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Development of chemical conversion coating technology by environment friendly method for Zn electroplated steel

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Abstract : Zinc confers high corrosion resistance by acting as a sacrificial anode, and a zinc coating improves the appearance of steel. Chromate conversion coating (CCC) films are still one of the most efficient surface treatments for steel. Although such films can self-repair via the dissolution of Cr(VI), dissolved Cr(VI) have adverse effects on humans, and the environment. Therefore, we examined the corrosion protection property and morphology of colloidal silica conversion films as an alternative to CCC films. The corrosion behavior was investigated in 3% NaCl solution using electrochemical techniques, including electrochemical impedance spectroscopy, open circuit potential, and the salt spray test (SST). Corrosion was implied by the appearance of red rust on the specimen surface. In corrosion resistance at 3% NaCl solution, red rust appeared at 15-20, 55-70, and 83-98 days on Zn-electroplated steel, colloidal silica conversion-coated specimens, and CCC-coated specimens, respectively. In the salt spray test, the colloidal silica film provided better corrosion protection than CCC films, *i.e.*, red rust appeared at 96 hours on the Zn-electroplated steel sheet, at 432 hours with the CCC films, and at 888 hours with silica conversion coating.

Key words : Corrosion Protection Property, Colloidal Silica, Chemical Conversion Coating, Electrochemical Impedance Spectroscopy, Open Circuit Potential, Salt Spray Test

1. Introduction

With the heightened awareness of the need to protect terrestrial environments, strict regulations have been enacted governing the discharge of harmful matter that might cause environmental pollution. The regulations governing chromium, especially Cr(VI), are strict. The Water Pollution Control Law in Japan mandates that Cr (VI) emissions must be below 0.5 mg/L, since Cr(VI) is carcinogenic, and in drinking water, the concentration must be below 0.05 mg/L.[1] According to the pollutant release and transfer resister (PRTR) system and the environmental contaminant discharge movement quantitative register, the amount of Cr(VI) used must be decreased.[2] Since some countries have limited the amount of Cr(VI) used to 5 g per automobile after the year 2002, automobile manufactures hope to use chromium-free conversion, which does not use Cr(VI), in new designs.[3-5] In addition, to conserve resources and energy, it is necessary to develop a new surface finishing method to solve these problems. Therefore, we studied a new non-chromate-type chemical conversion coating method[6], and considered its environmental impact, using Zn-electroplated steel sheets coated with colloidal silica that contains silicon dioxide as the main component.

2. Experimental Section

The Zn-electroplated steel sheets (10 ×5 cm) used for chemical conversion coating were cleaned with acetone at 298 K, and the zinc surface was activated using 2 wt% nitric acid solution. Each sheet was masked with tape, except for a 24-cm^2 area (6 ×4 cm). After cleaning with water, the specimen was immersed in the chemical conversion coating solution for 90 sec with agitation. The standard conversion solution contained colloidal silica (Snowtex, Nissan Chemical Industries Ltd.) consisting of 10 - 20 nm SiO_2 particles at a concentration of 200 mM together with 4.2 mM $Ti(SO_4)_2$, 1.8 mM $CoSO_4$, and 4.2 mM $C_2H_4(COOH)_2$. Then, it was washed with water, and dried with warm air at 353 K for 5 min. The film that formed on the Zn-electroplated steel sheet was 7~8 μm thick.

Frequency response measurement equipment (FRA, Solartron: SI 1260) and a potentiostat (Solartron: SI 1287) connected to a personal computer using a GPIB interface were used to examine the specimens. The corrosive solution used was 500 ml of 3 mass % NaCl solution. To keep the dissolved oxygen concentration in the corrosion solution uniform, it was bubbled with air. The dissolved oxygen concentration of the corrosive solution during the experiment was 7.5~8 ppm. The impedance experiment used the bipolar method with a counter and working electrodes. Measurements were made at an applied voltage of 10 mV over a frequency range of 10 kHz to 10 mHz, at 10 points per

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decade (per column). The temperature of the corrosive solution was maintained at 303 K, and the corrosion resistance value (R_{ct}) was measured for 8 days.

The surface morphology of the chemical conversion coating was observed using an optical microscope (Olympus SZX12) and SEM (Hitachi S-800), and Fourier transform IR spectroscopy (FT-IR). The zeta potential test was carried out at an applied potential of 50 V. In total, 200 particles were measured. The range of potentials from -100 to +100 mV was divided in 10mV sections. The number of silica particles present in each section was measured. Then, average values were obtained, which followed a normal distribution.

The salt spray test (SST) was conducted using the method outlined in JIS H8502, paragraph 7. The SST was carried out at a spray rate of 1.5 ± 0.5mL(h • 80cm^2) The corrosive solution was 3 mass % NaCl, pH 6.5~7.2. The temperature of the corrosive solution was 303 K ; the humidity was at least 98% ; and the spraying was continuous. Four specimens were tested : Zn-electroplated, silica chemical conversion-coated, silica chemical conversion-coated with poly-vinyl alcohol (PVA) in the coating solution, and chromate chemical conversion (CCC)-coated steel sheets. The presence of rust was defined using the criteria in JIS H8502 paragraph 11. To identify white rust, the corroded area of the specimen surface was compared with a standard diagram. The area of corrosion was expressed as the percentage of the specimen area. The time at which red rust was seen on the specimen surface was also recorded.

3. Conclusions

Zeta-potential and FT-IR measurements indicate that colloidal silica containing sulfuric acid titanium forms Si-O-...Ti^{4+} bonds. The Ti^{4+}shifts the surface electric charge of the colloidal silica from negative to positive. The formation of red rust on Zn-electroplated, silica-coated, and silica-coated specimens with PVA immersed in 3 mass % NaCl took 15-20, 55-70, and 75-80 days, respectively. In the salt spray test, the silica coating was more resistant to red rust formation than CCC, which was the opposite of the electrochemical evaluation. Red rust formed after 432, 888, and 1444 hrs on the CCC-coated, silica-coated, and silica-coated with PVA specimens, respectively. Silica chemical conversion coating appears to have a high barrier function.

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