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Surface Modification of Expanded Graphite by Low Temperature Electroless Nickel Plating using Multiple Reducing Agents and Morphology Studies

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Abstract

Surface modification of expanded graphite was studied. A new bath formulation was developed, which allowed deposition of nickel using multiple reducing agent at low temperature on expanded graphite. This investigation leads to a development of good conductive filler with EMI properties, because among all the metals nickel particles are more effective for shielding effectiveness and high electrical resistivity. Conventional electroless coating methods of nickel from its salt requires temperature greater than or equal to 80°C. The present investigation was carried out at temperature 50-55°C using combination of three reducing agents namely sodium hypophosphite, hydrazine hydrate and sodium borohydrate in the ratio of 8.5:2:1. The pH was maintained at 10-11 throughout the process. Both uncoated and coated expanded graphite were characterized by the scanning electron microscope for morphology examination, energy dispersive spectroscopy for elemental and elemental mapping, X-ray diffraction analysis for phase identification of the coated materials.

Introduction

In recent years, the importance of deposition of conductive metallic coating on organic and inorganic substrate has gradually increased in applications such as food packaging, microelectronics packaging and coatings for electromagnetic interference (EMI) shielding and wear protection[1-3]. There are several advantages in electroless nickel plating such as low cost, easy formation of a continuous and uniform coating on the surface of substrate [4-6]. In recent studies, electroless Ni plating has been done on the nano inorganic particles, carbon nanotubes[7-8], SiC powder[9-10] and polystyrene resin balls[11].

A natural graphite flake is abundant and highly electrically conductive and has a unique layered nano-structure, layered structure has a c-axis lattice constant of 0.66nm and there are no reactive surface groups on the graphite layers. Expanded graphite (EG), a kind of modified graphite contains layered thickness is ranging from 20 to 50nm. The interlayer spacing expanded graphite is several hundred times along the c-axis[12-13]. It has been applied widely as a kind of functional carbon material used in sealing, catalyzing space fight, military affairs, environmental protections, etc[14-15].The expanded graphite keeps a layered structure similar to natural graphite flakes the with lager interlayer spacing[15]. A number of studies have been carried out on expanded graphite reinforced conductive polymer nano composite[16- 20] due to its high electrical conductivity.

The present method of nickel coating on expanded graphite is unique and energy efficient because of the low temperature needed for coating. While conventional coating methods of nickel from its salt requires temperatuere greater than or equal to 80°C. Present method which involves multiple reducing agents and requires temperature in the range of 50-55°C only. The combination needs three reducing agents namely sodium hypophosphite, hydrazine hydrate and sodium borohydride in ratio of 8.5:2:1. The combination of the three reducing agents not only offers more control over the coating process (the reaction is less vigorous) but also requires low temperatures (50-55°C). Moreover, the coating process can be used to coat nickel on a variety of substrates and the process is substrate independent. Same process has been adopted to coat Ni on expanded graphite. Ni electrical resistivity is higher compared to other metals and further nickel is magnetic can be used in EMI materials because of its effective for shielding effectiveness. This investigation shows nickel coated expanded graphite is a new conductive filler for future applications.

Experimental

Materials

Expanded graphite form Asbury (US), Nickel Chloride (Rankem 99.9%), Ammonia (Ranke 25%), Ammonium Sulphate (SD fine 99.9%), Sodium Hypophosphate (SD fine 99%), Hydrazine Hydrate (Finer 80%) and Sodium borohydrate (SD fine 99%). Distilled water was used during bath preparation and for filtration.

Methods: Electroless nickel plating bath

Electroless nickel plating was carried out through following process, including pre-treatment of expanded graphite, bath preparation, plating, post-treatment and drying of the final coated material. Expanded graphite was pre-treated with 5% alcohol at room temperature for 5 to 10 min to remove the contaminated diesel/external particles, then rinsed in deionised water and dried at 100°C for 1-2 hours. Ratio of expanded graphite to nickel is 1:0.5.

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The nickel bath was prepared with 41 g/L $NiCl_2.6H_20$, 133 ml/L NH_3 (25% aqueous solution) and 7.1 g/L $(NH_4)_2SO_4$ after getting clear solution pre-treated expanded graphite was immersed in the bath, then temperature raised to 50-55°C. 24.7 g $NaPO_2H_2$, 3 ml N_4H_2 and 1.2 g $NaBH_4$ reducing agent in the ratio of 8.5:2:1was dissolved in 300 ml of distilled water. Subsequently reducing solution was added drop wise to heated bath. p^H of the bath was maintained at 10-11 and temperature of 50-55°C throughout the process. Ni deposited on expanded graphite on over the time 45 min. In the post-treatment step, the Ni coated expanded graphite was rinsed with deionised water at room temperature for 30 min and dried in an oven at 100°C for 5 to 6 hrs.

Characterization

A Scanning Electron Microscope (Hitachi S3400) having tungsten filament and 50 nm resolution was used to characterize the surface morphology of the both uncoated and coated expanded graphite. Chemical composition by energy dispersive x-ray analysis (EDX Thermo scientific) was attached to SEM and also elemental mapping has been characterized to see the distribution of the Ni on expanded graphite. Phase identification of the nickel plated expanded graphite was evaluated using X-ray Diffraction (XRD, Rigaku Miniflex, Cu Kα radiation at 20kV and 40 mA).

Mechanism of electroless nickel plating

Nickel coating proceeds via three different steps.

The first step involves the formation of the blue ammonia complex as shown in the reactions Eq.(1)

$$[Ni(H_2O)_6]^{2+} + 6\ NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6\ H_2O \qquad \text{Eq.(1)}$$

The second step involves the half cell reaction of hypophosphate in alkaline solution as shown in the reactions Eq.(2)

$$H_2PO_2^- + 3\ OH^- \rightarrow HPO_3^{2-} + 2\ H_2O + 2\ e \qquad \text{Eq.(2)}$$

The third step involves the half cell reaction of the nickel hexamine ion, $[Ni(NH_3)_6]^{2+}$ as shown in the reactions Eq.(3)

$$[Ni(NH_3)_6]^{2+} + 2\ e^- \rightarrow Ni^0 + 6\ NH_3\ (aq) \qquad \text{Eq.(3)}$$

The overall reaction can be written as below

$$[Ni(NH_3)_6]^{2+} + 6\ H_2PO_2^- + 3\ OH^- \rightarrow Ni^0 + HPO_3^{2-} + 2\ H_2O + 6\ NH_3(aq)$$

$$3Ni^{2+} + N_2H.BH_3 + 3H_20 \rightarrow 3Ni + N_2H_4 + H_3BO_3 + 6H^+$$

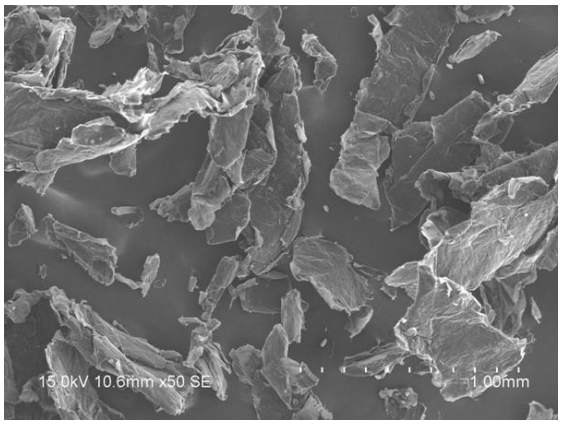
A side reaction that can occur is:

$$3Ni^{2+} + 2(N_2H_4.BH_3) \rightarrow 3H_2O + Ni_3B + 2N_2H_4 + 6H^+ + H_3BO_3 + 3/2H_2 \qquad \text{Eq.(4)}$$

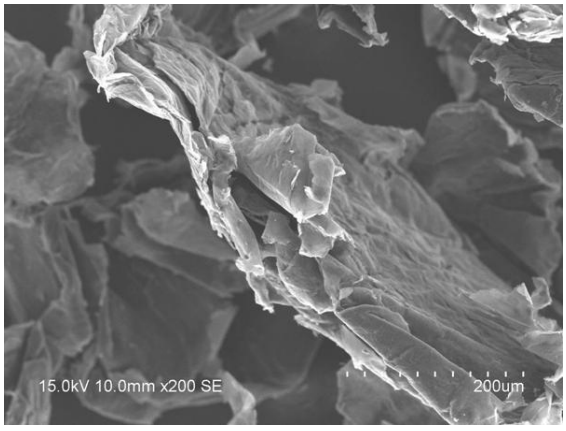
Results and Discussion

Morphology studies

Scanning electron microscope micrographs of both uncoated and coated expanded graphite were reported. Figure 1 (a, b and c) shows SEM micrographs of neat expanded graphite captured at different magnification. Figure 2 (a, b and c) shows SEM micrographs of Ni coated expanded graphite. The surface of expanded graphite had significantly changed. Coated expanded graphite surface was uniformly coated with nickel particles which were clearly visible and nickel particles were well dispersed on



(a)



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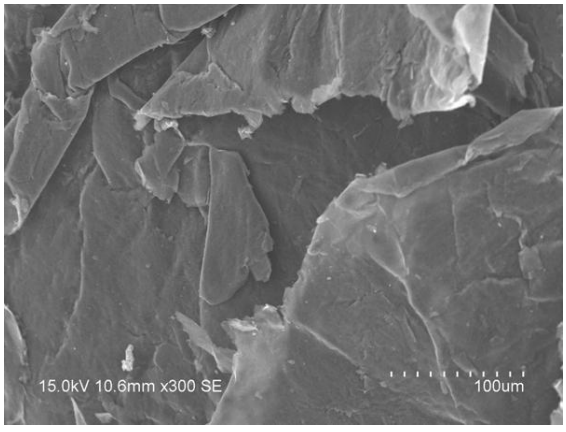
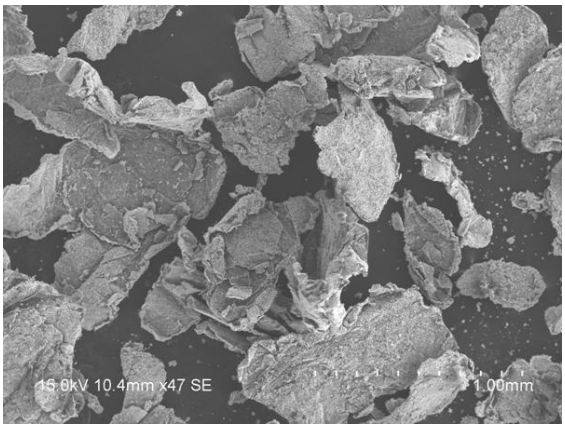


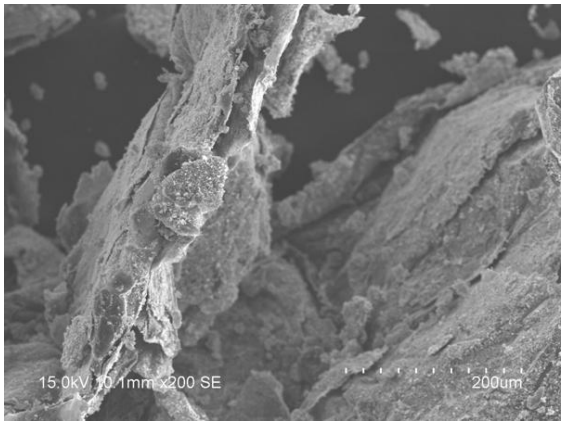
(c)

Figure 1: SEM micrographs of neat expanded graphite at (a) 50X, (b) 200X and (c) 300X

expanded graphite surfaces with the present electroless plating method. Figure 3 (A, B) evidence that enlarged microstructure of the expanded graphite indicates that the nickel particles are spherical shape and the approximate coated primary nickel particle size is from ~ 250 to 350 nm. Thin conductive Ni layer may affect their electrical and EMI properties. Elemental analysis of neat and nickel coated expanded graphite were investigated using thermo scientific having SDD detector at 20KV. Figure 4(A) neat expanded graphite shows the strong peak of carbon presence and (B) Ni coated expanded graphite, results showed the prominent presence of Ni and no impurities are observed on the surface, within the resolution limit of EDX, which further indicated high purity nickel plating was obtained using multiple reducing agents at low temperature, all above studies can conclude process is energy efficient elctroless plating technique.



(a)



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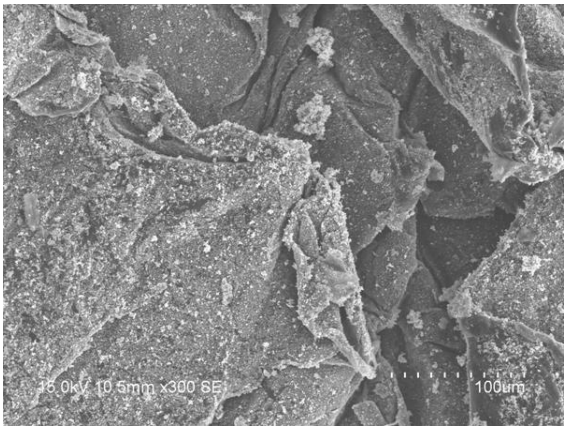
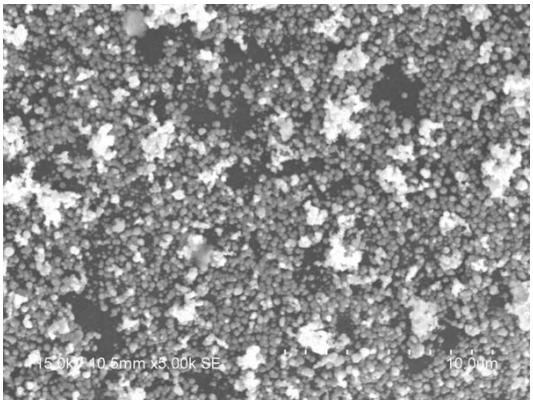
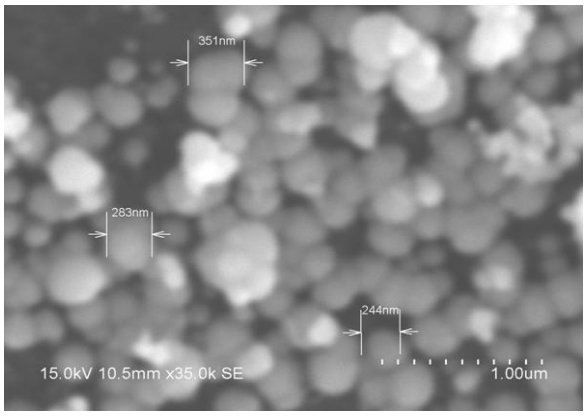


(c)

Figure 2: SEM micrographs of Ni coated expanded graphite at (a) 47X, (b) 200X and (c) 300X

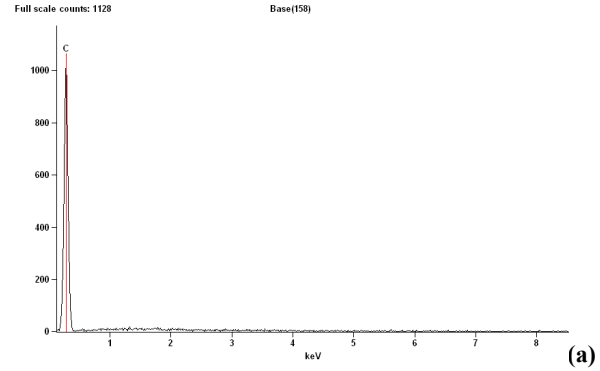


(a)

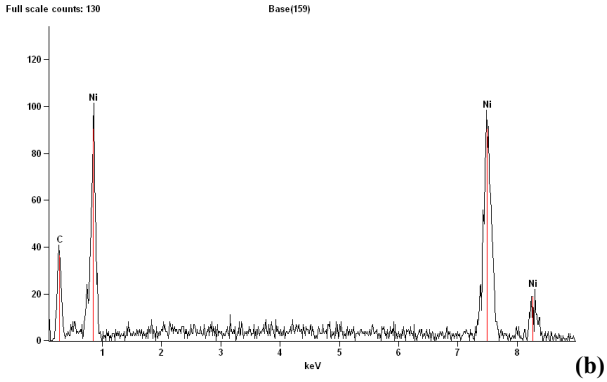


(b)

Figure 3: Magnified SEM micrograph of Ni coated expanded graphite at (a) 5000X and (b) 35000X



(a)



(b)

Figure 4: EDS of (a) Neat expanded graphite and (b) Ni coated expanded graphite

EDX with elemental mapping

Elemental mapping is useful tool to identified the elementals in large area of scan and also determine the distribution of nickel on coated expanded graphite. Figure 5 shows the elemental mapping on Ni coated expanded graphite. Mapping had done at the 20KV and scanning time of 30 min. Yellow and blue colour region represents the area scan of carbon (C, Kenergy lines) and Nickel (Ni, K energy lines).

X-ray Diffraction (XRD) analysis

Figure 6(A) shows the x-ray diffraction pattern of neat expanded graphite and Figure 6(B) shows the x-ray diffraction pattern of nickel coated expanded graphite. The four major strong characteristic peaks in standard nickel XRD is at 2θ 44.370°

51.596°, 76.084° and 92.094° corresponded to the crystal faces of (111), (200), (220) and (311) of Nickel respectively. Based on the XRD results on Ni coated expanded graphite shows the prominent 2θ peak at 44.370° and hkl (111) and it matched with the standard nickel XRD pattern of I/Io 100.The XRD pattern identified that the deposited nickel exhibited a characteristic face-centred cubic crystal-line structure, implying that nickel plated expanded graphite had ideal conductivity property.

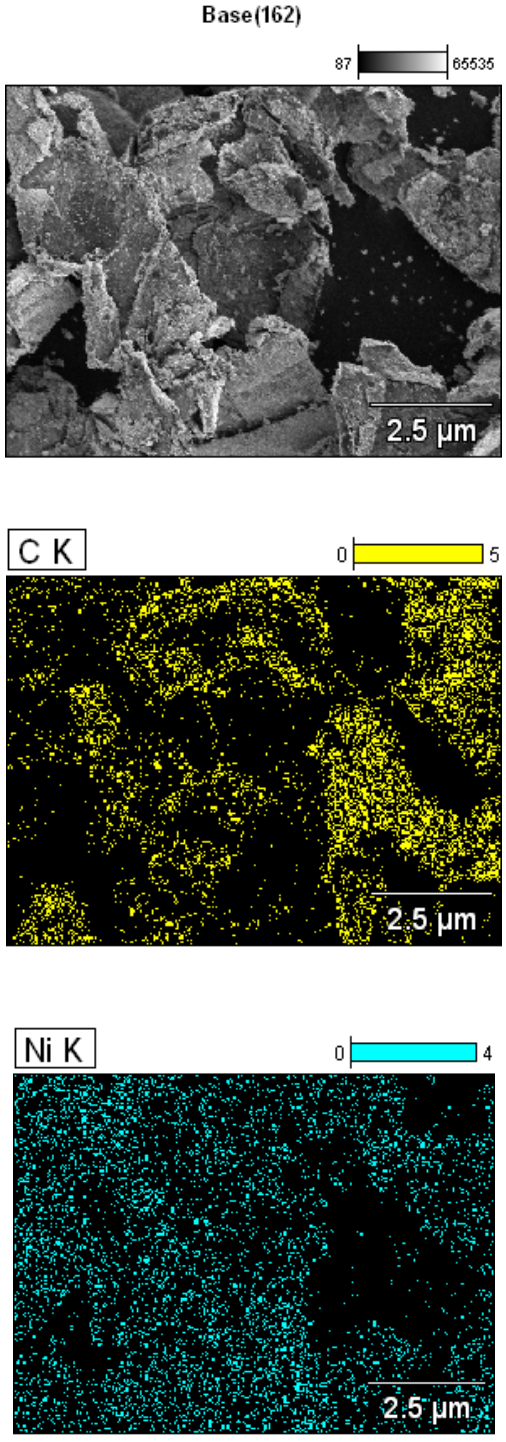


Figure 5: Elemental mapping of Ni coated expanded graphite

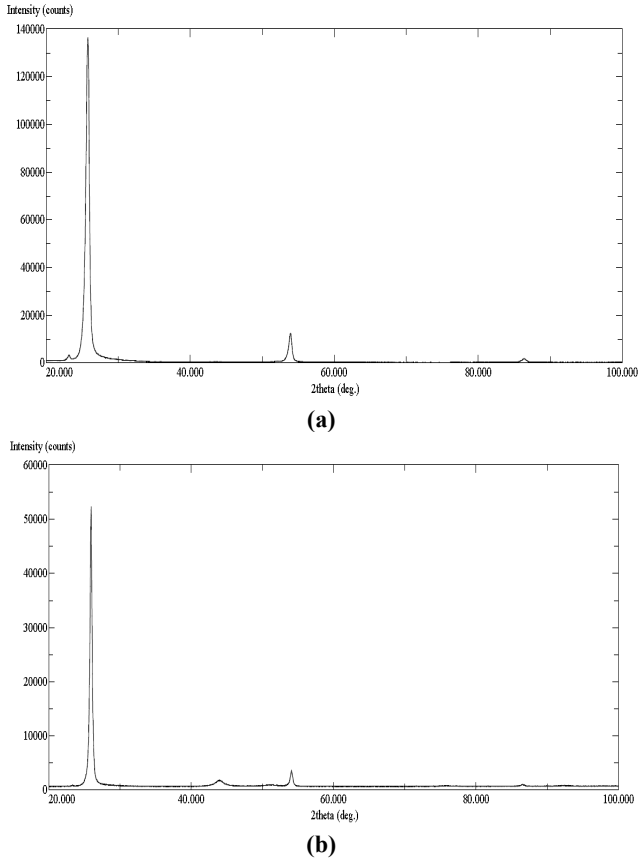


Figure 6: XRD of (a) neat expanded graphite and (b) Ni coated expanded graphite

Conclusions

Electroless nickel plating on expanded graphite using multiple reducing agents at low temperature has been demonstrated in this paper. The deposited nickel particles were subjected to a detailed characterization analysis by SEM, EDX, elemental mapping and XRD. The results showed that there was a uniformly distributed nickel layer on the expanded graphite. The nickel layer is composed of spherical shaped particles and characteristics of a face-centred cubic crystalline structure. This study shows one of the efficient plating technique and Ni coated expanded graphite could be consider as good electrically conductive. Among all the metals nickel particles are more effective for shielding effectiveness, because nickel is magnetic. So it will be good conductive filler for future applications. This investigation leads to a development of new conductive composite materials with high electromagnetic interference shielding effectiveness coupled with good electrical properties.

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