JOURNAL OF MATERIALS PROCESSING TECHNOLOGY 209 (2009) 3022–3029

journal homepage: www.elsevier.com/locate/jmatprotec

Influence of process parameters for coating of nickel–phosphorous on carbon fibers

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ARTICLE INFO

Article history:
Received 4 October 2007
Received in revised form 1 July 2008
Accepted 5 July 2008

Keywords:
Electroless coating
Carbon fiber
X-ray diffraction
SEM
TGA/DTA

ABSTRACT

The nickel–phosphorous (Ni–P) coating on carbon fiber was studied, using sodium hypophosphite as a reducing agent in alkaline medium. The effects of process parameters such as time, stabilizer concentrations, pH of the plating bath and plating bath's temperature on the electroless Ni–P coating efficiency were investigated. Structural study using X-ray diffraction (XRD) indicates that nickel deposition rate increases with increasing coating time and temperature. The nickel (Ni) recovery efficiency decreases with an increase of stabilizer concentration. From scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX), it has been confirmed that the coating thickness and nickel content increase with an increase of coating time and temperature. The bath temperature of 25 °C, pH of 9, and stabilizer concentration of 25 g/L is good to get a good and uniform coating of Ni on carbon fiber. Thermal stability was studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). From TGA study it is evident that the nickel coating increases thermal stability of the nickel-coated carbon fiber. *I–V* (current vs voltage) measurement shows Ni-coated fiber is more conducting in nature.

1. Introduction

Ni–P alloys have been extensively used in chemical, aerospace, automobile and textile industries due to their excellent wear resistance, corrosion resistance, solderability, polishability, magnetic properties, etc. (Matsubara et al., 2002). Today, the deposition process of electroless coating and thin film plays an important role in microelectronics and nanotechnology (Shacham-Diamond et al., 2003). Carbon fiber has excellent mechanical characteristics, including high tensile strength and high elastic modulus, as well as high thermal and electrical conductivities. Marshal et al. (1994) have reported that the polymer-based advanced composites filled with carbon fiber are good in adverse environments because of their excellent mechanical behavior and good durability over a wide range of temperature, pressure and weather. In recent years, many conductive polymer composites have been produced using carbon fiber as conductive reinforcements. It takes the advantage of fine conductivity of carbon fiber.

The single wall carbon nanotube (SWNT) has an outstanding tensile strength of ~37 GPa, stiffness of ~640 GPa, and Young's modulus of ~2.8 to 3.6 TPa (Ruoff and Lorents, 1995; Ebbesen and Ajayan, 1992) have reported the electrical conductivity of ~100 S/cm. The thermal conductivity of SWNT, which is 2000 W/mK has been reported by Che et al. (2000). Peigney et al. (2001) have reported the specific surface area of 1350 m^2/g. These properties of carbon nanotube (CNT) will have little value, unless they are incorporated into a matrix.

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doi:10.1016/j.jmatprotec.2008.07.006

Composite materials containing carbon fibers are, of course, already used in applications ranging from aerospace to sports equipments. In such materials the matrix can be plastic, epoxy, metal or carbon. The incorporation of carbon fiber into the matrix not only confers strength and elasticity to the material, but also greatly enhances toughness that is its ability to resist cracking. The ability to disperse CNT into polymer is a major problem for controlling the properties. Carbon nanotubes, these are in clumps or agglomerated with other carbonaceous materials, create defects and initiate failure in the composites. In addition, they reduce the efficiency of load bearing capacity of CNT. From this understanding an attempt will be made in near future to grow CNTs on the surface of nickel-coated carbon fiber. These CNT coated fibers will help to make strong composite materials. A transition metal is to be coated on the surface of carbon fiber to grow CNTs. Keeping this in mind, the carbon fiber is coated with nickel catalyst in this study. Now the question is about the process of nickel coating on carbon fiber at nano scale. Electroless coating is a suitable method, where a metallic film is coated on the surface of carbon fiber to increase the conductivity of fiber. When the conductivity of carbon fiber is increased it has lot of benefits for many suitable applications. Gimblett et al. (1989) have indicated that the carbon fiber containing phosphate groups provide a suitable protection for anti-oxidization. Marshall et al. (1992) have reported that when the content of phosphorous is more than 7–9 wt.%, the phase of electroless nickel phosphorous (Ni–P) alloys is amorphous in nature. The conductivity of amorphous electroless Ni–P alloy coating is poor than that of crystalline. Thus, the anti-oxidized ability of Ni–P coating is improved by optimizing the process parameters during nickel coating. The compositions of the coating strongly influence its properties and are controlled by various process parameters like pH, temperature, etc. (Lu and Zangari, 2002). In this paper, we have reported the effect of process parameters such as time, stabilizer concentration, pH of the plating bath and plating bath's temperature on the feasibility, efficiency and stability of Ni–P coating on carbon fiber.

2. Experimental approach

2.1. Materials

PAN based continuous carbon fiber used in this study was received from M/S FORTAFIL Industries, Inc., UK. Table 1 shows the structural parameters of this fiber measured in our laboratory. Nickel sulphate ($NiSO_4{\cdot}6H_2O$, 98.2%) was used as a source of nickel. Ammonium chloride (NH_4Cl, 99%) was used as a complexing agent to control the rate of release of the free nickel metal, and tri-sodium citrate ($Na_3C_6H_5O_7{\cdot}2H_2O$, 99–100%) was used as stabilizer to prevent the decomposition of the plating bath. M/S Qualigens Chemicals Inc., India supplied all these chemicals. Sodium hypophosphite ($Na_2H_2PO_2{\cdot}H_2O$, 99%) were obtained from M/S Loba Chemie Inc., India and used as a reducing agent, which also serves as a source of phosphorous in the coating. Ammonia solution (25%) was received from M/S Merck India Ltd., which was used to maintain the pH of solution.

Table 1 – Structure parameters of carbon fiber

Fiber type	Average diameter (μm)	d_{002} (Å)
Fortafill	6.8 ± 0.20	3.45

2.1.1. Pretreatment of carbon fiber surface

The carbon fiber surfaces are frequently given a surface treatment to improve its wetability with polymer. Before electroless plating, the coating of carbon fiber, which is known as sizing materials, were removed by immersing the fiber into the acetone solution for an hour and rinsed with deionized water. Then, the cleaned fibers were heated in an oven at a temperature of 100 °C for an hour in order to dry the fiber surface.

2.1.2. Electroless nickel deposition

The Ni–P coating was deposited on the carbon fiber's surface using an alkaline bath containing nickel sulphate as a source of nickel, and sodium hypophosphite as a reducing agent. Table 2 lists the bath composition and their important functions. After drying, the cleaned fibers were placed in the solution. To study the effect of tri-sodium citrate (stabilizer) concentration on the crystallinity and deposition rate, several baths with varying amount of stabilizer were prepared. The concentration of stabilizer used in these baths was 10, 25, 35 and 50 g/L. The effect of time and temperature on deposition was also carried out. The temperature was controlled through PID based temperature controller (model # 4001AJF, M/S OMEGA Engineering, Inc., USA) with an accuracy of ±1 °C (cold water of 15 °C was circulated around the beaker). To study the effect of pH, experiments were conducted with varying pH values of 7, 8, 9 and 10. The pH was measured by digital pH meter (model # LT-11, M/S Labtronics, Laboratory Instruments, India) with an accuracy of ±0.1 pH. It was mentioned by adding ammonium hydroxide in the solution.

In all these cases the stabilizer concentration was maintained at 25 g/L. To obtain experimental errors, 5 specimens were coated for each experimental condition, so that, the final results were average value of 5 measurements. The experimental error was reproducible within an error of ±5%.

Table 2 – Formulations and operating conditions for electroless nickel-plating bath

Chemical	Formulae	Functions	Concentration (g/L)
Nickel sulphate	$NiSO_4{\cdot}6H_2O$	Metallic ions	30
Sodium hypophosphite	$NaH_2PO_2{\cdot}H_2O$	Reducing agent	10
Ammonium chloride	NH_4Cl	Complexing agent	50
Tri-sodium citrate	$Na_3C_6H_5O_7{\cdot}2H_2O$	Stabilizer	10, 25, 35, 50
Ammonium hydroxide	NH_4OH	Alkalinity reserve	pH adjustment