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Surface metallization of ABS plastics for nickel plating by molecules grafted method

Heng Zhang[a], Zhixin Kang[a,*], Jing Sang[b], Hidetoshi Hirahara[b]

[a] Guangdong Key Laboratory for Advanced Metallic Materials Processing, School of Mechanical and Automotive Engineering, South China University of Technology, 381 Wushan, Guangzhou 510640, China

[b] Department of Chemistry and Biological Sciences, Faculty of Science and Engineering, Iwate University, 4-3-5, Ueda, Morioka 020-8551, Japan

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ABSTRACT

The surface activation of ABS plastics was achieved by novel palladium-free pretreatments that consisted of molecular grafting and self-assembling. Silver mirror reaction has been developed to prepare silver films on ABS plastics by solution spray. There is an excellent adhesion between the substrate and Ag films as the molecular bonding force is larger than the mechanical anchoring force by conventional sensitizing-activation method. A compact copper coating was prepared on the Ag films to make the products to adapt to a variety of environments, and double-nickel electroplated coats were achieved to enhance corrosion resistance. X-ray photoelectron spectroscopy (XPS) analysis provided useful data on surface functionality. X-ray diffraction (XRD) result revealed pure silver films on ABS. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were used to characterize the coatings morphologies.

1. Introduction

The surface metallization of ABS plastics combines inherent performances, such as thermal stability, excellent mechanical strength, and high resistance to chemical reagents [1–3]. Metallized plastics will also bring about the characteristics of the metal, such as conductivity, magnetic shielding, abrasion resistance and decorative properties [4–7]. It is increasingly high required for corrosion-resistant, lightweight products in modern industries. The metallization of engineering plastics has been widely used in electrical and electronic, automotive, computer body parts, office equipment, machinery and other industries [8–10]. There are various types of engineering plastics that can be metalized in industrial production, such as polypropylene, polyamide, acrylonitrile-butadiene-styrene copolymer, polyethylene terephthalate [11–13], of which ABS is the most widely used metalized engineering plastic because the butadiene is dispersed uniformly in the acrylonitrile-styrene matrix, which making the metal bond to the substrate closely [14,15].

One of the more important processes in the conventional surface metallization of ABS plastics is sensitizing-activation [16,17]. After the pretreatment of soak cleaning, the substrate is etched firstly by using a hot sulfuric-chromic acid bath. The purpose is to oxidize the butadiene which dispersed uniformly in the acrylonitrile-styrene matrix to obtain distributed micro-pores evenly [18,19]. Furthermore, colloidal palladium is deposited into the etched micro-pores through chemical redox reaction [20,21]. Through a series of cumbersome processes, the ABS plastics can be metallized followed by electroless plating and electroplating. The structure of adherent metal coatings on the substrate is called 'anchor effect' vividly [22–24]. Moreover, it is reported that hexavalent chromium is toxic to human body [25]. As a result, it is necessary to develop convenient palladium-free methods, and several works have been reported. Teixeira et al. [26] studied the results of etching morphologies with different group solutions of sulfuric acid, with hydrogen peroxide and/or nitric acid, replacing chromic acid, as oxidants. The reasonable solution components perform as well as the chromic-based baths eventually. Bazzaoui et al. [7,21] proposed a direct metal electroplating on ABS plastics, after the critical pretreatments, that consists of a black, adherent PPy polymerization on ABS, so that plastic became conductors. They showed the homogeneous copper films were successfully prepared on PPy/ABS nucleus. Magallón-Cacho et al. [27] presented an alternative surface treatment with substantially lower levels concerning environmental impact, which indicated the heterogeneous photocatalysis with titanium dioxide is an oxidative treatment for the ABS surface modification that generates enough and appropriate roughness to allow an optimum metallization. Laser Direct Structuring (LDS) technology become more popular in recent years, by adding a certain amount of metal compound crystals before plastics injection, metal particles were deposited uniformly in the matrix

* Corresponding author.
E-mail address: zxkang@scut.edu.cn (Z. Kang).

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Table 1
Step and operational conditions of pretreatment.

Step	Specific parameter
Cleaning	Absolute ethanol, ultrasonic cleaning, 3 min
Molecular grafting of P-TES	P-TES 0.8 g/L (absolute ethanol alcohol solution), 10 s
Self-assembling of N-TES	N-TES 1 g/L, 20 min
Solution spray of silver	$AgNO_3$ 17 g/L, $NH_3{\cdot}H_2O$ (25%) 150 mL/L, $(CHO)_2$ 1 mol/L, $N(CH_2CH_2OH)_3$ 0.1 mmol/L

through the laser activation [28,29], which could ensure the electric conductivity of plastics sample followed by electroless plating that metal patterns are formed [30]. However, which made a high demand for laser equipment and technological parameter.

In the present work, a simple method without palladium and chromium is presented to replace conventional sensitizing-activation. The adhesion between the film and substrate was greatly enhanced by molecular grafting and self-assembling. The dense corrosion-resistant nickel coatings can be achieved on ABS substrate after the solution spray of silver films.

2. Experimental

2.1. Materials

ABS sheets with PE films covered that were purchased from the Anheda Plastic Products Co. Ltd. (Shenzhen China), The powdery monomer of P-TES 6-azide-2,4-bis (3-triethoxysilyl) propylamino-1,3,5 triazine and N-TES 6-azide-2,4 dithiol monosodium (3-triethoxysilyl) propylamino-1,3,5 triazine were obtained from laboratory (Sulfur Chemical Institute, Japan). All the chemical reagents used were analytical pure reagent grade and they were commercially available. The solutions were prepared using distilled water or absolute ethanol.

2.2. Palladium-free treatments

The ABS sheets with the size of 50 mm × 40 mm × 1 mm plates were used in this paper. The processes of solution spray and the pretreatments include cleaning, molecular grafting and self-assembling were shown in Table 1.

2.2.1. Surface modification of ABS

The experiments were achieved at room temperature as follows: Firstly, the ABS sheets were cleaned with absolute ethanol through ultrasonic cleaner for 5 min and then immersed into P-TES solution for 10 s. The foils was exposed to an ultraviolet lamp that emits ultraviolet radiation at the wavelength of 265 nm for 3.5 min to promote the monomer of P-TES to graft with ABS by chemical bonding, after that rinsed by absolute ethanol for several times. At last, the sheets were dipped into an aqueous solution of N-TES for 20 min so that the molecular membrane can form self-assembled structures adequately on the substrate [10].

Table 2
Solution components and conditions of copper electroplating.

Solution components	Concentration	Conditions
Copper sulfate	220 g/L	j = 0.5–1.5 A/dm^2
Sulfuric acid	60 g/L	T = 30 °C
Chloride ion	30 mg/L	t = 20 min
Polyethylene glycol	20 mg/L	

Table 3
Solution components and conditions of semi-bright nickel electroplating.

Solution components	Concentration	Conditions
Nickel sulfate	240 g/L	j = 2–4 A/dm^2
Nickel chloride	30 g/L	T = 30 °C
Boric acid	40 g/L	t = 5 min, pH = 4.4 ± 0.1

Table 4
Solution components and conditions of bright nickel electroplating.

Solution components	Concentration	Conditions
Nickel sulfate	240 g/L	j = 2–4 A/dm^2
Nickel chloride	30 g/L	T = 30 °C
Boric acid	40 g/L	t = 5 min
Sodium dodecyl sulfate	0.2 g/L	pH = 3.5 ± 0.1
Additives	10 mL/L	

2.2.2. Silver films solution spray

Before silver plating, the modified ABS sheets were immersed into an aqueous solution containing 0.1 mol/L $SnCl_2$ and 40 mL/L HCl for 1 min to wet surface. The spraying process uses two devices simultaneously, one with the silver ammonia solution, Tollen's reagent, and the other with the reducing agent solution, glyoxal, and triethanolamine. The spraying direction is perpendicular to the surface of the sample, and the distance between spray nozzles with the dimension of 500 μm and sample was 15 cm, the deposition took about 8 s per every 10 spray

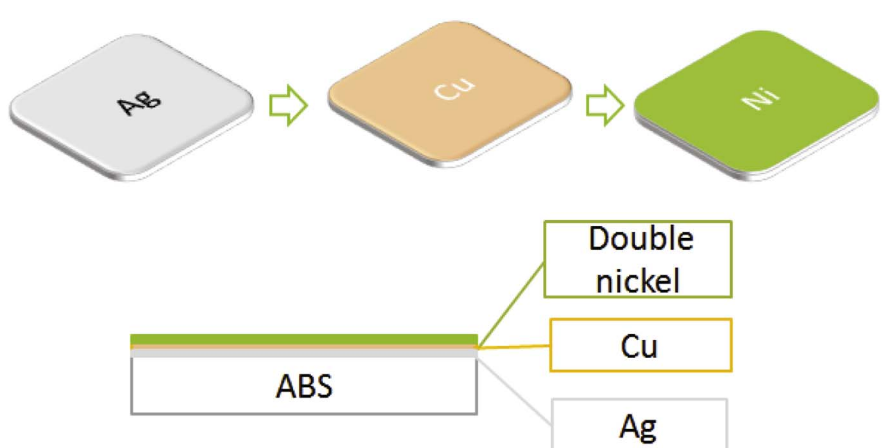

Fig. 1. Schematic illustration of electroplating.