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ScienceDirect

Surface & Coatings Technology 202 (2008) 2591 – 2602

SURFACE & COATINGS TECHNOLOGY

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Synthesis and corrosion protection study of poly(*o*-ethylaniline) coatings on copper

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Received 16 April 2007; accepted in revised form 19 September 2007
Available online 13 November 2007

Abstract

Poly(*o*-ethylaniline) coatings were synthesized on copper (Cu) by electrochemical polymerization of *o*-ethylaniline in an aqueous salicylate solution by using cyclic voltammetry. The characterization of these coatings was carried out by cyclic voltammetry, UV–visible absorption spectroscopy, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The results of these characterizations indicate that the aqueous salicylate solution is a suitable medium for the electrochemical polymerization of *o*-ethylaniline to generate strongly adherent and smooth poly(*o*-ethylaniline) coatings on Cu substrates. The performance of poly(*o*-ethylaniline) as protective coating against corrosion of Cu in aqueous 3% NaCl was assessed by the potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS). The results of these studies demonstrate that the poly(*o*-ethylaniline) coating has ability to protect the Cu against corrosion. The corrosion potential was about 0.078 V versus SCE more positive in aqueous 3% NaCl for the poly(*o*-ethylaniline) coated Cu (~ 15 μm thick) than that of uncoated Cu and reduces the corrosion rate of Cu almost by a factor of 70.

Keywords: Corrosion resistant coatings; Conducting polymers; Poly(*o*-ethylaniline) coatings; Copper; Electrochemical polymerization; Cyclic voltammetry

1. Introduction

During the last decade, the electrically conducting polymers have been a center of scientific interest and active multidisciplinary research due to their excellent potentialities for widespread technological applications [1–5]. One of the most important applications of these materials which attracting considerable attention in most recent times is in corrosion protection of oxidizable metals [6–18]. However, conducting polymer coatings have been controversially discussed as being useful for corrosion protection of oxidizable metals during last couple of years. It is widely accepted that conducting polymer coatings reduce the corrosion rate of oxidizable metals, but they perform well only under certain special conditions. Recently, it has been reported that conducting polymer coatings perform well during immersion experiments as long as there are no large defects in the coating [19–21].

The electrochemical polymerization is a simple, relatively inexpensive and most convenient route for synthesizing novel conducting polymers on metallic surfaces [1,2]. Although, the conducting polymers are found to be the most promising materials for corrosion protection, the electrochemical polymerization of conducting polymers is not easy on oxidizable metals. DeBerry [22] was the first to show that the electrochemically synthesized polyaniline acts as corrosion protective layer on stainless steel in 1 M H_2SO_4. Since then, several research groups [6–18] have systematically investigated the electrochemical synthesis of various conducting polymers on oxidizable metals for corrosion protection purposes. The common feature of these investigations is that the electrochemical synthesis of conducting polymer coatings on oxidizable metals is preceded by the dissolution of the base metal at a potential lower than the oxidation potential of monomer. Thus, the oxidation of the metal appears

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doi:10.1016/j.surfcoat.2007.09.025

as a simultaneous and competitive oxidation process at the potentials adequate for the formation of polymer. Hence, a successful electrochemical synthesis of conducting polymer coatings on oxidizable metals demands a careful choice of the solvent and/or supporting electrolyte and the establishment of electrochemical parameters, which will strongly passivate the metal without impeding the electrochemical polymerization process.

Copper (Cu) is widely used reactive metal in electrical and electronic devices. It is rapidly replacing aluminum as the interconnect material of choice in integrated circuits, particularly microprocessors, because of its low resistivity and its improved electromigration performance [23]. Despite the fact that copper is noble, it readily corrodes in a variety of environments [24]. However, only very few studies [25–27] have been carried out on the corrosion protection of copper by conducting polymer coatings in spite of its use in wide range of technological applications. There are only two reports dealing with the direct electrochemical polymerization of pyrrole on pure Cu. Fenelon et al. [25] have successfully electropolymerized the pyrrole on Cu from a near-neutral sodium oxalate solution to generate a homogeneous and adherent polypyrrole films. It was observed that these films exhibit significant corrosion protection properties in acidified and neutral 0.1 M NaCl solution. Cascalheira et al. [26] recently reported the formation of strongly adherent polypyrrole coatings on Cu from an aqueous salicylate solution. In most of the other studies, the conducting polymers were first synthesized chemically and then deposited on the metal surface. For example, Brusic et al. [27] have deposited the films of polyaniline and its derivatives on Cu by spin coating technique and studied the corrosion protection properties as a function of the applied potential and temperature.

More recently, we have investigated the electrochemical polymerization of *o*-anisidine and *o*-toluidine on Cu substrates from a near-neutral sodium oxalate solution using cyclic voltammetry [28,29]. It was found that the aqueous sodium oxalate solution is a suitable medium for synthesizing uniform and strongly adherent poly (*o*-anisidine) and poly(*o*-toluidine) coatings on Cu. The synthesis of these coatings was facilitated by the formation of copper oxalate passive layer, which inhibits the Cu dissolution without impeding the electrochemical polymerization process. Further, it was shown that these coatings have remarkable potential to protect Cu against corrosion in chloride environment.

With the objective to search for new conducting polymers applicable for corrosion protection of oxidizable metals, we have made an attempt to synthesize strongly adherent poly(*o*-ethylaniline) coatings on Cu substrates by electrochemical polymerization from aqueous salicylate medium and examined the ability of these coatings to serve as corrosion protective coatings on Cu. To the best of our knowledge, there are no reports in the literature dealing with the direct deposition of poly(*o*-ethylaniline) coatings on Cu from aqueous salicylate medium.

The reasons for selecting the *o*-ethylaniline monomer are many and obvious. These reasons are — (a) The monomer *o*-ethylaniline is commercially available at low cost. (b) This study explores the possibility of utilizing the poly(*o*-ethylaniline) as alternative to polyaniline for corrosion protection of Cu. (c) The *o*-ethylaniline monomer has quite good solubility in water and therefore it is possible to develop an electrochemical polymerization recipe using aqueous media which will reduce the use of hazardous chemicals as well as the cost of waste disposal.

The results reported in this paper have shown that the electrochemical polymerization of *o*-ethylaniline from the aqueous salicylate solution results into the formation of uniform, compact and strongly adherent poly(*o*-ethylaniline) coating on Cu substrate. The evaluation of the corrosion protection performance of these coatings reveals that poly(*o*-ethylaniline) can be considered as a potential coating material for protection of Cu against corrosion in aqueous 3% NaCl.

2. Experimental

Analytical reagents (AR) grade chemicals were used throughout the present study. The *o*-ethylaniline monomer was double distilled prior to its use. The aqueous sodium salicylate ($NaC_7H_5O_3$) solution was used as the supporting electrolyte. The concentrations of sodium salicylate and *o*-ethylaniline were kept constant at 0.1 M and 0.05 M, respectively.

The Cu (99.98% purity) substrates (size ~1×1.5 cm and 0.5 mm thick) were cut from a piece of Cu plate. The substrates were polished with a series of emery papers, followed by thorough rinsing in acetone and double distilled water and dried in air. Prior to any experiment, the substrates were treated as described and freshly used with no further storage.

The poly(*o*-ethylaniline) coatings were synthesized by electrochemical polymerization of *o*-ethylaniline on Cu substrates from aqueous salicylate solution using cyclic voltammetry. The electrochemical polymerization was carried out in a single compartment three electrode cell with Cu as working electrode (150 mm^2), platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. The cyclic voltammetric conditions were maintained using a SI 1280B Solartron Electrochemical Measurement System (U.K.) controlled by corrosion software (CorrWare, Electrochemistry/Corrosion Software, Scribner Associates Inc. supplied by Solartron, U.K.) [32]. The synthesis was carried out by cycling continuously the electrode potential between – 1.0 V versus SCE and 1.8 V versus SCE at a potential scan rate of 0.02 V/s. The number of cycles was varied from 1 to 25. After deposition the working electrode was removed from the electrolyte and rinsed with double distilled water and dried in air.

The FTIR transmission spectrum of poly(*o*-ethylaniline) coating was recorded in horizontally attenuated total reflectance (HATR) mode in the spectral range 4000–400 cm^{-1} using a Perkin Elmer spectrometer, 1600 Series II, U.S.A. The UV–visible absorption spectrum was recorded *ex situ* at room temperature in the wavelength range 300–1100 nm using microprocessor controlled double beam UV–visible spectrophotometer (Hitachi, Model U2000). SEM was employed to characterize the surface morphology with a Leica Cambridge 440 Microscope (U.K.).

The adhesion of the poly(*o*-ethylaniline) coating was determined by the standard sellotape test (TESA–4204 BDF)