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Preparation and characterization of nickel-cobalt-diamond electro-composites by sediment co-deposition

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Abstract

Nickel-diamond and nickel-cobalt diamond coatings were produced by electrodeposition using sedimentation technique on mild steel substrate and their tribological properties evaluated. Electrodeposition was carried out from a conventional Watts bath with cobalt addition. The conditions to obtain nickel-cobalt alloy were optimized first and then the conditions for obtaining diamond composites from both systems were investigated. Natural diamond powder of $6-12 \mu m$ size was used in the study. The volume percent incorporation of diamond powder in the coatings was investigated with respect to its concentration and cobalt concentration in bath, cathode current density, pH and temperature. The diamond powder distribution in the composite coatings, as examined with SEM, are uniform at low powder concentration in the bath and agglomerated at high concentrations. Physical properties of the composites including hardness, wear resistance and roughness were measured. Presence of cobalt increased volume percent incorporation of diamond powder, hardness and wear resistance of the coatings. © 2006 Elsevier B.V. All rights reserved.

Keywords: Composites; Natural diamond; Mechanical properties; Microstructure

1. Introduction

Diamond and diamond based composite coatings are considered as super abrasive materials harder than other materials. Due to their superior tribological properties, these materials are industrially important. Though the exceptional properties of diamonds are well known, it is difficult to make any component using only diamond powder. This has necessitated the growth of composite market throughout the world.

Diamond tools are used for cutting, shaping and finishing of numerous materials such as rocks — granite, marble, sandstone, refractories, concrete, ceramics, glass and cemented carbides. Diamond tools range from dresser tools, grinding wheels, segmented saws to precisely shaped single crystal diamond tools for the accurate generation of surfaces to tolerances in the micrometer to nanometer range as in the case of turning computer hard discs. Electroplated super abrasive tools involve a single layer of highly concentrated ultra-hard abrasive material such as diamond electro-co-deposited along with a hard and durable nickel layer onto a metal substrate of the required form/profile. These electroplated products are multi-purpose tools that can be manufactured using diamond powder of a wide range of micron sizes for a variety of applications. The superiority of electroplated tools lie in their high cutting efficiency and longer tool life, made possible by their excellent grit protrusion and high diamond concentration.

Ultra dispersed diamond particles in a nickel matrix are increasingly attracting considerable scientific and technological interest by virtue of their unique mechanical and tribological properties including higher hardness, lower friction coefficient and inertness to chemical attack [1–6]. Yogodkina et al. [7] studied the structure, physicochemical and structure of Nidiamond composites and Reddy et al. [8] and Lukschandel [9] studied the properties of electro less Ni-diamond coatings. Abi-Akar et al. [10] investigated the effect of gravity on co-deposition of the above composites. Sato et al. [4] studied the above process on the grinding wheel while Lee et al. [11] compared the Ni-nano diamond co-deposition from direct current and pulse current.

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Table 1 Conditions used for plating Ni-diamond and Ni-Co-diamond composite coatings

Variable	1	2	3	4	5
Temperature (°C)		30	45	60	
pH	2.5	3.5	4.5		
Current density (A/dm ²)		1	2	3	4
Diamond Concentration (g/l)	1	2.5	5	10	15
Cobalt as sulphate ^a (g/l)	1	2.5	5	7.5	10

^a Only for producing Ni-Co-diamond deposits.

The particle surface state is of great importance to the codeposition process. It has been widely accepted that this could be achieved by the surface modification of these particles [12-14]. More probably, surface modification can be achieved through organic surface-active agents. Attempts to increase the incorporation of the co-deposited particles using various organic surfactants in the electrolyte have been reported by many researchers [12–14]. On the other hand, inorganic additives for modification of the particle surface state are much more important and practical, since the addition of organic additives can cause disadvantages such as instability in the electrolyte, high stress or brittleness of the composite deposits, etc. Presently few studies have concentrated on effects of inorganic additives like cobalt on the co-deposition process [15-20]. It is assumed that Co²⁺ ions are adsorbed on diamond particles much easier compared with Ni²⁺, which might give particle surfaces a more positive charge [17]. In the present work effect of cobalt addition on nickel-diamond co-deposition has been studied and their tribological properties were investigated by evaluating the microstructure, micro hardness, surface roughness and wear resistance.

2. Experimental

2.1. The electrolyte

The conventional Watts bath of the following composition was used.

Nickel sulphate:	250 g/l
Nickel chloride:	30 g/l
Boric acid:	40 g/l

The electrolyte was purified in the conventional manner for removal of organic and inorganic impurities [21]. The pH value of the electrolyte was adjusted electrometrically using dilute H_2SO_4 or KOH. The temperature of the electrolyte was maintained at the set value using a thermostat. 0.01-g/l sodium lauryl sulphate was added to the electrolyte as anti-pitting agent before plating.

2.2. Plating procedure

Deposition was carried out on a 500 ml capacity using sedimentation technique [2]. Nickel anodes and mild steel cathodes were used. For estimation of volume percent stainless steel cathodes were used. The cathodes of 7.5×2.5 cm area

were mechanically polished, degreased, bent to 90° , suitably masked to expose an effective plating area of 6.25 cm², electro cleaned, first cathodically and then anodically, washed rinsed and then introduced into the plating electrolyte with the area to be plated in the horizontal plane closer to the bottom of the cell facing the anode. A bagged nickel anode bent similarly was placed above the area to be coated. Diamond powder was added to the electrolyte in the form of a slurry.

The solution was stirred using a magnetic stirrer. Stirring was given initially for 30 s to bring all the diamond powder into the suspension and then stopped. The deposition was continued for 15 min to allow the particles to settle on the substrate while the deposition proceeded. The same process was repeated to obtain deposit thickness of 25 μ m.

The volume percent of diamond incorporation in the deposits were estimated gravimetrically. Deposits were stripped in 50% (v/v) nitric acid, which was filtered, and the mass of diamond powder in the deposit was estimated gravimetrically. Knowing the mass of the deposit and the incorporated powder and the density of nickel and diamond powder, the volume percent incorporation was calculated. Each experiment was carried out with a fresh solution and the values reported are the average of three readings.

2.3. Ni-diamond deposition

Natural grade polycrystalline diamond powder of $6-12 \ \mu m$ sizes supplied by M/s Dev Ashish, Mumbai was used. Prior to the co-deposition, the diamond particles were ultrasonically dispersed in the bath for 10 min.

Initially, experiments were conducted at a fixed diamond concentration of 5 g/l, varying the plating parameters like temperature, pH, current density as shown in Table 1. Based on the volume percent, and nature of deposits, the optimum operating conditions were fixed. Adopting this, experiments were conducted at varying diamond concentrations in the bath.



Fig. 1. a) Set-up used for measuring wear resistance. b) Wear disc showing the wear track.



Fig. 2. Effect of diamond concentration in the nickel bath on its vol.% incorporation in the deposit. pH 3.5; 30 °C; Current density, A/dm² : \blacksquare 1; \blacksquare 2; \blacktriangle 3; \lor 4.

2.4. Ni-Co-diamond deposition

Admixtures of cobalt in nickel-diamond composite impart superior mechanical properties, especially in terms of hardness



b)



Fig. 3. SEM micrograph of nickel diamond composite plated at 1 A/dm², 30 $^{\circ}$ C, pH3.5, and diamond concentration in bath: a) 1.0 g/l; b) 5.0 g/l.



Fig. 4. Effect of nickel bath temperature on the vol.% diamond incorporation at different current densities, 30 °C, pH 3.5. Current density, A/dm²: ■ 1; ● 2; ▲3; ▼4.

and wear resistance. Moreover, its ability to dissolve carbon permits wetting of the diamond particles and improves their bond with the matrix [19,22,23]. As suggested by Lee et al. [15], experiments were conducted to optimize the operating variables and cobalt concentration in the solution to produce a nickel alloy containing around 10%-cobalt. The range of parameters studied are as given in Table 1. The concentration of cobalt as its sulphate, added to the Watts bath was varied from 1–10 g/l. Other conditions are similar to Ni-diamond composite plating. Ni and Co percentages in the deposit were determined using X-ray Fluorescence Spectroscopy (XRF).

2.5. Properties evaluation

Hardness of the deposits was determined using Mitutoyo micro hardness tester at a load of 50 g. The final value quoted for the hardness of a deposit was the average of 10 measurements.

Surface roughness of the composite was determined by means of Mitutoyo Roughness testing instrument.

Wear resistance of the composite coating was measured using Ducom's pin on disk wear testing machine. Testing was conducted under dry lubricant condition. The material surface to be tested was fixed on the wear disc and load is applied to pin by adding weight to the pan. The pin used here was a high-speed steel containing 5% cobalt of hardness 65 HRC (833 HV). The pin tip is rounded to have point contact with the surface. The tests were done at various loads, distances and speeds and the rotating track diameter was around 14 mm. Fig. 1 shows the apparatus used for testing wear and friction of composite coatings. The wear rate was calculated using equation,

Wear rate = V/SF where,

V is wear volume in cm³, *S* is sliding distance in cm (measured using formulae $2 \times 3.14 \times R \times N \times t$. where *R* is the wear track diameter in cm, *N* is No of revolution of wear disc per minute, *T* is time in minutes) *F* is the normal load in N. Wear track diameter and normal load used here was 14 mm and 7.5 N. Wear volume was estimated from the wear rate displayed. Experiments were conducted to determine the effect of diamond volume percent and cobalt content on wear rate.

Table 2

Surface morphologies of composite coatings were examined by scanning electron microscope.

3. Results and discussion

Sediment co-deposition is done by occasional stirring of the dispersoid and allowing it to settle slowly as the deposition progresses.

3.1. Ni-diamond deposition

3.1.1. Effect of diamond powder concentration

The effect of diamond concentration in the bath on the diamond content of the deposits is shown in Fig. 2. The volume percent of diamond particles in the composite increased by raising its concentration in the bath up to 5 g/l. Similar trend has been reported by Zahavi and Hazan [24] and in several different systems [5,25,26]. Fig. 3a and b show the SEM micrographs of deposits obtained at two different concentrations in the electrolyte. With 1 g/l, though the particle incorporation in the deposit is less the extent of agglomeration of particles is also less. But, with 5 g/l, the particle incorporation in the deposit is

a)



Fig. 5. SEM micrograph of nickel diamond composite plated at pH 3.5 with diamond concentration in the bath 5.0 g/l. a) 4 A/dm², 50 °C and b) 30 °C.

27-May-05

500µm

0mm 25.0kV x100

Effect of pH on the volume percent diamond incorp	oration and hardness of
deposits (Diamond concentration 5 g/l; 30 °C)	

pН	C.D. A/dm ²	C.D. A/dm ² Diamond (vol.%)	
2.5	1	48.40	434
2.5	2	45.90	410
2.5	3	40.35	390
2.5	4	38.44	365
3.5	1	48.30	460
3.5	2	45.20	432
3.5	3	43.23	420
3.5	4	42.58	_
4.5	1	39.40	421
4.5	2	44.35	398
4.5	3	37.26	380
4.5	4	29.24	_

more but the extent of agglomeration of particles is also high. At still higher concentrations the volume percent showed a decreasing trend probably due to the blocking effect of the powder [1] on the surface area available for plating. In absence of sufficient metal available for holding/binding the particles, the deposits became more powdery in nature and withered off while handling, washing and drying.

3.1.2. Effect of current density

Fig. 2 also shows the effect of current density on the percentage incorporation of diamond in the deposit. With increasing current density, the incorporation decreases. Many authors have reported similar trend [27]. In composite plating the actual current density prevailing at the cathode is considerably higher than the apparent current density since the exposed area for deposition is very less. This condition is more effective in sediment co-deposition due to higher particle incorporation. So, at higher apparent current densities (>2 A/dm²), the rate of metal deposition increases considerably and hence the volume percent decreases. According to Lee et al. [5] charge transfer at the cathode controls the rate of nickel deposition; however, diamond particles did not transfer charge even though the particles move to the cathode electrophoretically. At higher current densities



Fig. 6. Effect of cobalt concentration in the nickel bath on the cobalt content of the deposit pH 3.5; 32 °C; Current density A/dm²: \blacksquare 1; O 2; \blacktriangle 3; \blacktriangledown 4. \blacklozenge Composition reference line.

nickel covered almost all the diamond particles, which got completely engulfed in the nickel deposit.

3.1.3. Effect of bath temperature

Fig. 4 shows the effect of varying the current density under different operating temperatures. At high operating temperature, the metal deposition rate increases reducing the volume percent diamond incorporation. Fig. 5a and b show the SEM micrographs of nickel diamond composites plated at 50 °C and at 30 °C at 4 A/dm² showing a reduction in diamond content at 50 °C.

3.1.4. Effect of solution pH

Table 2 shows the effect of pH on the volume percent diamond incorporation in the deposit. The diamond content in the deposit shows a maximum at pH 2.5–3.5. According to Lee et al. [5] the zeta potential for diamond particles decreased linearly with pH, and the point of zero charge (pzc) pH appeared to be 3.2. So, at pH 2.5 the particles are positively charged and reached the cathode by their own charge. Since the optimized pH of the





Fig. 7. SEM micrograph of a) nickel diamond composite plated at 1 A/dm², 30 °C, pH 3.5, diamond concentration in the bath 5.0 g/l; b) Ni–Co-diamond in the same conditions with 7.5 g/l Co in the bath.



Fig. 8. Effect of cobalt concentration in the bath on the diamond content of the deposit. pH 3.5; 30 °C; Diamond concentration in bath 5.0 g/l; Current density A/dm^2 : \blacksquare 1; \bigoplus 2; \blacktriangle 3.

plating bath is 3.5, diamond particles would be near negatively charged. Hence, Ni²⁺ ions should have got adsorbed on negatively charged diamond particles making co-deposition easy.

3.2. Ni-Co-diamond deposition

3.2.1. Effect of cobalt addition in a nickel bath

Fig. 6 shows the effect of cobalt addition in the nickel bath. As the cobalt concentration increases, its content in the deposit increases. As shown by Lee et al. [15] the conditions to obtain 10-15% cobalt in the alloy were selected. It is obvious that the system shows anomalous behavior in which the wt.% cobalt in the deposit is much higher than its content in the deposit. Cobalt wt.% of 2.99 in the bath, $1-2 \text{ A/dm}^2$, pH 3.5, and 30 °C were fixed as optimum conditions to obtain the above alloy. Fig. 7(a and b) shows the SEM micrograph of nickel and Ni–10%Co deposits. Marginal reduction in grain size (around 3 µm for nickel and 1µm for Ni–Co) is noticed leading to increase in hardness of the coating.



Fig. 9. Effect of current density on the diamond contents of the Ni and Ni–Co deposits. pH 3.5; 30 °C; Current density 1A/dm²; diamond 5g/l; ■ Ni-diamond; ● Ni–Co-diamond.



Fig. 10. SEM micrograph of nickel-cobalt-diamond composite plated at 1 A/dm², 30 $^{\circ}$ C, pH 3.5 and diamond in bath 5 g/l.

3.2.2. Effect of current density

Fig. 8 shows the effect of cobalt wt.% in the bath on the diamond volume percent incorporation in nickel–cobalt alloy deposit at different current densities. As current density increases, the volume percent decreases. It is observed that 2.99% of cobalt in the bath is most suited to obtain maximum diamond incorporation in the deposit. The incorporation is highest at 1 A/dm² at 3.5 pH and 30 °C.

3.2.3. Effect of cobalt content in composite plating

With higher cobalt content in the deposit, the diamond incorporation decreases (Fig. 8). Noticeable increase in volume percent of diamond particles in the metal matrix was observed with the addition of Co^{2+} to the Ni/diamond plating bath (Fig. 9). In addition, the distribution of diamond particles in the composite coatings deposited from the electrolyte with Co^{2+} is much more uniform with less agglomeration (Fig. 10) than that of composite coatings without Co^{2+} in the electrolyte (compare with Fig. 3b). The above results showed that the addition of Co^{2+} in the Ni/diamond plating bath significantly improved the amount and uniformity of dispersed diamond particles in the



Fig. 11. Effect of diamond concentration in the bath on the wear rate and hardness of Ni-diamond deposits. pH 3.5; 1 A/dm²; 30 °C.



Fig. 12. Effect of cobalt contents in the deposit on the hardness and wear rate of deposits pH 3.5; 1A/dm²; 30 °C; ● Ni–Co-diamond ■ Ni–Co.

metal matrix. It has been shown by Wang et al. [17] that Co^{2+} adsorbed on diamond particles much easily than Ni²⁺, which might give surfaces a more positive charge and hence increases the electrostatic attraction between the diamond particle and the



Fig. 13. SEM micrograph of wear track of a) Ni-diamond and b) Ni–Co-diamond composite.



Fig. 14. Effect of diamond concentration in the bath on the roughness of deposits. pH 3.5; 1 A/dm²; 30 °C; ● Ni-diamond; ■ Ni–Co-diamond.

negatively charged cathode. As a result, a higher content of diamond particles are co-deposited in the matrix.

3.2.4. Hardness

Ni-diamond and Ni-Co-diamond composites exhibited higher hardness as compared to the Ni and Ni-Co coatings (230 and 440 Hv respectively [15]), which is linked with the dispersion hardening effect caused by the incorporation of diamond particles in the metal matrix. Moreover, the Ni-Codiamond composite coating showed the highest micro hardness. It is well known that the hardness and other mechanical properties of metal matrix composites depend on the amount of the dispersed phase, operating conditions and the characteristics of the matrix [28]. For the above two matrixes, the hardness value of the Ni-Co matrix is higher than that of a Ni matrix. However, with the addition of Co^{2+} in the Ni/diamond plating bath, the micro hardness of composite coating increased from 460 Hv to 700 Hv when plated at 1 A/dm², pH 3.5 and at 30 °C (Figs. 11 and 12). It is obvious that this hardness improvement is due to the higher content of diamond particles embedded in the Ni-Co matrix.

3.2.5. Wear resistance

The results of wear tests for the Ni and Ni-Co composite coatings under the dry sliding conditions are summarized in Figs. 11 and 12. It is observed that both type of Ni-based composite coatings exhibited lower wear rates when compared with pure Ni coatings, which can be attributed to the dispersion-strengthening effect with the incorporation of diamond particles. Wear rate of the nickel-cobalt composite is much lower than that of the nickel composite. The reinforced particles have reduced the direct contact between the matrix and the steel ball during the sliding wear test that reduced the adhesion wear between the two pure metal counter bodies and impede the wear process [17]. As mentioned above, the addition of Co^{2+} in the electrolyte resulted in a more uniform distribution and higher content of diamond particles in the matrix, which enhanced the load bearing capability and avoided direct metalto-metal (nickel to steel) contact and as a result, improved the wear performance. However, in case of the Ni/diamond composite with relatively lower amount of incorporation and high agglomeration, after a short period of wear test, the agglomerated diamond particles in the nickel matrix are easily pulled out of the matrix since they are not fully encapsulated by nickel. The debris moves along with the steel ball, and causes additional damage to the coating (Fig. 13a and b). Better anti-wear performance of Ni–Co-diamond composite can also be attributed to the higher hardness of Ni–Co matrix than that of pure nickel matrix [15].

3.2.6. Surface roughness

The surface roughness of the Ni–Co-diamond composite layer containing around 52% diamond powder was lower than that of Ni-diamond composite layer containing around 45% powder (Fig. 14). R_a value for the surface roughness of Ni-diamond composite is 0.99 and that of Ni–Co-diamond is around 0.82 µm. The decrease in surface roughness with addition of cobalt content in the deposit is due to the reduction in extent of agglomeration of particles despite their higher incorporation.

4. Conclusion

The percent of diamond incorporation in the deposit depends on bath operating temperature, pH, current density and diamond concentration in the bath. Presence of cobalt in the nickel-diamond plating solution increases volume percent incorporation of particles and also reduces their agglomeration in the deposit. Highest powder incorporation in the deposit was found at pH 3.5,1 A/dm², 30 °C and with 5 g/l diamond concentration in the bath.

Micro-hardness of the deposits depends also on their diamond content besides operating conditions. Micro-hardness of the Nidiamond composite coating was found to be around 460 Hv. With the addition of cobalt ion the nickel-plating bath, the micro hardness of the composite increases to 700 Hv. The increase in hardness is due to increased particle co-deposition and reduced agglomeration.

The wear rate of nickel–cobalt-diamond composite is approximately three times lower when compared to that of Ni-diamond composite coating. The anti-wear performance of the composite coating increased with the diamond concentration up to 5 g/l in the bath and became relatively steady with further increase in diamond concentration.

Surface roughness of nickel–cobalt-diamond composite is less than nickel-diamond composite. This is due to the reduction in agglomeration of particles despite their higher incorporation in the deposit due to the presence of cobalt.

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