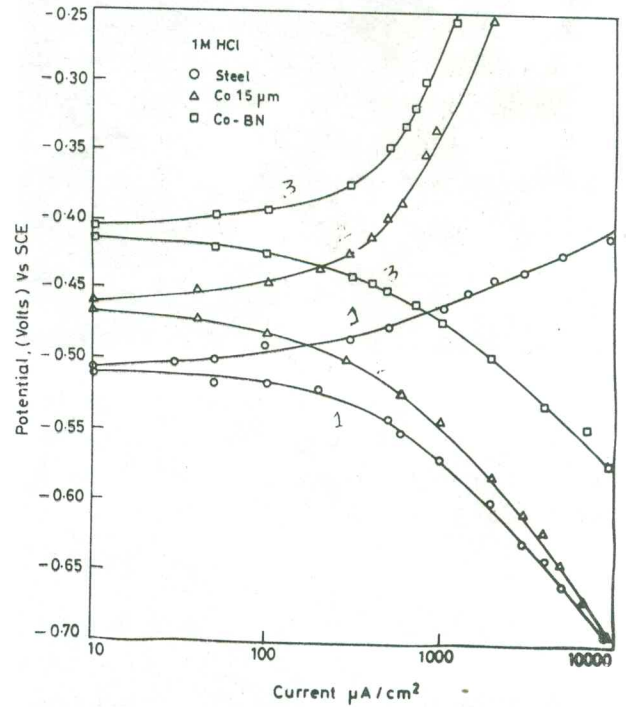

Fig 8. Galvanostatic polarization curves for corrosion of mild steel (1), Co (2) and Co-BN composite (3) in 1 M HCl solution. Deposit thickness 15 μm

In 1 M Hydrochloric acid solution

Figs. 7 and 8 show the galvanostatic behaviour of mild steel, cobalt and cobalt-boron nitride composite coatings in 1 M hydrochloric acid. From these curves, E_{corr} and I_{corr} were calculated (Table II). From the curves it is clear that both composite coatings, irrespective of the thickness shifts the corrosion potential, E_{corr}, towards anodic direction. In case of Co-BN composites, the shift is almost 100 mV towards anodic direction and for cobalt coatings alone, the shift is not to that

extent. This indicates that addition of boron nitride to the composite has more pronounced effect in bringing down the I_{corr} in acid medium considerably. The corrosion current is reduced from 150 to 30 μA.cm^{-2} indicating that by adding boron nitride to cobalt matrix one can prevent the dissolution of mild steel almost 3 times. In this study also the thickness of the coating does not alter the corrosion behaviour to a great extent. At lower coating thickness i.e. at 7.5 μm, by incorporating boron nitride, one can achieve the same kind of corrosion protection as achieved by increasing the coating thickness to 15 μm.

Structure of Co-BN composite

Fig. 9 shows the SEM photograph of Co-BN composites electrodeposited at 5 A.dm^{-2}. The Co matrix reveals a coarse grained structures (Fig. 9a). Introduction of BN particles into the Co matrix shows a modified structure resulting with a fine-grained structure (Figs. 9b and 9c). A
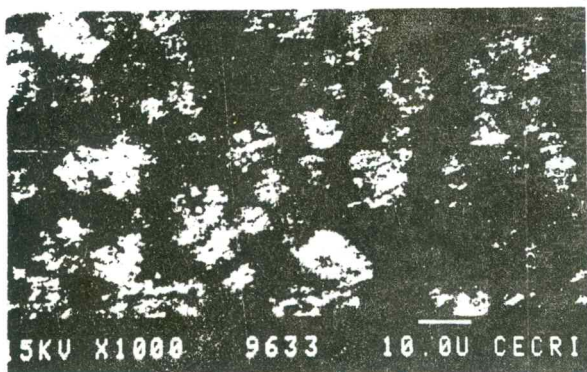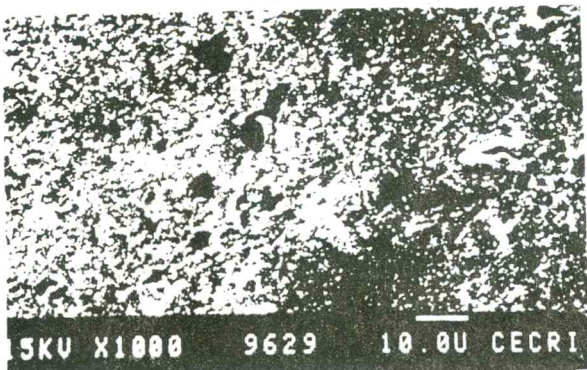
TABLE II: Corrosion data of Co-BN (25 vol%) in 1 M HCl solution by galvanostaticpolarization method

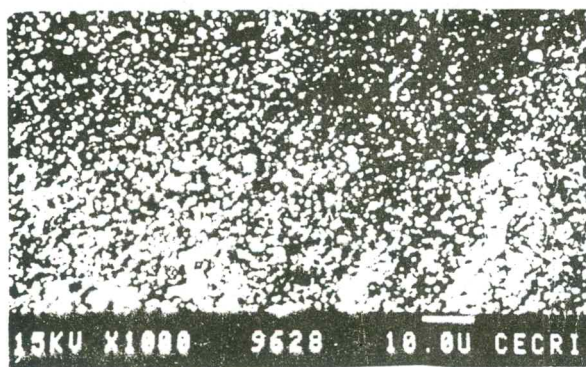| Sample	Thickness (μm)	E_{corr} mV vs SCE	I_{corr} μA.cm^{-2}
Mild steel	—	-510	150
Co	7.5	-480	40
Co-BN	7.5	-395	30
Co	15.0	-465	40
Co-BN	15.0	-405	25

Fig. 9a

Fig. 9b

Fig. 9c

Fig 9. SEM structure of electrodeposited Co & Co-BN composites
(a) Co deposit (b) Co-BN (10 g.l^{-1}) (c) Co-BN (30 g.l^{-1})

complete coverage of the surface with BN particles can be seen at 30 g.l^{-1} suspension.

CONCLUSION

¤ BN particles can be incorporated into a cobalt matrix by conventional electro codeposition method using a sulphate bath consisting of 290 g.l^{-1} cobalt sulphate, 40 g.l^{-1} boric acid, 0.1 g.l^{-1} sodium lauryl sulphate and 30 g.l^{-1} BN.

¤ An optimum incorporation of BN (25 vol%) was obtained by operating the bath at 5 A.dm^{-2} at pH 2 and at 323 K for a BN particle content of 30 g.l^{-1} in the bath.

¤ The vol% incorporation of BN particles into the Co matrix increased with increasing BN content in the bath and current density.

¤ The Co-BN (25 vol%) composites of 7.5 μm thickness offer 2-3 times more protection against corrosion on steel in 5% NaCl and 1 M HCl solutions.

REFERENCES

1. V O Nwoko and L L Shreir, *J Appl Electrochem,* **3** (1973) 137
2. G R Lakshminarayanan, E S Chen and F K Chen, *Plat Surf Finish,* **63** (1976) 35
3. F K Sautter, *J Electrochem Soc,* **110** (1963) 577
4. G N K Ramesh Bapu, V S Muralidharan and K I Vasu, *Plat and Surf Finish,* **78** (1991) 126
5. G N K Ramesh Bapu and M Mohammed Yusuf, *Materials Chemistry and Physics,* **36** (1993) 134
6. N Guglielmi, *J Electrochem Soc,* **119** (1972) 1009
7. J P Celis and J R Roos, *J Electrochem Soc,* **124** (1977) 1508