

Characterization of carbon fabric coated with Ni-P and Ni-P-ZrO₂-Al₂O₃ by electroless technique

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Ni-P and Ni-P-ZrO₂-Al₂O₃ (Ni-P-X) composite coatings on carbon fiber woven fabric have been attempted by electroless (EL) coating technique. For producing Ni-P EL coating, a sodium hypophosphite is used as reducing agent in alkaline bath whereas for producing composite coating, in the same bath, the co-precipitation of Al₂O₃ along with ZrO₂ by a chemical reaction has been used. The bath used was maintained at pH value of 9 ± 0.25 and a temperature of $90 \pm 2^\circ\text{C}$ for all the coatings under investigation. The morphology of coatings has been studied under SEM and the phases have been identified by XRD and TEM. The phases like microcrystalline nickel, amorphous nickel, Ni₅P₄ and Ni₁₂P₅ have been identified to be present. The grain size of these phases has been seen to be in the range of 5–10 nm. The tensile strength of as-coated and heat treated samples of both the types of coatings have been compared with that of uncoated fabric. The UTS values of uncoated carbon fabric used has been found to be 3.7 N/mm² whereas that for heat treated after coating the fabric samples with Ni-P and Ni-P-ZrO₂-Al₂O₃ EL coatings have been observed to be 11.1 and 12.4 N/mm² respectively. © 2002 Kluwer Academic Publishers

1. Introduction

Carbon fiber or fabrics are century old engineering materials, which were first produced by Edison for their use in electric lamps and also as electrical conductors [1]. Its increasing use in metal matrix composites (MMCs) has made this material more popular as an engineering material. The interfacial chemical reaction between the carbon fiber with the matrix affects the MMCs performance irrespective of the synthesizing routes adopted. The better wettability of fibers/fabric with the matrix has been considered of utmost importance [2]. The non-wetting of dispersoid with the matrix can lower the performance of the composite as a result of discontinuity at the interface. One of the ways to get rid of these difficulties is by coating the fibers/fabric. It can be said that the metallic coatings improve metallurgical characteristics like wear resistance, corrosion resistance, mechanical strength in general and also improve the wettability characteristic of fabric. It is also possible to attain the distinct properties to MMCs by giving suitable heat treatment after coating or by the addition of alloying elements in the matrix of the alloy [3]. The nature of nickel base EL coatings is well understood and they are easy to process [4]. The performance of MMCs largely depends upon the morphology of the less common phases present in the coatings, thickness and nature of the coatings [5].

Considering the above factors, with respect to the use of carbon fabric as filler in the fabrication of MMCs,

the present investigation is an attempt to coat the carbon fabric by electroless, EL, technique. The EL coatings under investigation are Ni-P and Ni-P-ZrO₂-Al₂O₃, (Ni-P-X). These coatings are characterized by Scanning Electron Microscopy (SEM) to assess continuity of the phase and the uniformity of coating on carbon fabric. Electron Probe Micro Analyser (EPMA) was used for quantitative elemental analysis of the contents present in the coating. The morphology and phases present in the coating are analyzed by Transmission Electron Microscopy (TEM) and X-ray diffraction (XRD) techniques. The tensile strength of as-coated and heat treated samples of both Ni-P and Ni-P-X EL coatings are compared with uncoated samples.

2. Experimental details

2.1. Specification of carbon fabric

The carbon fabric has been used as the substrate for EL coatings in the present investigation. The specifications of the carbon fabric are as follows:

Carbon—94%, Ash contents—1% max, Na—500 ppm, Breaking strength: Warp—138 kpa; Fill—103 kpa, Specific gravity—1780–1980 kg/m³, Weight—225–325 g/m², Thickness—0.4–0.5 mm, Surface resistivity—0.62–1.55 kohm/m², Weaving type—8 H.S., pH value—7–11, and Width: 820–1100 mm.

TABLE I Bath components and operating conditions for EL coating (8)

Particulars	Description
Temperature	90°C
Time of coating	5 min
pH	9.0
Metal salt	Nickel sulphate
Reducing agent	Sodium hypophosphite
Complexing agent	Sodium citrate
Stabilizer	Ammonium sulphate and chloride
pH control reagent	Ammonia solutions
Co-precipitation elements (for composite coatings)	Aluminium chloride and zirconium oxychloride

2.2. Surface preparation of the substrate

Since EL coating is a catalytic chemical reduction process, surface preparation of the substrate is vital to achieve a sound deposit. A properly prepared substrate surface is the one where all surface contamination have been removed mechanically and/or chemically, while maintaining its dimensional tolerances [6]. The following procedure was adopted for the preparation of cut samples ($25 \times 80 \text{ mm}^2$) of carbon fabric for EL coating. Samples were taken individually and cleaned with distilled water by rinsing the sample followed by rinsing in acetone and in methanol. Sensitization of the cleaned samples was carried out by immersing in 0.1% SnCl_2 solution for 1 min and subsequently immersing in freshly prepared 0.01% PdCl_2 solution for 5 min. It is to be noted that after each rinse, the sample was dried before proceeding to the subsequent step.

2.3. Synthesis of electroless coatings and heat treatment

In the present investigation the Ni-P and Ni-P-X coatings were deposited on carbon fabric samples. Sodium hypophosphite reduced alkaline bath [5] was used for Ni-P EL coating on carbon fabric samples. The bath components and operating conditions are reported in Table I and to obtain Ni-P-X, composite coating, *in situ* co-precipitation [7] followed by co-deposition [8] was attempted.

The EL coated samples were heat treated at $400 \pm 5^\circ\text{C}$ for 1 h in a tube furnace in purified argon atmosphere.

2.4. Characterization of electroless coatings

2.4.1. Metallographic studies

The coatings were characterized by SEM (Leo 435 VP model) and continuity and the phase uniformity of coating on carbon fabric was assessed. The surface morphology of carbon fabric samples in uncoated, as-coated and heat treated conditions were studied by using SEM. For determining the coating composition, EPMA (JOEL, JXA-8600 M model) was used in which point analysis was carried out. The average of five points has been reported in this work.

2.4.2. Phase analysis

The phases present in the coating were analyzed by TEM (Philips) and XRD (Philips-PW 1140/90 model)

techniques. The SAD pattern in TEM was used to confirm the structure of the EL coating.

2.4.3. Tensile loading

Fabric samples of $25 \text{ mm} \times 80 \text{ mm}$ were used for tensile testing. Different samples coated by EL technique were heat treated at 400°C for 1 h and subjected to tensile tests by using the Hounsfield Tensometer (H25 KS model). The tensile strengths of as-coated and heat treated samples for both Ni-P- and Ni-P-X EL coatings were compared with uncoated samples.

3. Results and discussions

Carbon fabric could be coated with the Ni-P and Ni-P based composite by EL technique successfully and the reproduction of the same has been confirmed. In EL coatings, the process begins with nucleating at several isolated sites and then growth occurs both laterally and vertically to cover the entire surface of the substrate [5]. When co-precipitation of Al_2O_3 and ZrO_2 has been obtained simultaneously within the traditional EL nickel bath, very fine precipitates co-deposited along with the Ni-P alloy coating [8]. In this way, Ni-P based composite coating has been obtained. During the coating period, a large number of nucleation sites has been developed on a catalytically sensitized surface and Ni-P alloy coating started immediately. While the growth in both lateral and vertical directions occur, the fine precipitates of Al_2O_3 and ZrO_2 get co-deposited within the matrix to form an adherent Ni-P-X composite coating. The remainder of the co-precipitation product has been collected after filtering by a filter paper followed by thorough washing by distilled water. This co-precipitation reaction product, i.e., powder, which was available for co-deposition was examined under SEM and the micrograph has been shown in Fig. 1. These fine particles of $5\text{--}10 \mu\text{m}$ range of size have been co-deposited in Ni-P matrix resulting in the composite coating.

The uniform coating over the fibers in carbon fabric was achieved. The visual examination revealed that brightness is one of the obvious differences in Ni-P and Ni-P-X coatings, when compared with uncoated sample. The Ni-P coating has found to be the brightest whereas the Ni-P-X coating has been found to be

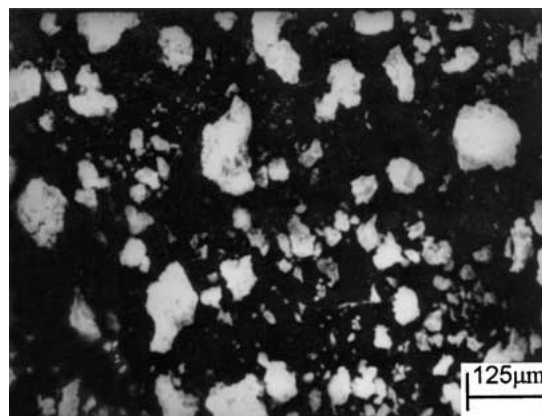


Figure 1 SEM micrograph of co-precipitation reaction powder available for the co-deposition.

duller in appearance than Ni-P coating. In the case of the Ni-P-X coatings, the dull golden spread of color is an indication of the presence of zirconia along with other phases like Ni_5P_2 , Ni_{12}P_5 and NiP_2 (Ni_xP_y) and oxide of aluminium, which has been confirmed by SEM spectrograph. The Ni-P-X coated carbon fabric under SEM has been shown in Fig. 2, uniform coating around all the strands of the fabric is apparent. The SEM micrographs of carbon fabric (uncoated) have been shown in Fig. 3a and b. The cleaned carbon fabric was clearly evident from the photos in longitudinal and cross sectional positions from Fig. 3a and b respectively. The micrographs of Ni-P as-coated showed the uniform coating of an al-

loy Ni-P, on carbon fabric as seen in Fig. 4a and b. The globules of coating developed could be observed from Fig. 4a, whereas Fig. 5a and b shows similar feature in the Ni-P-X coated carbon fabric. This composite coating of $\sim 0.8 \mu\text{m}$ can also be easily distinguished from uncoated or Ni-P coated carbon fabric. The composite particles have been seen to be entrapped in Ni-P-matrix, which is evident from Fig. 5a and b, i.e., in longitudinal and cross sectional positions of the fibers of the carbon fabric respectively. The results of quantitative analysis carried out by EPMA have been shown in Table II.

The phases present in the uncoated, as-coated and heat treated samples have been determined by subjecting them to XRD. Fig. 6 shows the XRD pattern obtained for uncoated carbon fabric sample. All the peaks of carbon have been evidenced by this XRD pattern, which shows that the fabric used did not contain any other impurities. Fig. 7a and c shows the diffraction patterns obtained for as-coated samples with Ni-P and Ni-P-X coatings respectively, whereas Fig. 7b and d is

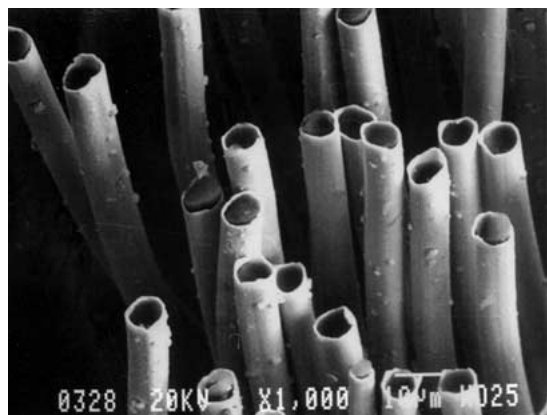
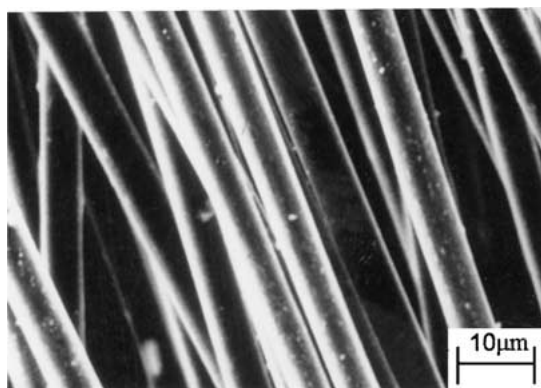


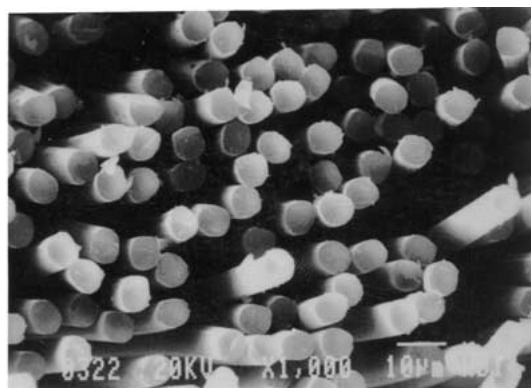
Figure 2 SEM photo of Ni-P-X coated carbon fabric.

TABLE II Quantitative analysis of EL Ni-P-X coating determined by EPMA

Element/Compound	Wt. %
P	9.5
Al_2O_3	0.025
ZrO_2	0.287
Ni	Balance

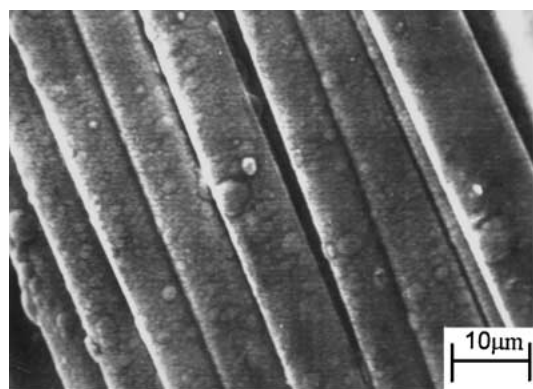


(a)



(b)

Figure 3 SEM micrographs of uncoated carbon fabric in: (a) longitudinal position and (b) cross sectional position.



(a)



(b)

Figure 4 SEM micrograph of Ni-P coated on carbon fabric in: (a) longitudinal position and (b) cross sectional position.

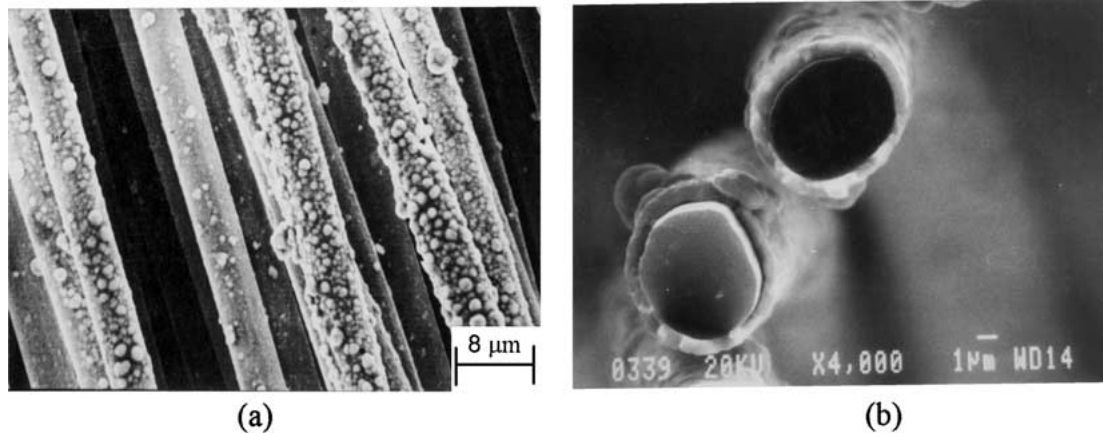


Figure 5 SEM micrograph of Ni-P-X coated carbon fabric in: (a) longitudinal position and (b) cross sectional position.

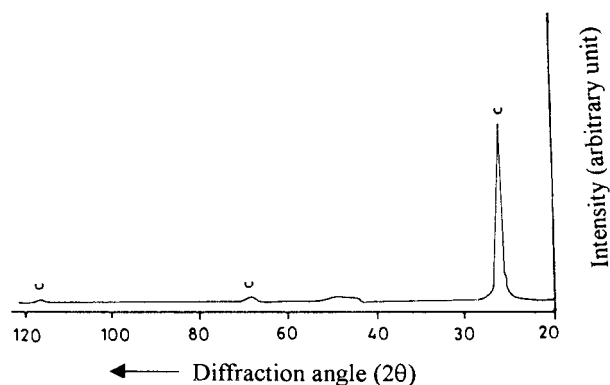


Figure 6 XRD pattern of uncoated carbon fabric sample.

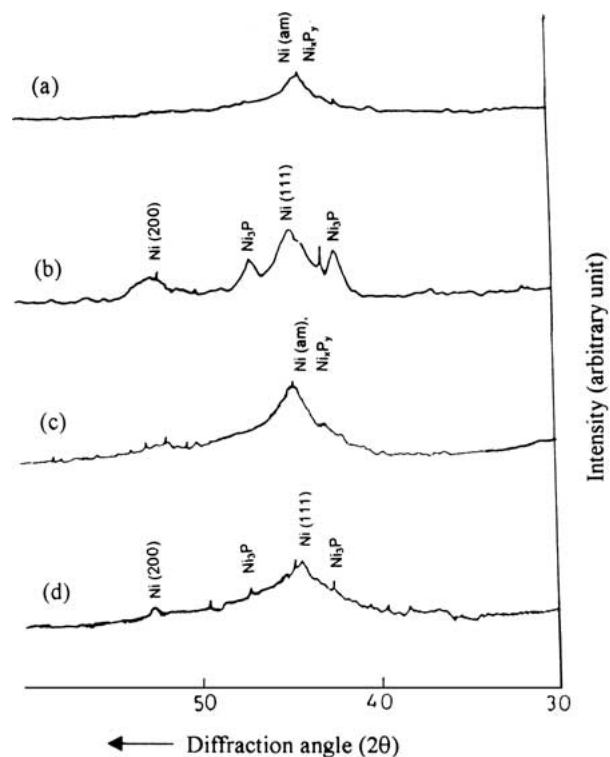


Figure 7 XRD patterns of as-coated and heat treated carbon fabric samples: (a) Ni-P as-coated, (b) Ni-P heat treated, (c) Ni-P-X as-coated and (d) Ni-P-X heat treated.

for those samples which have been heat treated after coating with Ni-P and Ni-P-X respectively. The phases microcrystalline nickel, amorphous nickel, Ni_5P_2 and Ni_{12}P_5 have been identified to be present in the as-coated condition. When phosphorus atoms have gone into the nickel lattice of FCC structure, distortion of the FCC lattice occurs so that a small and a broad peak for nickel exists in the XRD pattern of as-coated carbon fabric. Fig. 7a and c shows the XRD pattern of as-coated Ni-P and Ni-P-X carbon fabric. It has been observed that the coating on carbon fabric is amorphous in nature, which is further supported by the SAD pattern under TEM, which will be discussed later. Such amorphous nature of composite coating has been reported elsewhere [6]. The XRD patterns obtained for Ni-P and Ni-P-X coated fabric and heat treated at 400°C for 1 h in an argon atmosphere have been reported in Fig. 7b and d respectively. From these figures it has been noted that the heat treatment changes the nature of the coating from amorphous to crystalline. During heat treatment of Ni-P-X coated carbon fabric it has been seen (Fig. 7d), that the Ni_3P phase has started nucleating like in the Ni-P coatings (Fig. 7b) but the growth rate is hindered due to the presence of 'X', which acts as a grain refiner. The amorphous nature of the EL coatings on the carbon fabric has been evident from the Fig. 8a to c, which show the bright field, dark field and SAD pattern observed with the Ni-P-X coatings. The SAD pattern shows a diffused ring either corresponding to Ni (111) in amorphous state or nanocrystallites. Similar results for as-coated Ni-P foil have been reported elsewhere [5]. The amorphous nature of the EL coating is due to the presence of phosphorus atoms distorting the crystal lattice of nickel. Fine grains of 5–15 nm size (Fig. 8a and b), uniformly distributed in the matrix are identified as Ni, Al_2O_3 , ZrO_2 .

Fig. 9 represents the SEM spectrograph indicating the presence of Ni, P, Al_2O_3 and ZrO_2 . A typical line of $10.84 \mu\text{m}$ has been selected from the surface of the Ni-P-X coated specimen under SEM and then spectrographic analysis along the line was carried out. This spectrographic analysis is expected to provide the composition of different elements along the selected line and also the profile of the line. Fairly flat profile of the coating along the line is observed in part (I) of Fig. 9

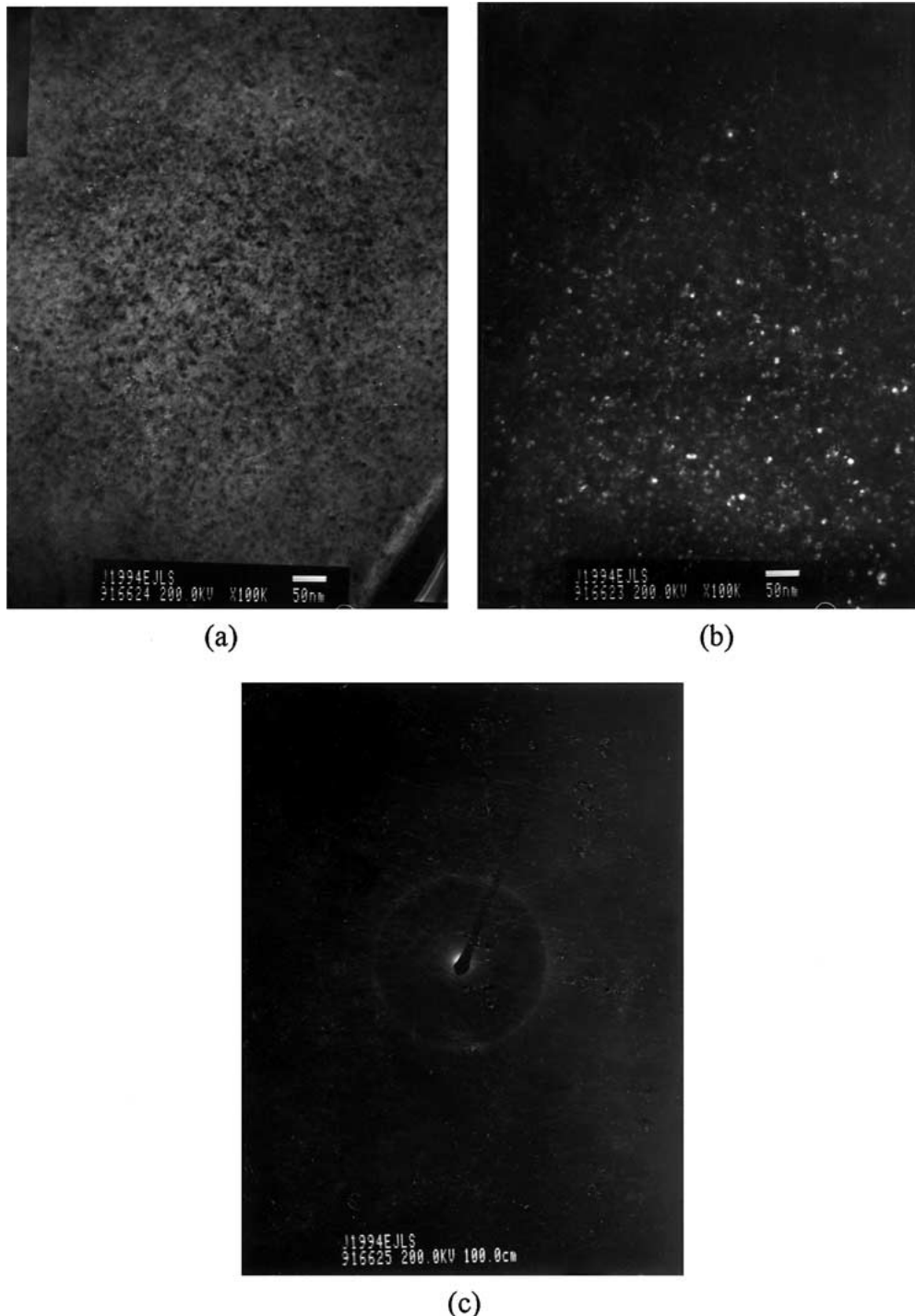


Figure 8 TEM micrographs of Ni-P-X coating on carbon fabric: (a) bright field image and (b) dark field image and (c) SAD pattern.

while other parts, viz., (II), (III), (IV), (V), (VI) and (VII) represent the presence of different elements including O K_{α} , Al K_{α} , P K_{α} , Zr L_{α} , Ni K_{α} and Zr K_{α} respectively. Fig. 9 reveals that peaks for the presence of Ni and P are more predominant and those for other trace elements are relatively smaller, which may be attributed to small amounts of Al, Zr and O in the Ni-P-X coating. The same phases also have been confirmed by a point analysis and have been represented in Fig. 10. From the above figure it can be inferred that the carbon content of the surface has not appeared in the coating, this shows that uniform coating has been obtained without having any porosity.

The tensile tests have been carried out on the specimens of carbon fabric in different conditions

including uncoated, as-coated Ni-P-X, heat treated after Ni-P coating and heat treated after Ni-P-X coating and load vs. extension curves obtained are shown respectively in Fig. 11a to d. Lower tensile failure loads of 41 N and 71 N corresponding to uncoated and as-coated Ni-P-X carbon fabric were noticed as seen in Fig. 11a and b. And it has been observed that the Ni-P-X coated and heat treated sample failed under tension at a load of 136 N and that for Ni-P coated and heat treated is found to be 126 N as seen in Fig. 11d and c. The UTS of the fabric specimens have been determined by assuming maximum packing density of the fiber tows into the fabric by referring to the specifications of the carbon fabric as given earlier. UTS of Ni-P-X as-coated carbon fabric so calculated

have been found to be 6.3 N/mm² while after heat treatment at 400°C for 1 h, the corresponding values is found to be 12.4 N/mm². The Ni-P coated and heat treated fabric shows lower UTS, i.e., 11.1 N/mm². And the UTS for un-coated carbon fabric has been

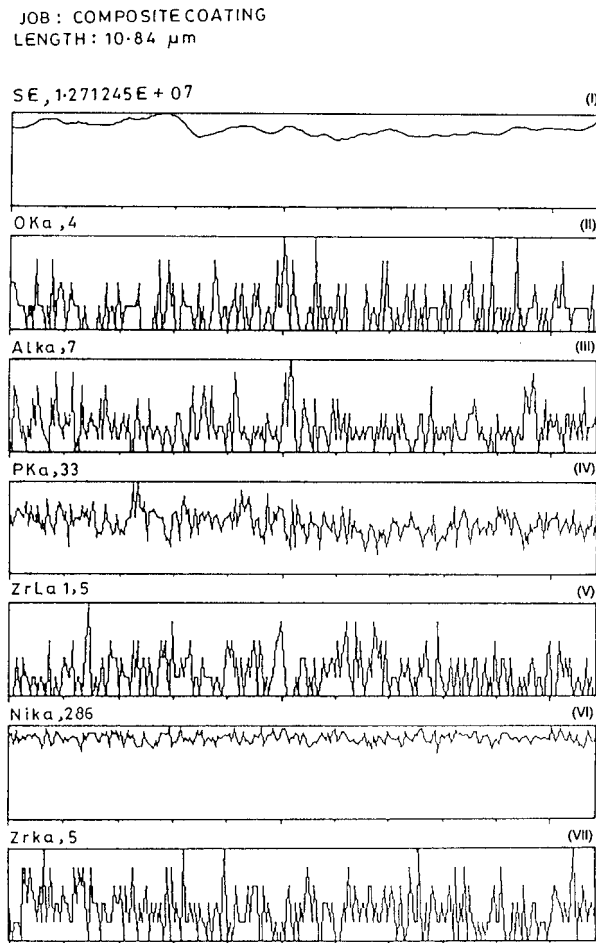


Figure 9 SEM spectrographic line analysis of Ni-P-X coating.

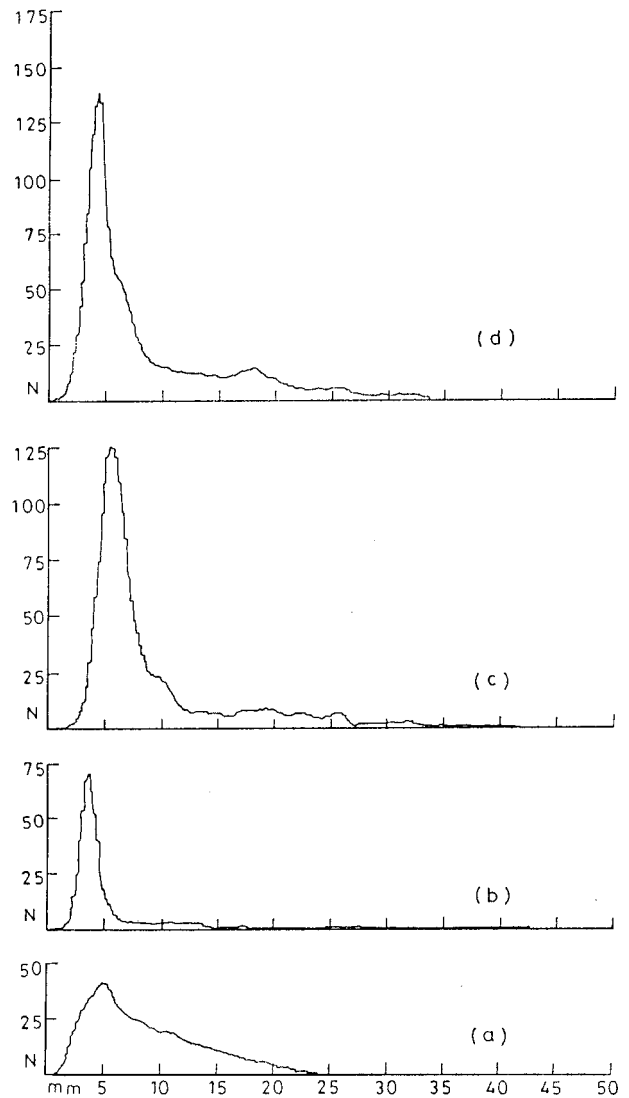


Figure 11 Tensile failure loads for various electroless coated carbon fabric samples. (a) uncoated carbon fabric, (b) as-coated Ni-P-X, (c) coated and heat treated Ni-P and (d) coated and heat treated Ni-P-X.

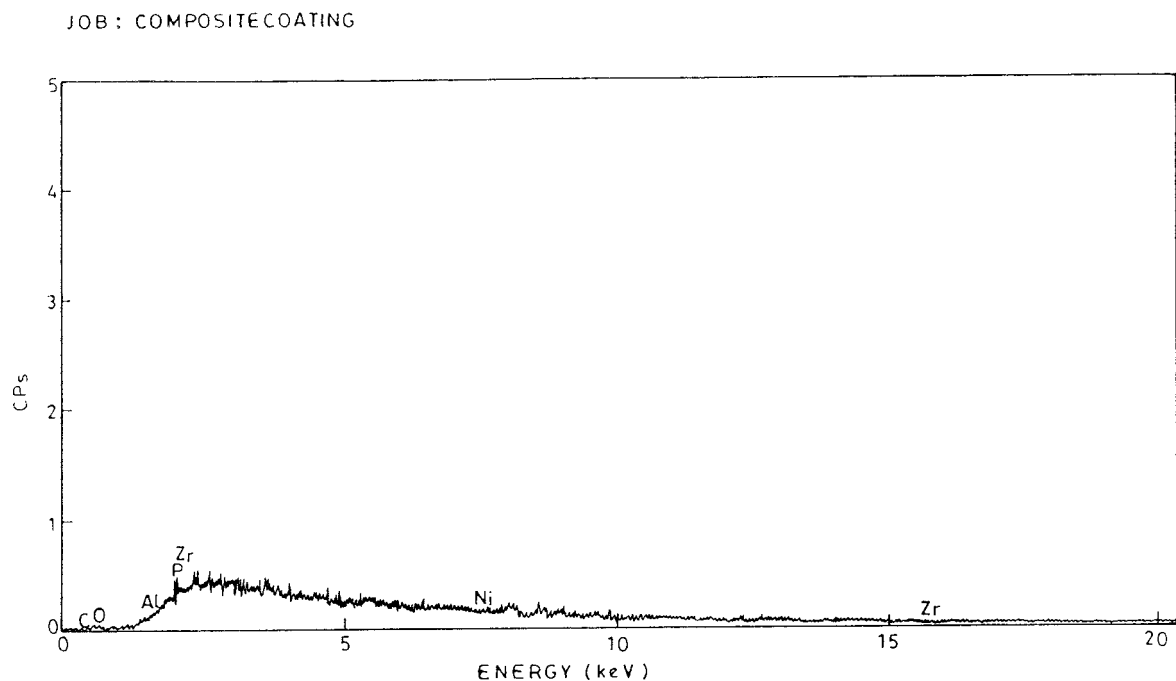


Figure 10 SEM EDAX for a point on the Ni-P-X coating.

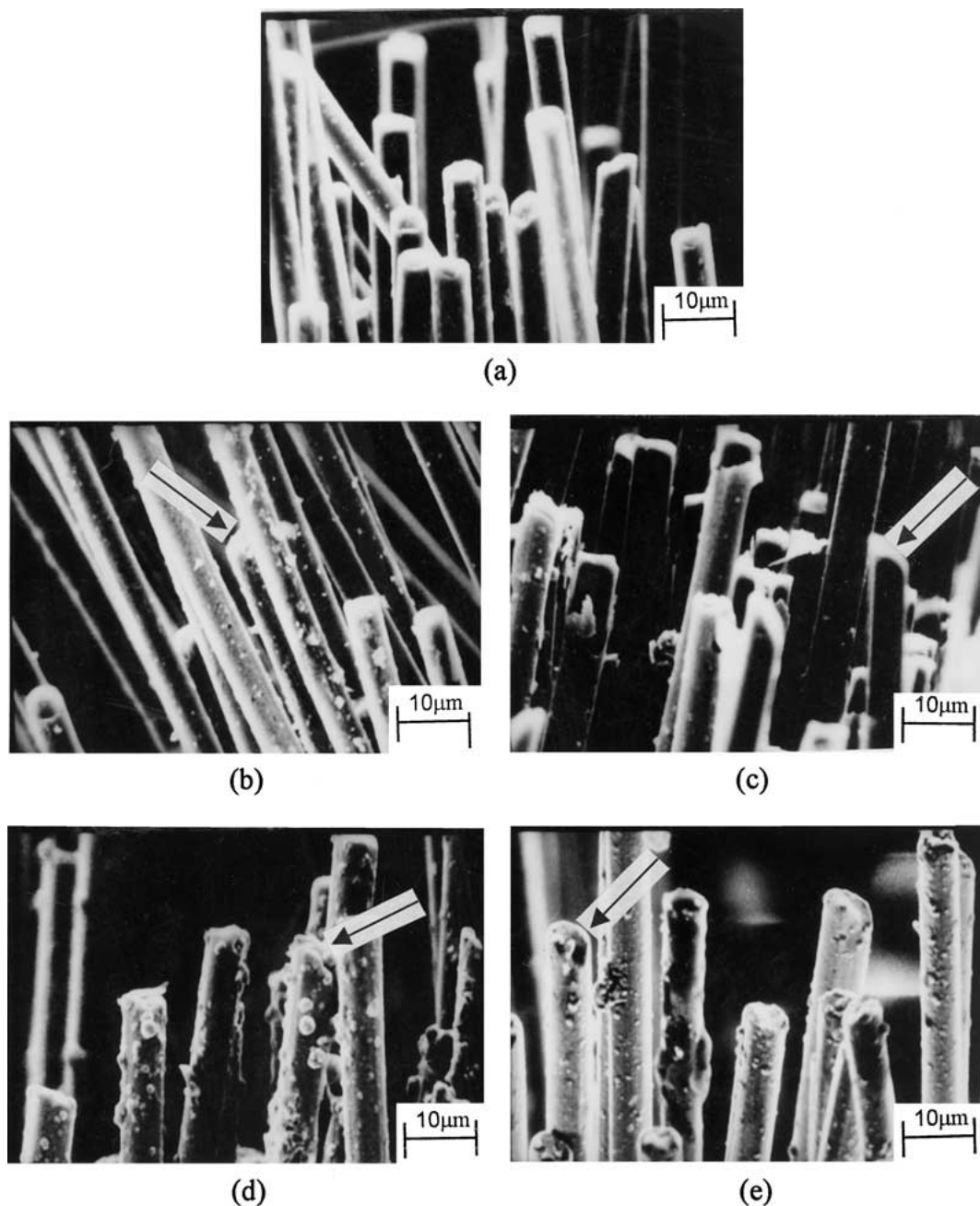


Figure 12 SEM fractograph of the carbon fabric samples: (a) uncoated carbon fabric, (b) as-coated Ni-P, (c) as-coated Ni-P-X, (d) coated and heat treated Ni-P and (e) coated and heat treated Ni-P-X.

observed to be 3.7 N/mm^2 . The UTS of carbon fabric increases by about ~ 1.7 times by electroless coating and after heat treatment further it increases by ~ 3.25 times while comparing with uncoated fabric. This improvement is due to the nucleation of Ni_3P phase as a result of heat treatment. The Ni_3P phase is hard ($\sim 1100 \text{ VHN}$), and when embedded in the softer Ni-P ($\sim 530 \text{ VHN}$) matrix it improves the strength of the material. The co-deposition of ZrO_2 and Al_2O_3 particles has shown further improvement in UTS value of coated and heat treated carbon fabric.

The SEM fractographs of carbon fabric samples in uncoated, as-coated Ni-P, as-coated Ni-P-X, heat treated Ni-P and heat treated Ni-P-X coatings have been shown in the Fig. 12a to e respectively. The fracture of carbon fabric has been seen to be of a brittle nature (Fig. 12a), whereas that with the coating is not so ev-

ident. From the Fig. 12b and c, the ductile fracture of as-coated Ni-P and Ni-P-X coatings has been observed at lateral surfaces, but the cores, i.e., carbon fiber, fracture is of a brittle nature similar to that seen in uncoated fibers of the fabric. The heat treated carbon fabric after Ni-P and Ni-P-X coatings is also seen to have the brittle nature of fracture, as inferred from Fig. 12d and e respectively. This brittle fracture feature is shown in the corresponding Fig. 12b to e by arrows. The coating around the fiber is primarily of Ni based alloy, which is ductile in nature. The coatings on carbon fabric in the present investigation, carbon occupies a predominant region, i.e., with higher volume fraction while comparing with that of Ni based coated regions. Hence, the coated fibers effectively tend to have a brittle fracture. This can be ascribed to lower percent elongation during tensile testing as seen in Fig. 11a to d.

4. Conclusions

By the EL technique uniform and continuous coating of Ni-P and Ni-P based composite coatings could be successfully achieved on carbon fabric. The mechanism of coating seems to be the deposition of Ni-P alloy by forming several nucleation sites to start with and grow laterally and vertically along with entrapment of the composite particles during growth of the EL coating.

The *in situ* co-precipitation of Al₂O₃ and ZrO₂ has been successfully used for composite coatings by EL technique. The EL coatings in the present study showed the amorphous nature in 'as-coated' conditions.

Under tensile loads, the EL Ni-P-X coated carbon fabric exhibited about 1.7 times increase in ultimate tensile strength than uncoated carbon fabric. Also, further increase in UTS values by about 3.25 times has been observed when EL Ni-P and Ni-P-X coated carbon fabric samples were heat treated at 400°C for 1 h.

The brittle fracture of uncoated carbon fabric and heat treated carbon fabric after the EL coating has been seen but the fracture at the lateral surface of the carbon fibers, which is in as-coated condition is found to be ductile in nature.

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