CHAPTER 3

PREPARATION AND CHARACTERISATION OF NICKEL-DIAMOND ELECTRO COMPOSITE COATINGS

3.1 DESIGN OF EXPERIMENTS

Experiments planned and conducted most judiciously to use the data most effectively with minimum number of experiments. Statistical design of experiments is the process of planning the experiments so that appropriate data could be collected which may be analyzed by statistical methods resulting in valid and objective conclusions.

Experiments were planned to fulfill the following requirements:

- To get the homogeneous distribution of diamond powder over the whole range of controllable factors to be investigated;
- To reduce the number of experiments;
- To establish a relationship between different input variables and the output parameters accurately within the selected range of investigations.

3.2 $3^K$ FACTORIAL DESIGN FOR THREE FACTORS

$3^K$ factorial design is the most widely used factorial design having three levels for each ‘K’ factors. The three levels of factors are referred to as
low (-1), intermediate (0) and high (+1). If there are three factors under study and each factor is at three levels arranged in a factorial experiment, then this constitutes a $3^3$ factorial design. Each main effect has two degrees of freedom; each two-factor interaction has four degrees of freedom. If they are $n$ replicates, then there are $(n \times 3^3 - 1)$ degrees of freedom and $3^3(n-1)$ degrees of freedom for error. This investigation is designed as above. Ni-diamond electro composite coating was obtained for the combination of three different process variables as shown in the Table 3.1 below.

<table>
<thead>
<tr>
<th>Table 3.1</th>
<th>Level designation of electroplating variables</th>
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<tbody>
<tr>
<td>Level</td>
<td>$i$ (A/dm$^2$)</td>
</tr>
<tr>
<td>-------</td>
<td>---------------</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
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3.3 PREPARATION OF NICKEL-DIAMOND ELECTRO COMPOSITE COATING

3.3.1 Electrodeposition technique

Electrodeposition of particle in metal matrix are of two types

i) Conventional Co-deposition technique (CECD)

ii) Sediment Co-deposition technique. (SECD)

In CECD technique co-deposition is done by keeping the anode and the cathode vertically. Particles in the electrolyte are placed in suspension by continuous stirring. The disadvantage of this technology is that it requires higher amount of particles in the electrolyte for getting the same amount of particle inclusions in the deposit as that obtained by SECD technique. This is due to the fact that co-deposition occurs against gravitational force.
In the case of sediment co-deposition technique concentration of particle in the electrolyte is relatively less for the same amount of incorporation as the process is supported by gravitational force. Here both anode and cathode are placed horizontally. Also volume fraction of diamond particle in the deposit for a given plating condition is high compared to that of conventional co-deposition technique. This helps in reducing the capital investment on diamond powder and hence the production cost. So Sediment co-deposition technique is adopted here for co-deposition of particles in metal matrix.

3.3.2 Preparation of bath

The conventional Watts bath of the following composition was prepared for 10 liters.

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

To remove the organic impurities present in the solution, activated charcoal treatment was given. For removing inorganic impurities i.e., metallic impurities dummy electrolysis was carried out using corrugated stainless steel cathode and nickel anode. The formation of white nickel deposited on the corrugated cathode was taken as indicative of freedom from inorganic impurities. The pH of the electrolyte was adjusted electrometrically using dilute H₂SO₄ or NaOH. 0.01-g/l sodium lauryl sulphate was added to the electrolyte as surface active agent. The temperature of the electrolyte was maintained up to 60°C using a thermostat.
3.3.3 Preparation of substrate

Before plating process, the substrate was subjected to pretreatment process. The pretreatment depend on the type of substrate used. Pretreatment given for mild steel differs from that of high-speed steel (HSS). Pretreatment is given to make the substrate free of surface oxide, to remove any greasy material and to make the surface water wettable. The substrate surface is mirror polished using buffing machine. Then the substrate was subjected to cathodic cleaning for 120sec and anodic cleaning for 30sec using a bath containing sodium hydroxide (30g/l) and sodium carbonate (30g/l).

3.3.4 Plating procedure

Deposition was carried out in a 500 ml capacity cell using sedimentation technique. Rolled nickel anode and mild steel cathodes were used. The cathodes of $7.5 \times 2.5$ cm area were mechanically polished, degreased and bent to $90^\circ$. They were suitably masked to expose an effective plating area of $6.25$ cm$^2$, electro cleaned, first cathodically and then anodically, washed rinsed and then introduced into the plating bath 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 with an inter electrode distance of 3 cms. Diamond powder (6 to 12 $\mu$m) was added to the electrolyte in the form of 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 minutes to allow the particles to settle on the substrate while the deposition proceeded. The same process was repeated to obtain deposit thickness of 25 $\mu$m.

The experimental setup used for Nickel-diamond electro deposition by sediment co deposition technique (SCED) is shown in Figure.3.1.
3.3.5 **Nickel-diamond deposition**

Natural grade polycrystalline diamond powder of 6–12 μm size was used. Prior to the co-deposition, the diamond particles were ultrasonically dispersed in the bath for 10 min. Experiments were conducted at a fixed diamond concentration of 5 g/l, varying the plating parameters like temperature, pH, and current density. Ranges of coating parameters in the coating process are as follows:

- **Current density**, $i = 1$ to $3 \text{ A/dm}^2$
- **PH value** = 2.5 to 4.5;
- **Temperature** = 30 to 60 °C.
3.4 CHARACTERISATION OF NICKEL-DIAMOND COMPOSITE COATINGS

3.4.1 Volume fraction of diamond deposition (Vfd)

The volume percent of diamond incorporation in the deposits was 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 powders, the volume percent incorporation was calculated as

\[
V_{fd} = \frac{\text{Volume of diamond powder in deposit}}{\text{Total volume of nickel and diamond powders in deposit}} \times 100
\]

Each experiment was carried out using a fresh solution and the values of the average of three readings were reported.

3.4.2 Hardness (VHN)

Micro-hardness of the coatings was determined using MITUTOYO Vickers micro hardness testing equipment with a load of 50g for 15 sec. For the selected load, the substrate effect on hardness can be avoided. The indented surface was viewed at 400X magnification and the slider position was adjusted to the indentation diagonal and for the given \( D_1 \) and \( D_2 \) value, micro hardness was automatically calculated by the system based on equation (3.2) shown below.

\[
HV = \frac{\text{Load (kgf)}}{\text{Area of Pyramidal Impression (mm}^2\text{)}}
\]
The hardness was measured in four different locations and the readings reported are the average of eight readings.

### 3.4.3 Wear resistance

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 was applied to pin by adding weight to the pan. The pin used here was high-speed steel containing 5% cobalt of hardness 833HV. 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. Figure 3.2 shows the apparatus used for testing wear and friction of composite coatings and Figure 3.3 is the wear disc showing the wear track. The wear rate was calculated using equation (3.3)

\[
\text{Wear rate} = \frac{V}{SF} \tag{3.3}
\]

where

- \(V\) is wear volume in \(\text{cm}^3\)
- \(S\) is sliding distance in cm measured using formulae \(2 \times 3.14 \times R \times N \times T\).
- \(R\) 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 newton.
Figure 3.2 Pin on disc wear setup used for measuring wear resistance.

Figure 3.3 Wear disc showing the wear track.

Wear track diameter and normal load used here was 10 mm and 7.5 N. Experiments were conducted to determine the effect of diamond volume percent and cobalt content on wear rate.

3.4.4 Surface roughness

Surface roughness of the composite coating is measured using Mitutoyo surface roughness testing instrument. Measurements were made
with the instrument using diamond stylus in differential inductance measuring method. The surface roughness values are reported in terms of $R_a$ values in microns. $R_a$ is the universally recognized and most used international parameter of roughness. It is the arithmetic mean of the absolute departures of the roughness profile from the mean line. The advantage of this parameter is that it lends itself to electrical integrating stylus instruments which provide a direct meter reading.

### 3.4.5 Surface morphology

The surface morphology and microstructure of the coatings were investigated using Scanning Electron Microscope (SEM). The micrographs were used to assess the effect of pH, current density, temperature, and presence of cobalt on the structure of deposits and homogeneity of dispersion of diamond in the deposit.

The cross section of the composite electro deposits were also examined using SEM. Samples of 1cm x 1cm size were mounted in araldite resin and allowed to harden for 48 hours. The cross section of the specimen were then metallographically polished with successive grades of emery paper in a polishing wheel (1/0 – 5/0). The cross sections were then etched in freshly prepared alcohol-nitric acid mixture, washed, dried and then examined with SEM.

The specimens were also subjected to X-ray diffraction analysis. X-ray diffraction analysis is based on Bragg’s law i.e. $n\lambda = 2d \sin \theta$, where $n$ is an integer, $\lambda$ is the wave length of X-rays, $d$ is the spacing between the planes in the atomic lattice and $\theta$ is the angle between the incident ray and the scattering planes.
X-ray diffraction was obtained by PANalytical make X’pert PRO diffractometer system and the pattern was analyzed using X’pert High score software. The XRD pattern revealed the presence of diamond particles in the nickel-diamond and nickel-cobalt-diamond composite coated specimen.

3.5 PREPARATION OF NICKEL-COBALT-DIAMOND ELECTRO COMPOSITE COATINGS

Admixtures of cobalt in nickel-diamond composite impart superior mechanical properties, especially in terms of hardness and wear resistance. Its ability to dissolve carbon permitted wetting of the diamond particles and improved their bond strength with the matrix. Experiments were conducted to optimize the operating variables and cobalt concentration in the solution to produce a nickel alloy containing around 10%-cobalt. The concentration of cobalt was varied by addition of cobalt sulphate to the Watts bath (1–10 g/l). Other conditions were similar to nickel-diamond composite plating. Nickel and cobalt percentages in the deposit were determined using X-ray Fluorescence Spectroscopy (XRF).

3.6 CHARACTERISATION OF NICKEL-COBALT-DIAMOND ELECTRO COMPOSITE COATINGS

The characters of nickel-cobalt-diamond composite coated specimen such as micro hardness, wear resistance and surface roughness were measured as elaborated for the Nickel-diamond composite coatings. Surface morphology studies were made with the help of the Scanning electron microscope and X-ray diffraction method.