Applied Surface Science 387 (2016) 252–259

Contents lists available at ScienceDirect

Applied Surface Science

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

Titanium composite conversion coating formation on CRS In the presence of Mo and Ni ions: Electrochemical and microstructure characterizations

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ARTICLE INFO

Article history:
Received 23 April 2016
Received in revised form 29 May 2016
Accepted 16 June 2016
Available online 18 June 2016

Keywords:
Ti-based conversion coating
Nickel
Molybdate
EIS
XPS
Corrosion

ABSTRACT

There have been an increasing interest in finding a replacement for the chromating process due to environmental and health concerns. Hence, in this study Chrome-free chemical conversion coatings were deposited on the surface of cold-rolled steel (CRS) on the basis of Titanium (TiCC), Titanium-Nickel (TiNiCC) and titanium-molybdate (TiMoCC) based conversion coating solutions. The surface characterization was performed by field emission scanning electron microscope (FESEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and contact angle measuring device. Also, the corrosion behavior was assessed by the means of potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. FESEM and AFM study show that the TiNiCC is denser and more uniform than that TiCC and TiMoCC since, TiMoCC conversion coating presents network feature, and there were abundant micro-cracks on the surface of the coating. XPS results confirmed the precipitation of Ti and Ni oxide/hydroxide, Mn dioxide/trioxide on the surface of different Ti-based conversion coatings. Electrochemical results revealed that all Ti-based conversion coatings have better anti-corrosion properties than bare CRS. Moreover, TiNiCC treatment inhibited the corrosion of CRS to a significant degree (polarization resistance (R_p) = 5510 Ω cm^2) in comparison with TiCC (R_p = 2705 Ω cm^2) and TiMoCC (R_p = 805 Ω cm^2).

1. Introduction

Corrosion is known as the destruction of materials due to interaction with corrosive environment [1]. Metals are used extensively in modern society in a range of applications from infrastructure to aircraft to consumer products. The protection of metals, primarily from corrosion, has been an active area of materials science for many years. Cold Rolled Steel (CRS) provides excellent press formability, surface finish, thickness and flatness tolerances. Steel producers use various organic and inorganic coatings to protect cold-rolled steel (CRS) sheets from corrosion during shipment and storage. Some coatings are designed to retard corrosion by controlling the electrochemistry, while others such as conversion and organic coatings create physical barriers to retard the corrosion rate in an oxidizing environment.

Conversion coatings are inorganic thin films (some conversion coatings also contain organic compounds as an additive) formed on the surface of metals and alloys by the reaction of the metal with baths of specific chemical composition [2]. The conversion coating provides corrosion protection and improves adhesion between the substrate and the second layer of the organic coating system [3]. Even though, the chromate based conversion coatings offer a very good initial adhesion with organic finishes, Cr^{+6} is known to be carcinogen. Moreover, its compounds are hazardous for environment and costly to be eliminated as waste products [4–7]. In fact, it is known that hexavalent chromium can cause lung cancer in humans as a result of inhalation exposure in certain occupational settings. Hexavalent chromium was recognized as a known carcinogen by the World Health Organization (WHO) and by the U.S. Environmental Protection Agency (EPA) but it is also toxic and can lead to allergic contact dermatitis as a result of direct skin exposure to powders or liquids containing hexavalent chromium [8,9]. In addition, Cr^{6+} has a high oxidizing potential and, thus, it is also dangerous for the environment.

Given the environmental and toxicity problems associated with the use of chromate-type conversion coating systems, there has been a thrust to use non chromium processes, i.e. zirconium

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http://dx.doi.org/10.1016/j.apsusc.2016.06.095

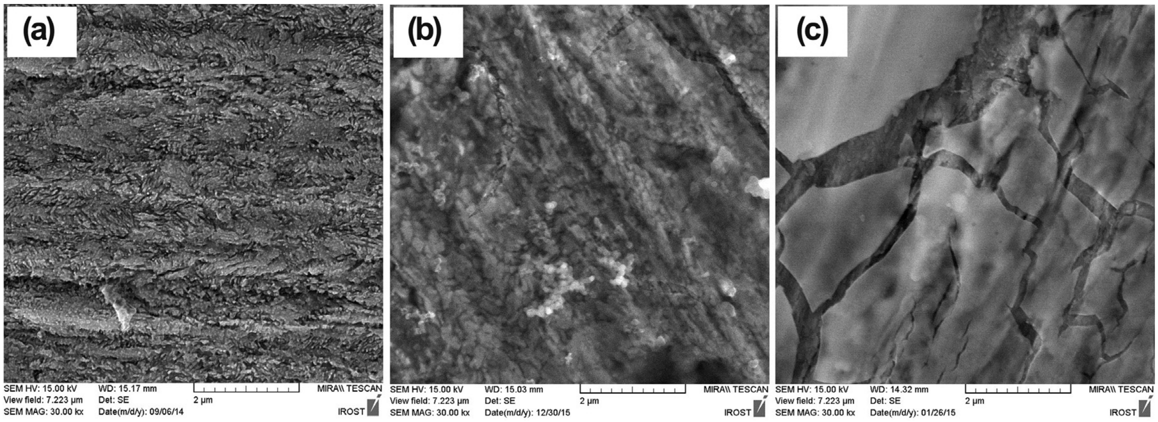

Fig. 1. FE-SEM images for samples treated in Ti-based (a), TiNi (b) and TiMo (c) conversion coatings.

[10–16] or titanium-containing systems [17–19], cerium [20–22], Lanthanum [23], Vanadium [24], molybdenum [25–27] systems.

Chromate-free treatments based on fluorotitanic acid are shown to be reliable alternatives to Cr(VI)-containing ones. Particularly, the greater chance of achieving promising Chromate-free conversion coatings comes with solutions based on titanium or zirconium compounds. Titanium-based conversion coatings performance regarding corrosion protection and adhesion were comprehensively studied when applied on aluminum alloys [28–34] and galvanized steel substrates [35,36]. Nonetheless, there is no available report providing their efficiency on cold rolled steel (CRS) substrates.

The effect of additives presence in conversion bath on the properties of the resulted coating was studied mostly for crystalline coatings [37–39]. However, some researchers have proposed the addition of some metal ions to amorphous conversion coatings [40–42]. Wilson et al. [36] found that the manganese (II) phosphate present in the Ti-based solution increases the coating deposition rate while the organic components increase resistance to the aggressive action of chloride ions. Lostak et al. [42] indicated that there is a significant film thickness increase by adding Cu^{2+} or Fe^{3+} ions to the modified zirconium oxide conversion layer applied on HDG steel substrates.

The current study aims to investigate the formation of the Ti-based conversion layer on CRS substrate using Cr-free surface treatment mainly composed of titanium chloride ($TiCl_4$) and modification in the presence of sodium molybdate (Na_2MoO_4) or nickel sulphate ($NiSO_4$). The effect of Mo and Ni ions presence on surface morphology and electrochemical behavior of Ti-based conversion coating applied on CRS substrate was studied utilizing FE-SEM/EDS, AFM, XPS, contact angle, EIS and DC Polarization.

2. Materials and methods

The material used in this research for evaluating the performance of novel environmentally friendly conversion coatings was CRS, which was supplied in the form of sheets with 40 mm × 20 mm × 0.7 mm dimensions. The CRS was obtained from Dongbu Company. The composition of the CRS in wt% was listed as following: 0.002% C, 0.009% P, 0.006% S, 0.04% Mn, 0.03% Al, and balanced Fe. Mechanical pretreatment was performed on the substrates using 400, 800 and 1200 grit SiC polishing papers followed by a washing and cleaning step by deionized (DI) water. Afterwards, 10 wt.% KOH solution and acetone were used to make the substrates ready for immersion. The constituents of the conversion solutions ($TiCl_4$, Na_2MoO_4, $NiSO_4$, DI water and pH adjusters) are provided in Table 1. pH adjustment of the solutions was performed with hydrochloric acid (HCl) and sodium hydroxide (NaOH). After the conversion process also, samples were washed with deionized water. It should be noted that after optimizing the Ti-based conversion solution on the basis of our previous research: (pH = 2), (Ti concentration = 1 g/lit), (immersion time = 5 min) and (temperature = 25 ± 2 °C) [18], Mo and Ni ions were added to Ti-based solution with different concentrations. In each concentration the effects of immersion times and solution pH on anti-corrosion performance were investigated by EIS, DC polarization and FESEM techniques. Example of optimization for TiMoCC sample could be found in supplementary file (Figs. S1–3).Consequently, regarding electrochemical results the best TiMoCC and TiNiCC samples were selected for further studies.

Table 1
Details about sample's designations and the composition of the corresponding conversion solutions. "Bare" designates the non-treated CRS sample.

Sample\Components	$TiCl_4$ (gr/lit)	Na_2MoO_4 (gr/lit)	$NiSO_4$ (gr/lit)
TiCC	1	–	–
TiMoCC	1	1	–
TiNiCC	1	–	1
Bare	–	–	–

A Scanning Electron Microscope (TESCAN, Model VEGAII) equipped with an Energy dispersive X-ray spectrum (Model RONTEC, QUANTAX Software) was utilized for morphological evaluation. The former was used to obtain surface morphology and the latter was used to provide information about micro-zone composition.

X-ray Photoelectron Spectroscopy was conducted on the conversion coatings in order for the chemical composition to be determined (Model X-Ray 8025-BesTec). All spectra were obtained using a monochromated Al Kα beam. The take-off angle of the detected photoelectrons was 45° with respect to the surface normal. The CasaXPS and xpspeak software performed the analysis.

Electrochemical analysis by AUTOLAB PGSTAT 302 N EIS instrument was carried out at room temperature (25 ± 2 °C) where frequency range was selected to be 10 kHz to 10 mHz and the perturbation amplitude was 10 mV with respect to the open circuit potential (OCP). Hot melt mixture of bees wax and colophony was used to expose a defined area of 1 cm^2 to the test solution (3.5 wt% sodium chloride solution (100 ± 2 mL)). The conventional three-electrode set up was used where the working electrode was the specimen, a platinum rod was served as the counter electrode and Ag/AgCl was the reference electrode. Obtained data were analyzed with Nova 1.8 software. The potentiodynamic polarization curves were acquired by polarizing the samples in the range of −200 mV up to +200 mV with respect to the open circuit poten-