

# Preparation of Electroless Deposition and Characterization of Ni-P coated Graphite Particles

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**Abstract**—Electroless alkaline bath is used to coat Ni-P graphite particles of sizes 50-100  $\mu\text{m}$ , avg 75  $\mu\text{m}$ . Surface treatments to graphite particles, a mandatory process before actual electroless plating, must be given so that particles should be free from dust and quickly react with chemicals. This is done in three stages namely degreasing, sensitization and activation. Electroless nickel (EN) was plated using a sodium hypophosphite bath. Effect of plating time, size of the powder and weight of the powder were studied. For different samples keeping other parameter (quantity of salts in the bath, pH and temperature) constant, the time period is varied in order to know the effect of time on coating. Two coating trials one for 22 min and the other for 40 min were performed. It was found that extent of coating was more in 40 min trial than in 22 min trial. This reveals that coating increases with increase in time. SEM photographs and EDS spectra report, before and after EN plating confirm that uniform and continuous layer of nickel is deposited on the surface of the graphite particles. The micro structure studies carried out with SEM on the uncoated and coated graphite particles reveal: uncoated particles show irregular and fractured surfaces while the surface of the coated particles revealed the presence of Ni-P globules. Excess loading of graphite particles in the bath revealed decreased wt % of Ni deposition on graphite particles. However further increase in weight can be attained by placing the same powder in a fresh bath or replenishing the old bath to obtain desired Ni-P alloy mass.

**Keywords**—*Electroless plating, Electroless nickel, graphite, Ni-P globules, surface treatment.*

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## I. INTRODUCTION

Graphite particles are one of the resourceful engineering materials which have taken indispensable position in the metal matrix composites (MMCs). The interfacial reaction and wettability of these particles with the metal matrix plays a key role in processing as well as in the performance of the MMCs. These problems could be tackled well enough by applying metallic coatings over the graphite particles which improves the wettability and several other metallurgical characteristics of the MMCs [1]. Electroless coatings can be divided into three main categories like (i) alloy coatings, (ii) composite coatings and (iii) metallic coatings. By the controlled chemical reduction reaction, the electroless coating chemistry has emerged as one of the leading growth areas in the surface engineering, metal finishing etc. Amongst the wide range of coating processes, electroless process stands unique for the reason of direct metallization on any material with much ease and can be performed with simple experimental setup [2]. Electroless plating has been of great importance in fabrication of composite materials to coat the surfaces to achieve better mechanical properties mainly corrosion resistance, wear resistance, hardness, tensile strength and so on.

The electrochemical reduction of nickel during electroless plating is a fairly simple reaction. It is well known that the electroless nickel coating (EN) is the autocatalytic deposition of Ni-P alloy from an aqueous solution on to a substrate without the application of external current [3-7]. EN coatings provide characteristics that expand the physical properties beyond those of pure nickel coating systems. These coatings are widely used in the mechanical, chemical and electronic industries because of their unique corrosion and wear resistance, hardness, lubricity, uniformity of deposit regardless of geometries, solderability, bonding and nonmagnetic properties [8, 9]. The structure, composition, plating rate and properties of electroless Ni-P coatings are determined by several factors of which pH, temperature, nickel ion concentration and hypophosphite concentration are significant. Randin and Hinterman [10] determined that the phosphorous content of the deposit increases as the pH of the bath decreases. Plating bath temperature increases the plating rate although a very high temperature can lead to decomposition of the plating bath. Electroless deposition process has undergone numerous modifications to meet the challenging needs of

a variety of industrial applications since Brenner and Riddell invented the process in 1946. The original Ni–P plating on metals has been adapted to deposit on the surface of ceramic particles. Studies related to plating of metal on to ceramic substrates such as SiC, Al<sub>2</sub>O<sub>3</sub>, carbon nano-tubes and graphite[11-14] which do not have catalytic surface have employed the use of sensitization step (SnCl<sub>2</sub>) followed by activation (PdCl<sub>2</sub>), prior to plating [15]. Nickel plating on ceramic particles is difficult because it does not have catalytically active surface. As far as deposition of metal on the surface of graphite particles by electroless plating is concerned very few literature is available.

## II. EXPERIMENTAL PROCEDURE

### A. Pretreatment of graphite particles

Since the electroless nickel plating is completely a chemical process, surface treatment of graphite particles was done. The treatment includes degreasing, sensitization and activation. Weighed samples of graphite particles were packed in filter paper bags and undergone pre-treatment as explained below:

**Degreasing:** Removal of dirt from the substrate (graphite particles) is mandatory to ensure optimum EL coating on the substrate. Acetone (C<sub>3</sub>H<sub>6</sub>O) is used as degreasing agent generally. It is always the chemical generally preferred for surface cleansing action. The filter paper bag containing the graphite was immersed in a beaker containing acetone for 2 minutes.

**Sensitization:** After removal from the acetone, the bag was dried and then dipped in a beaker containing 0.1% stannous chloride (SnCl<sub>2</sub>.2H<sub>2</sub>O) solution for 2 minutes. Sensitization was done to make the surface of the substrate to quickly react to the forthcoming EL chemical reaction process.

**Activation:** The bag was removed from stannous chloride solution and consequently dipped into 0.01% palladium chloride (PdCl<sub>2</sub>) solution for 2 minutes. Activation enhances the rate of chemical reaction by catalyzing the surface of substrate. Palladium chloride is considered to be the most helpful catalyzing agent in chemical reactions.

After this treatment, the bag was dried using a hot air drier until the graphite particles get detached from the filter paper and then carefully stored to be used in the next process.

### A. Electroless Nickel Plating

This step is the core process of the entire experiment. In this process, a Nano sized coating of Nickel was obtained on the graphite particles. This is purely a chemical process carried out in chemical labs with utmost cleanliness and care. Handling of tens of chemicals and lab equipments is very important. Alkaline EL bath was used to produce Ni–P coated graphite particles.

After pretreatment, graphite powders were introduced in the electroless nickel plating bath. Electroless nickel was plated using a sodium hypophosphite bath and the composition of the bath is given in Table 1. Nickel sulphate is the source for metal ions, sodium hypophosphite is the reducing agent, sodium citrate is used as a complex agent and ammonium chloride acts as a buffering agent to control pH of the bath during plating process. The chemicals used in this experiment were all of analytical reagent grade.

TABLE I: BATH COMPOSITION

Sl no.	Chemical	Formula	Quantity(g/l)
1.	Nickel Sulphate	NiSO <sub>4</sub> .6H <sub>2</sub> O	30
2.	Sodium Hypophosphite	NaH <sub>2</sub> PO <sub>2</sub> .H <sub>2</sub> O	16
3.	Sodium Citrate	Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> .H <sub>2</sub> O	80
4.	Ammonium Chloride	NH <sub>4</sub> Cl	50

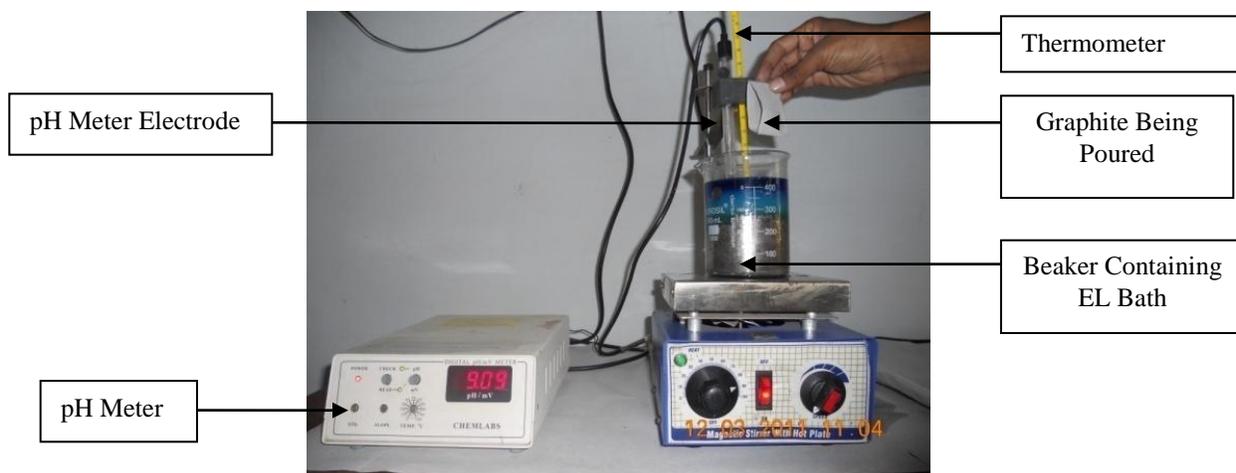


Fig.1 Electroless coating process.

The arrangement for the EL coating process was done as shown in the (Fig.1). The glass beaker containing the EL bath, with graphite poured in it, was placed over the magnetic stirrer. A magnetic bead was dropped into the beaker. While the blades of the magnetic stirrer rotate, the magnetic bead also made continuous revolutions in the beaker thus setting up a vigorous stirring of the EL bath. For regular checking of the pH, the electrode of the electronic pH meter was kept dipped in the bath. Also, a thermometer was dipped in it for continuous checking of temperature (Fig.1). The operating temperature and pH chosen for EL coating of graphite particles were maintained at  $90 \pm 2^\circ\text{C}$  and  $9 \pm 0.25$  respectively. The pH of the bath was checked frequently and maintained by adding ammonia solution.

Samples of different weights of pre-treated graphite particles were taken for each trial and coated in the EL bath for different time periods in minutes. The EL coating bath solution was stirred manually to keep the graphite particles in suspension to ensure complete coating. The concentration of nickel salt, concentration of sodium citrate, amount of graphite particles, and time of coating were kept constant throughout the experiments. To study the effect concentration of stabilizer and reducing agent on deposition, experiments were repeated by varying one of these parameters (in this case, time of coating) while keeping the other parameters constant. The variation in deposition was quantified by weighing the sample before and after coating process. Once the coating was done for the required time, the coated graphite particles were filtered, washed thoroughly with distilled water and dried in an oven at  $80^\circ\text{C}$  for 2 hr to remove moisture completely from the coated graphite. It was also placed in desiccators for the same purpose. It was then weighed and subjected to characterization. Samples were characterized by using SEM. The surface morphology of the powders was observed by Scanning electron microscope (SEM). EDS (energy dispersive X-ray spectroscopy) method is employed to know the extent of Ni coating over the surfaces.

### III. CHARACTERIZATION

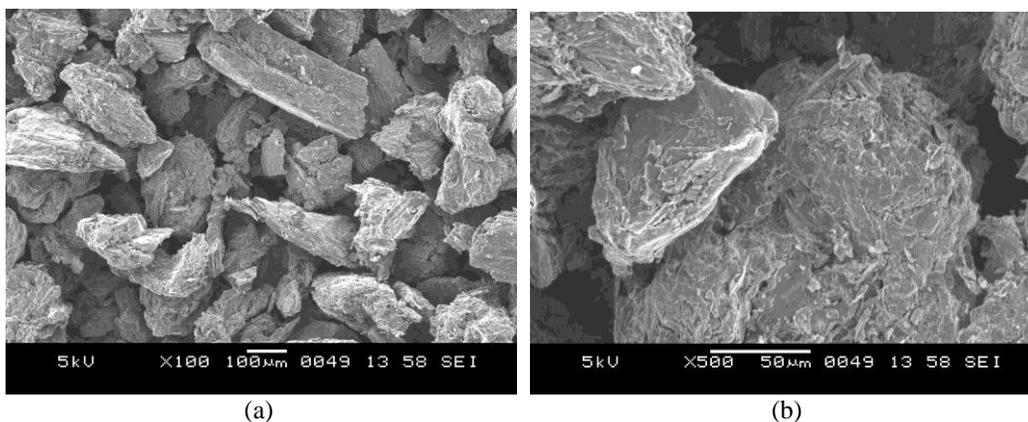
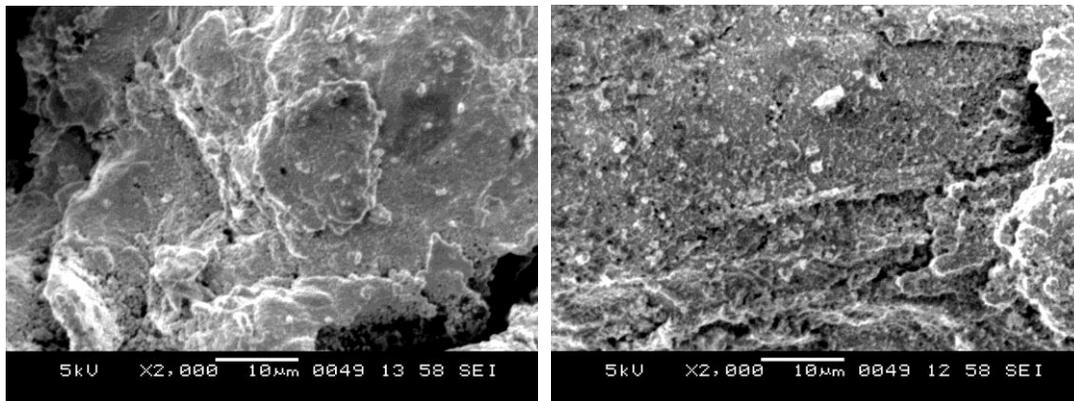
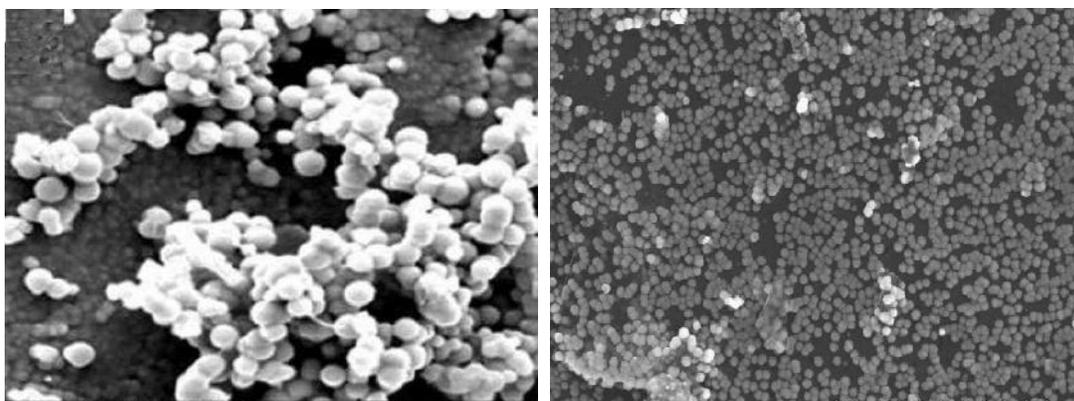


Fig.2. (a) (b): SEM photographs of uncoated graphite



(a) 22 min coated graphite particles

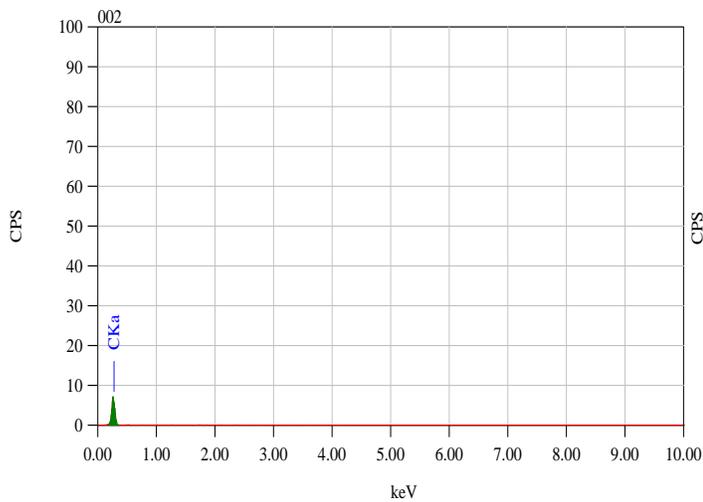
(b) 40 min coated graphite particles



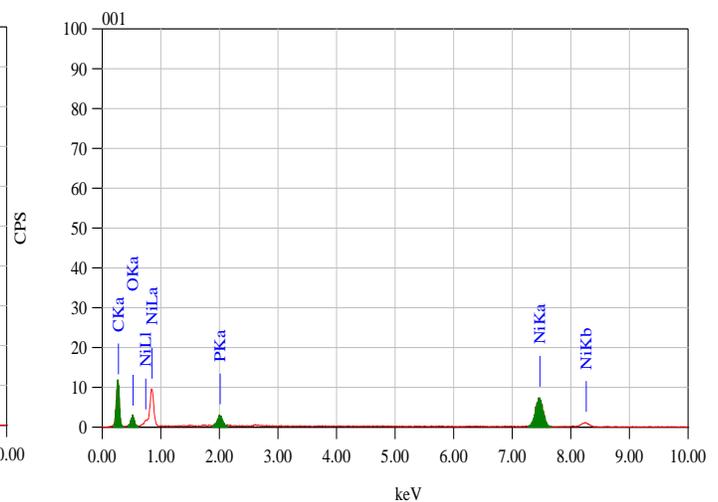
(c) Nickel Globules

(d) Granular Nickel on graphite surface

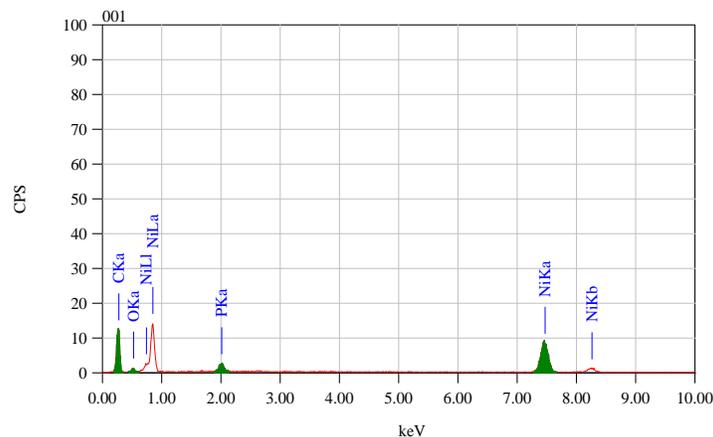
Figs.3 (a), (b), (c) & (d): SEM photographs of coated graphite particles (high magnifications)



(a) Uncoated graphite particles



(b) 22 min Nickel coated graphite particles



(c) 40 min Nickel coated graphite particles

Figs.4. EDS Spectra of (a) Uncoated, (b) 22 min coated and (c) 40 min coated graphite particles.

TABLE II: CHANGE IN WT % OF C, NI, P, & O ON GRAPHITE WITH TIME FOR VARIOUS PARTICLE LOADING SIZES

Weight of the powder (g)	Plating time (min)	C (Wt %)	Ni (Wt %)	P (Wt %)	O (Wt %)
08	22	58.25	27.46	1.87	2.45
08	40	61.60	34.12	2	2.28

The SEM micrographs of uncoated graphite particles at different magnifications exhibiting fractured and irregular surfaces are illustrated in Fig 2 (a) and (b) and those of coated graphite surfaces are shown in Figs 3 (a), (b), (c) and (d). These pictures clearly depict coating of nickel globules on the surfaces. EDS results show the absence/presence of Ni on the surfaces of uncoated/coated graphite particles in terms of mass percentage. Fig 4 (a) reveals that, only the mass of the carbon is dominant in the sample since there is no coating done. Fig. 4 (b) clearly shows the presence of nickel on graphite particles that underwent coating for 22 minutes and Fig. 4 (c) shows the presence of nickel on graphite particles that underwent coating for 40 minutes. The difference between the two is that, the percentage of nickel in the latter is more than that of the former (Table.2).

#### IV. RESULTS AND DISCUSSIONS

The sensitization and activation step for graphite is done by chemical treatment. By doing so, adsorbed gases on the surface of graphite particles is driven off, resulting in a clean active surface, which enhances wettability of the powders in the aqueous solution for the metal-ion species. The adsorbed Ni<sup>2+</sup> ions in the presence of the activated catalytic surface is reduced by the adsorbed H<sup>+</sup> ions and the plating proceeds so long as there is sufficient availability of metal ions and reducing agent. Nickel reduction on the surface is confirmed by evolution of hydrogen from the substrate surface. In this case, initially very vigorous reaction is observed during the plating reaction. The weight of the nickel deposited on the graphite powder as a function of time is depicted in the EDS spectra diagrams. The weight of the nickel deposited on the graphite powder, as a function of time and weight of loaded powder is shown in Table 2. In this process it is observed that the extent of coating increases with increase in time. Still, the nickel content on the powder can further be increased by removing the powder from the bath after 15–30 min plating, washing with distilled water and continuing plating in a fresh solution. Increase in the loading of graphite powder in the bath also leads to decrease in nickel content on the powders. This is due to increase in effective surface area to be coated, for the same amount of nickel ions. Therefore, time of coating is increased to 22 min and 40 min. Irrespective of the change in powder size, there is no variation in the nickel content deposited on the powders. A higher loading results in higher available surface area of graphite for the same number of metal ions in the bath. Hence, a higher powder load results in a lower nickel wt. % in the powder. Phosphorus analysis of the coated powders is not done due to the trace level availability in the system. The amount of phosphorus estimated is around 10 wt. % of the total weight of the coating (Ni–P). Thus it can be concluded that the total phosphorus content



would account for 10% of nickel content of the coating on graphite powders. Also, other element that gets entangled is oxygen which is only 2% by weight as found by the EDS spectra whose effect on the coating is also negligible.

Scanning electron microscopy is used to study the morphology of coated and uncoated graphite powders. Figs 2 (a) and (b) demonstrate the microstructures of uncoated particles while Figs 3 (a), (b), (c) and (d) demonstrate that of coated graphite particles. A typical cauliflower structure of nickel deposition is observed at higher magnification (Fig 3d). Given that the particle size of graphite is in the range of 50–150  $\mu\text{m}$ , the grain size of nickel is found to be in the range of 15–50 nm. EDS analysis of the coated powders is done to analyze the nickel and phosphorus content in the deposit. Figs. 4 (a), (b) and (c) and Table 2 clearly reveal the peaks for C, O, Ni and P. The reduction of nickel ion onto the catalyzed graphite particles could be inferred during the coating process by the evolution of hydrogen gas from the substrate.

## V. CONCLUSIONS

Observing the complete experimentation and characterization outcomes, we can draw the following conclusions:

- (1) After pre-treatment of the powders, uniform nickel–phosphorus coating was successfully achieved on graphite powders by electroless deposition process. This is proved by SEM photographs and EDS spectra.
- (2) For 22 minutes coating the weight of Nickel deposited is 27.46%, while for 44 minutes coating deposition is 34.12%. This indicates that the amount of deposition increases with the increase in time period of coating.
- (3) Weight percentage of phosphorus for 22 min trial and 40 min trial is respectively 1.87 and 2 while the weight of oxygen for the two trials is 2.45% and 2.28% respectively. This indicates clearly that, the phosphorus and oxygen coatings are negligible as compared to nickel coating. Hence their affects are negligible on the properties of MMCs that have coated graphite reinforcements.
- (4) EL Ni–P coating is found to be uniform over the complete surface including the intricate gaps and surface defects in the graphite particles.
- (5) The plating rate increases with increase in time.
- (6) Electroless Nickel plating is the surface coating process that does not make use of electricity.
- (7) The so far produced EL Ni-P coated graphite particles are ready to be used as dispersoids for fabricating MMCs.

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