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A study of the low temperature plasma polymerization on enhancing interface of painted cold rolled steel in salt bath

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Abstract

Enhanced corrosion protection of painted cold rolled steel (CRS) by low temperature plasma polymerization was investigated. It was found that the surface treatment on CRS prior to painting by plasma cleaning with hydrogen plasmas and then plasma coating by plasma polymerization with tetraethyl orthosilicate (TEOS) plasmas in room temperature (23 °C) can be used for improving the corrosion protection of painted CRS. Tape adhesion tests (ASTM 3359 Method) demonstrated this improvement, with a rating of “0” for untreated CRS for aging at 3.5% NaCl solution for 6 days and “5” for hydrogen plasma-cleaned and TEOS plasma-deposited CRS at certain plasma conditions even for aging at 3.5% NaCl solution for 10 days. The results of this study indicated the performance of corrosion protection on painted CRS was dependent on the surface characteristics of CRS, the wettability of CRS and the work of adhesion of paint to CRS. In this study, the work of adhesion of paint to CRS and the wettability of CRS were calculated from the surface free energy of paint and CRS. The surface free energy of paint and CRS were calculated by the contact angle measurement using sessile drop method, the surface characteristic such as surface morphology of CRS was monitored by atomic force microscopy (AFM) and the surface composition of CRS was characterized by using Electron Spectroscopy for Chemical Analysis (ESCA).

Keywords: Corrosion; Adhesion; PECVD; CRS; AFM; ESCA

1. Introduction

To prevent a coating layer delamination from the substrate during service, adhesion between a metal and a polymer such as paints and coatings is an important issue in the application of biomedical and electronic devices [1–8]. The pretreatment of metals before painting usually includes a phosphate conversion layer with a post rinse which has traditionally been an aqueous chromate solution [9,10]. However, chromate is considered toxic and carcinogenic. As a result, environmental regulations have prompted research and development of non-chromate pretreatment of metals. Extensive technologies such as in situ phosphating coatings [11], epoxy-silicone based coatings [12], organosilane coatings [13], parylene C coatings [14] and plasma-polymerized organosilanes [15–20] have been developed to treat steel surfaces for better corrosion protection by improving paint adhesion.

Plasma polymerization is essentially a plasma-enhanced chemical vapor deposition (PECVD) process resulting in the deposition of an organic polymer [21]. It refers to the deposition of polymer films through plasma dissociation and excitation of an organic monomer gas and subsequent deposition and polymerization of the excited species on the surface of a substrate. Plasma polymerization has been recognized as a new technology to make polymers that have high thermal and chemical stability and offer good adhesion to metal and polymer substrates [22,23]. The most important advantage of this technique over conventional methods may be that it is a dry process that consumes the minimum amount of effluents. From the viewpoint of environmental friendliness and recycling capability, the technique has significant merit as an alternative approach to protecting coated steel.

Conventional methods such as wet chemical etching, solvent degreasing and mechanical treatments tend to leave

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traces of materials used in the cleaning process on the cleaned surfaces [24–27]. Plasma cleaning of metals is a well-known process that effectively removes organic contaminants without leaving materials used in the cleaning process. In the present study, an attempt was made to use plasma cleaning combined with plasma-polymerized organosilanes in a reactor, replacing the series of conventional processes such as alkaline cleaning and phosphating in separate chambers, with totally dry and environmentally friendly processes.

Yasuda et al. [28] proposed the adhesion of a polymer to CRS was strongly affected by the surface morphology of CRS. In this study, the surface morphology of CRS was monitored by AFM for discussion on how to affect the corrosion resistance of painted CRS.

Wettability is a necessary criterion for adhesion of a liquid on a solid substrate [29]. The wetting of a surface can be described in thermodynamic terms. The surface tension of the coating in its liquid state and the surface free energy of both the substrate and the solid coating are important parameters which can influence the strength of the interfacial bond and adhesion development. The surface tension effects of the coating of paint in its liquid state and the solid state on the adhesion of paint to CRS were not discussed in this study because only one kind of paint was used. The work of adhesion for two phases was used to interpret how the dispersive and polar (non-dispersive) forces affect the interfacial strength of two phases [30]. In this study, the effects of work of adhesion of the substrate for CRS with paint by using various pre-treatments such as $Ar-H_2$ plasma cleaning and a combination of $Ar-H_2$ plasma cleaning and $TEOS-H_2$ plasma polymerization on the adhesion of paint to CRS were investigated.

Maeda [31] and Santagata et al. [32] showed that the adhesion of an organic coating to steel was strongly affected by the surface chemistry of CRS. In this study, the surface composition of CRS was monitored by ESCA to determine how it affects the corrosion protection of painted CRS.

In this study, how the surface characteristics such as surface morphology and surface chemistry of CRS, the wettability of CRS, and the work of adhesion of paint to CRS affect the enhancing corrosion protection of painted CRS was investigated. The enhancing corrosion protection of painted CRS was measured as the enhancement on the aging resistance on the adhesion of paint to CRS. The aging resistance on the adhesion of paint to CRS was determined by measuring the aged adhesion performance of paint to CRS after immersion in a 3.5 wt.% NaCl solution for 1–10 days. The adhesion performance of paint to CRS was evaluated using the ASTM 3359 tape adhesion test.

2. Experimental

2.1. Materials

A 1.6 mm thick and 50 mm × 50 mm wide CRS plate of JIS-G3101 SS41 was used for this study. The contents of elements such as P and S are all required to be less than 0.05% in SS41. The mechanical properties such as yield strength larger than 245 N/mm^2, tensile strength for 402–510 N/mm^2 and elongation larger than 21% for 5 tested pieces of SS41 are also stipulated. The thermosetting powder coating type of paint was used for spraying on cold rolled steel. The paint was composed of the powder of polyester, epoxy and pigment. The powder paint was sprayed on CRS and then melted to a liquid as it oven cured at 200 °C for 1.5 h. Then it was cooled down to room temperature (23 °C) and then solidified to a solid coating.

2.2. Equipment

The plasma cleaning of CRS was carried out in a low temperature glow discharge plasma chamber. Hydrogen and argon gases were fed into the reactor at a hydrogen flow rate of 0.5 sccm and an argon flow rate of 8 sccm. Other plasma settings were adjusted as follows: power at 200 W, chamber pressure at 60 mTorr and duration for plasma modification for 20 min. The pressure of the reactor chamber was decreased to less than 5 mTorr and with a pressure leak rate of less than 0.1 mTorr/min, i.e. the leak flow rate of air in the chamber is less than 1% of the flow rate of inlet gases such as hydrogen and argon. As the chamber pressure stabilized, radio frequency (RF) power was applied to create the hydrogen plasmas. After plasma cleaning, the RF power was turned off. Gases were pumped out and system pressure returned to background pressure (around 5 mTorr). The vacuum was broken by opening a valve to admit air into the chamber. Once the chamber pressure reached atmospheric pressure (typically within 5 min), the plasma-cleaned CRS was taken out for further treatment and testing.

After plasma cleaning, CRS is further coated with plasma-polymerized organosilicon by TEOS plasmas at a TEOS flow rate of 4 sccm and hydrogen flow rate of 0.5 sccm, with power of 200 W and duration at 1–5 min. The TEOS plasma-polymerized CRS was then taken out from the vacuum chamber for further treatment and testing.

2.3. Tape adhesion test

The corrosion protection of painted CRS was described by the aged adhesion performance of paint to CRS after immersed in 3.5 wt.% NaCl solution for 1–10 days. The adhesion performance of paint to CRS was evaluated using the ASTM 3359 tape adhesion test. The painted CRS samples were scribed with six cross-cuts with a knife before immersion in a 3.5 wt.% NaCl solution. The six parallel cuts were about 2 cm apart. Pressure-sensitive tape (Permacel #99) was applied to the surface over the cross-cut area and then removed, and the amount of paint removed served as the measure of adhesion. Ratings ranged from “0” to “5”, depending upon the number of squares left. The classification of adhesion test results is “0” when greater than 65%