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3-D Porous Metal Structure Preparation by a Template Method of Electroless Plating Process for the Application of Exhaust Filter

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Abstract: Metal porous structures are of interest as functional materials for application like membrane, filter, catalyst, etc. In the present work, electroless deposition on polyurethane (PU) foam has been carried out for the preparation of such metal porous structures. A modified activation process was developed for electroless Ni–P coating on PU foam and it was modified by replacing the conventional sensitization and activation steps involving the use of $SnCl_2$ and $PdCl_2$ with the reactive mixture of Nickel Sulphate and Sodium Boro Hydride. The deposition of Ni-P layer was characterized by Scanning Electron Microscope (SEM), Energy Dispersive Spectrometer (EDS) and X-Ray Diffraction (XRD) and indicated Ni-P coating on PU foam of thickness approximately 35 μm in 2 h of processing time. The study on Ni-P coated PU foam for filter of exhaust gas of diesel engine shown 38% better performance than conventional ceramic filter. Uniform and continuous coating throughout the PU foam is a challenge for its application both as functional and structural application.
Keywords: Electroless Ni-P coating, foam, polyurethane, filter.

Introduction

Porous materials found in natural structures such as bone, coral, etc. are inspirational for synthetically produced such as cork and sponge are interest for their lightweight structure. The materials out of polymers and ceramics have been widely exploited in wide range of applications like filter, catalyst bed and membrane for functional property and structural member like metallic and ceramic foam for low strength to weight property. Generally they are classified under porous metals (metals having a large volume of porosity, typically 75-95%) and metal foams (metals with pores deliberately integrated into their structure through a foaming process) depend on their structure. Closed cell foams, which have gas-filled pores separated from each other by metal cell walls, have good strength and are mainly used for structural applications. Open cell foams, which contain a continuous network of metallic struts and the enclosed pores in each strut frame are connected (in most cases these materials are actually porous or cellular metals), are weaker and are mainly used in functional applications[1-2]. There are many different ways to produce porous metals and metallic foams and these methods are usually classified into four different types of production, using liquid metals, powdered metals, metal vapor or metal ions. Various ways of producing porous metals are powder sintering (pressure less sintering, gas entrapment, reactive processing, addition of space holding fillers, additive manufacturing) , Slurry processing

(metal powder slurries, slurry coating on PU foams, slip reaction from sintering, foaming by mechanical whisking), foaming of compacted powder precursors and electro-deposition on a porous structure[3].

The conventional activation process includes two-step method using sensitization solution of $SnCl_2$ and then activation solution of $PdCl_2$, or one-step method using a mixture of $SnCl_2$ and $PdCl_2$. However, these methods involve numerous problems such as the use of highly toxic tin and the uncontrollable process which results in the waste of Pd and the failure of plating. The other most common approaches for activation of conductive structures on the flexible substrates are based on printing method using silver nanoparticle inks which typically require a sintering step.

In the present work, electroless deposition on polyurethane (PU) foam has been carried out for the preparation of such metal porous structures. A modified activation process was developed for electroless Ni–P coating on PU foam with the reactive mixture of Nickel Sulphate and Sodium Boro Hydride. The porous structure performance as exhaust filter also been analyzed.

Experimental Procedure

Materials and Pre-Treatment

Commercially available sponge is used for synthesizing porous structure. Polyurethane foams of dimensions 30x30x10 mm³ were sectioned for coating. PU foam have pore size of ~ 0.18 mm. The specimens were cleaned, degreased in solution of 35 g/L NaOH, 25 g/L Na_2CO_3, 10 g/L Na_3PO_4 at 70 ºC for 5 min to remove the dirt and release agent on the surface of polyurethane foam. Then the samples were rinsed then in distilled water and etched in a mixture of 1 g/L $KMnO_4$ and 0.5 mL/L H2SO4 solution at 45 ºC for 5 min[4].

Activation by Immersion in Reactive Solution

Activation by Nickel Sulphate and Sodium Boro Hydride

A reactive mixture containing metallic salt of Nickel Sulphate of 0.05 M concentration and reducing mixture containing sodium boro hydride of 0.05 molar concentration and sodium hydroxide of 0.017 molar concentration was prepared[6]. The polyurethane samples were immersed in reactive mixture and subjected to microwave heating. This step is continuously done until a uniform deposition of Ni_2B on the surface of the substrate is visible. When nickel ions are present in the solution, the homogenous reaction represented by the following equation occurs, precipitating nickel boride:

$$8BH_4^+ + 4Ni^{2+} + 18H_2O \longrightarrow 2Ni_2B + 6H_3BO_3 + 25H_2 \qquad \text{------- eq (1)}$$
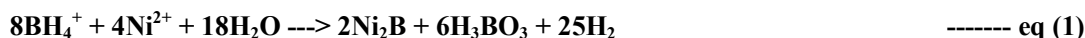
Microwave Assisted Heating

The samples immersed in reactive mixture were then subjected to microwave heating for the reason it results in uniform evaporation of water from core to shell when compared to other heating methods. For this process a house hold microwave oven (IFB 30 Sc4 Convection Microwave) was used. Power level 60 for a time period of 7 min was set for the cross-section of sponge taken.

Electroless Plating

After surface activation foam is immersed in the electroless plating solution for various time periods Activation of plating solution is attained at the temperature range 82-90ºC. The electroless plating machine consists of oil cum magnetic stirrer for heating the solution. The magnetic stirrer helps in homogenize mixture. The oil bath contains transformer oil with a flash point of 180 ºC. The specimen to be coated is supported by a rigid holder and is immersed slowly into electroless plating solution. The electroless plating solution used for the experiment is Ni-P electroless plating solution purchased commercially from ARTEK Pvt. Ltd.

Characterization Studies

Fourier Transform Infrared (FTIR) spectra of the samples were recorded using a Bruker .FTIR spectrometer (Model IFS 66 v) at room temp in the range 4000 – 500 cm⁻¹. The PU foam and Ni/PU foam was

cut and crushed into small pieces for analysis. Scanning electron micrographs (SEM) were taken with a JEOL, JSM 5610LV microscope to study the morphology. The sample was sputter coated with gold and fixed to stub of SEM with adhesive carbon tape. The Energy Dispersive Spectroscopy (EDS) was carried out using Oxford Instrument Nano Analysis INCA Energy 250 Microanalysis System in order to know the elemental composition. Phase analysis was studied using powder X-ray diffraction (Panalytical X'Pert Pro Powder XRD system) with 0.154056 nm Cu K_α radiation. Coated PU foam is crushed to powder and scanned in the range 10-90° (2Θ) value in a continuous mode with a scanning rate of 0.01 °/s.

Exhaust Filter Setup

Ni-P coated foam after characterization was evaluated for an application of exhaust filter in diesel engine of Internal Combustion Laboratory. A fixture for holding the sponge to the engine exhaust was constructed using coupling pipes welded to disc plates as shown in Fig.1. The experiment was carried for a period of 10 min with engine running on no-load condition. The weight of carbon residue collected by the metallic foam was calculated by weighing the foam before and after running the experiment. The amount of carbon residue collected was compared against a ceramic filter used in lab.
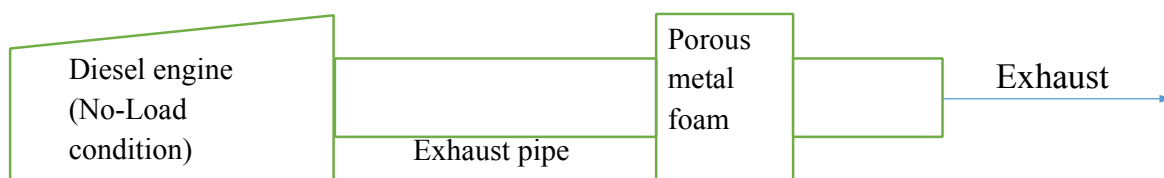

Fig 1. Exhaust filter setup for coated porous sponge

Results and Discussion

Characterization of Ni-P Coated Foam

Fig. 2 shows that the polymer foam is polyurethane by the presence of vibrational bands corresponding to functional groups C–H stretch of alkanes, N–O asymmetric stretch of nitro compounds and C–N stretch of aliphatic amines at the wave number 2863.81, 1534.03, 1219.83, 1077.25 cm^{-1}. So the chemical nature of the sponge is found to be PU. The FTIR spectrum for Ni/PU foam obtained was found to be similar to that of the PU foam.
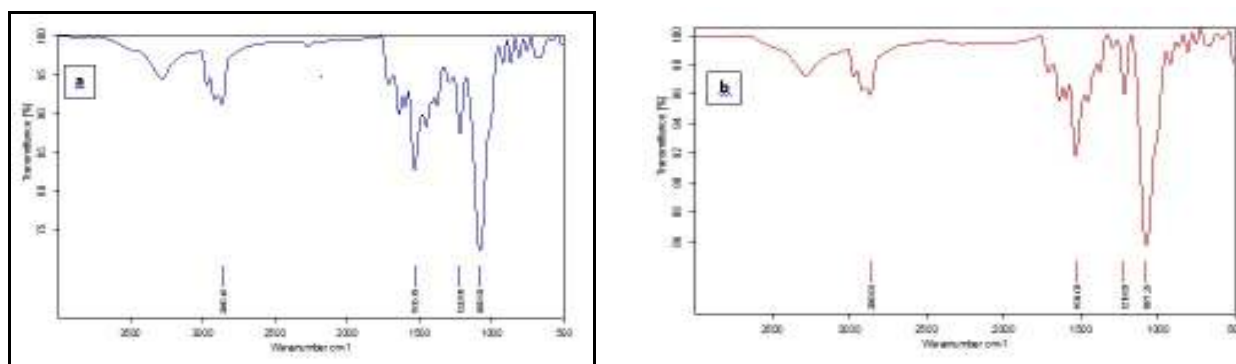

Fig.2 FTIR spectra for (a) PU foam and (b) Ni/PU foam

The SEM image of the PU foam before and after electroless deposition is shown in Fig. 3. A SEM micrograph shown in Fig. 3(b) revealed the layer thickness of 32±5 μm and the pore size of 166±5 μm measured with the help of Image J software. The surface of as deposited Ni-P coating consisted of nodular morphology and revealed the rough surface (Fig. 3 (b)). The formation of such nodular structures is a common feature[7].
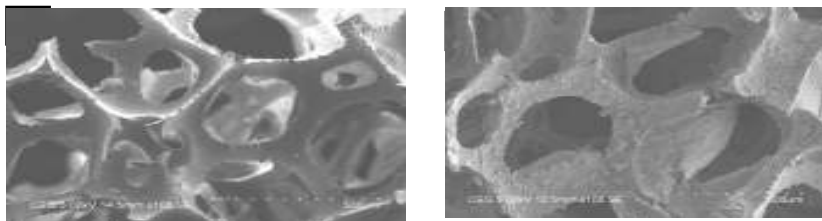
Fig. 3 SEM micrographs of (a) PU foam, (b) SE mode Image of Ni/PU foam

The composition of various elements over the Ni/PU foam activated by reactive mixture is analyzed using EDS analysis as shown in Fig. 4. It is clearly seen that the Ni is deposited in the surface of the PU foam.
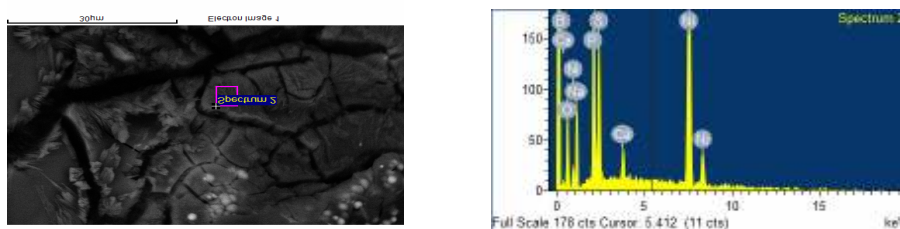

Fig.4 EDS spectra of the Ni/PU foam

According to EDS analysis shown in Fig. 4 (a) the electroless plated layer contained 96.79 at% of Ni and 3.17 at% of P, which is in a good accordance with previous published data for Ni–P coatings formed in an acidic media[8]. The composition analysis of Ni- P coated PU foam is shown in Table 1.

Table 1 Composition analysis of Ni- P coated PU foam

Element	Intensity cps	Weight %
C K	0.3181	0.01
P K	0.8850	3.64
Ni K	0.9696	9137
Total		100.00

In general metal layer formed by electroless plating is purely amorphous[7] but the XRD data demonstrated that the Ni–P layer becomes crystalline showing sharp peaks after heat treatment at 800°C. Peaks corresponding to metal Ni, Ni_3P and other Ni-P phases are observed on the diffraction pattern as shown in Fig.5.
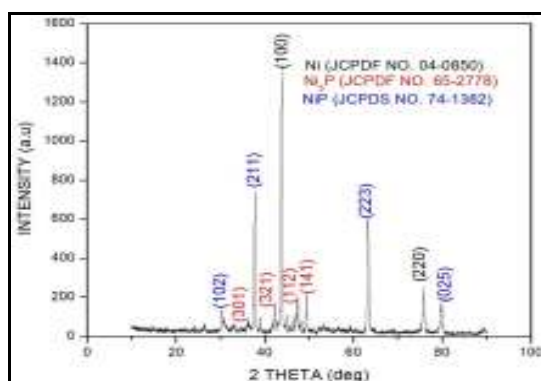

Fig.5 XRD pattern of heat treated Ni-P coating

Deposition Rate

Deposition rate for 120 min at interval of 30 min. was calculated by measuring the mass difference before and after electroless plating of Ni-P at regular intervals[4]. Deposition rate was faster at the early stages of plating and started decreasing after 60 min (Fig 6). This may be due to the reduction in amount of Ni ions in the electroless bath solution or reduced tendency of the coated layer to accept more Ni ions with increasing time and thickness.
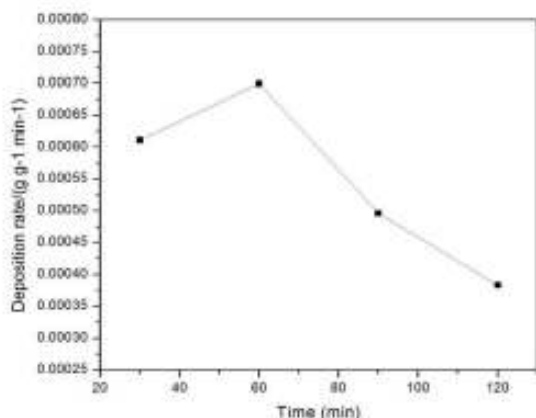

Fig 6 Deposition rate Variation with Coating duration

Performance as Filter

The mass of the coated sponge before using it as filter is found to be 3.0041 g. The engine is operated for 10 minute period. The coated sponge is then weighed and its mass after testing it for application is found as 3.2172 g. The mass difference between before and after testing is measured to be 0.2131 g and it gives the carbon residue collected by the coated sponge. Similarly, the carbon residue collected by ceramic filter is found to be 0.1546 g by taking the residue separately and weighing it in the weighing balance. Around 38 % increase in the collection of carbon residue by the Ni/PU foam when compared to the conventional ceramic filters because of the reduced pore size of 166 μm in Ni/PU foam.

Conclusion

A low cost method of activation of polymer substrate by using solution of metallic salt and a reducing solution was achieved using $NiSO_4$ and $NaBH_4$ with use of microwave heating. The SEM images of coated foam which was analyzed with image analyzer revealed a coating thickness of 32±5 μm and the average pore size of 166±5 μm. EDS analysis revealed that the composition of coating consist of nickel and phosphorous. XRD study corroborated well with the EDS data by the presence of distinct peaks of Ni and Ni_3P phases. The coated metallic foam tested for filter application showed 38 % better carbon residue trap than compared to that of the existing ceramic filters. There is need for optimization of surface activation and coating process for homogenous coating for foam of larger dimension as well as better mechanical strength.

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