Surface & Coatings Technology 219 (2013) 42–49

Contents lists available at SciVerse ScienceDirect

Surface & Coatings Technology

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

Effect of curing temperature on coating structure and corrosion resistance of ammonium zirconium carbonate on galvanized steel surface

Ryosuke Sako [a,*], Jun'ichi Sakai [b]

[a] Central Research Laboratories Nihon Parkerizing Co., Ltd., 2784,Ohkami, Hirutsuka, 254-0012 Japan
[b] Faculty of Science and Engineering Waseda University 3-4-1, Okubo, Shinjuku-ku, Tokyo, 169-8555 Japan

ARTICLE INFO

Article history:
Received 21 October 2012
Accepted in revised form 31 December 2012
Available online 11 January 2013

Keywords:
Chrome free
Corrosion
Conversion coating
TG–DTA
IR
Galvanized steel

ABSTRACT

The effect of curing temperature on the structure and corrosion resistance of an ammonium zirconium carbonate (AZC) coating on galvanized steel was investigated as an alternative to chromate. The corrosion resistance of the AZC coating was excellent when cured at 80 °C, but it decreased with an increase in the curing temperature; it was significantly inferior at curing temperatures over 160 °C. Two endothermic events were observed at 115 °C and 155 °C. The event at 115 °C resulted from the elimination of the water molecule coordinated to the zirconium atom, and the event at 155 °C resulted from the dehydration condensation of the hydroxide group involved in the bonds between zirconium, i.e., conversion of an ol-bridge to an oxo-bridge. Furthermore, it was observed that the cathode current of the coating plate cured at 160 °C or 200 °C, whose corrosion resistance was inferior to that at 80 °C or 120 °C in the salt spray test, increased. It is supposed that the dehydration occurring at 155 °C promoted shrinkage of the coating volume, which in turn caused the development of fissures on the coating surface. The fissures on the coating surface reduced the corrosion resistance significantly due to the increase in cathode current, which signifies the reduction of dissolved oxygen at the coating/metal interface.

1. Introduction

Most galvanized steels used in household electrical appliances are provided with chemical conversion treatment for rust prevention or paint adhesion. Chromate coatings containing hexavalent chromium salts have accounted for high market results as the conversion coating due to its superior corrosion resistance, and this coating has been applied on galvanized steel for many years [1–3]. In July 2006, the European Union (EU) instituted the Restriction of Hazardous Substances (RoHS), which prohibits the use of hexavalent chromium in EU countries owing to its carcinogenic nature. Many leading consumer electronics manufacturers have prohibited the use of not only hexavalent chromium compounds but also any other valence chromium compounds capable of converting to hexavalent compounds under the usage environment.

Over the past decade more alternatives for chromate such as cerium hydroxide [4], organosilicates [5], molybdates [6], and phenolic resins [7] have been examined and some of them have already been commercialized. These development trends and their functions have been reported by Moriya [8], Fujita [9] and Karube et al. [10].

Ammonium zirconium carbonate $(NH_4)_2[Zr(CO_3)_2(OH)_2]$ (denoted as AZC) has been applied as a crosslinking agent for water-soluble polymers in industry, and its structure in aqueous solutions has been reported by McAlpine [11].

The authors examined an inorganic film formed from AZC aqueous solution to apply onto galvanized steel surface as an alternative to chromate. Some patents regarding surface coating based on AZC have been published [12–14] and some of these coatings have been commercialized as an alternative to chromate for galvanized steel. However, there is no academic paper described the mechanism of the structure and corrosion resistance of the AZC coating. It is important to figure out the mechanism of structure and corrosion resistance of AZC coating film itself for future development of chromium free coating.

This paper describes the influence of curing temperature on the structure and corrosion resistance of the AZC film applied from an aqueous solution onto galvanized steel.

2. Material and methods

2.1. Sample preparation

The strip thickness of the electrogalvanized (EG) steel used, which is specified in JIS SECC E16, was 0.6 mm and the thickness of the EG coating was 2.8 μm (20 g/m^2 of Zn). The substrate plates were degreased by an alkali cleaner. They were then coated with the AZC aqueous solution (5 wt.% of Zr) using a bar coater and cured at different test temperatures (80 °C, 120 °C, 160 °C, and 200 °C) in the oven.

* Corresponding author. Tel.: +81 463 55 4431.
E-mail address: rsako@parker.co.jp (R. Sako).

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http://dx.doi.org/10.1016/j.surfcoat.2012.12.050

An aqueous solution of ammonium dichromate (5 wt.% of Cr) was adopted as a comparison and applied onto the surface of galvanized steel. The curing temperature was 80 °C.

The process and conditions for treatment are described in Table 1. The weights of the Zr coating and Cr coating were measured by fluorescence X-ray analysis.

2.2. Corrosion test

The plates, whose edges were covered with corrosion-protective tape, were subjected to a salt spray test (SST) following the JIS Z 2371 procedure. The white rust areas of the panels were estimated and displayed as a percentage after 12 h or 24 h of exposure in the SST. The appearances of the panel surfaces were photographed.

2.3. Analysis

2.3.1. Thermogravimetry and differential thermal analysis (TG–DTA) of AZC

TG–DTA (Seiko Instruments Inc., TG–DTA320) measurements of 20 mg of the dried solid, which was obtained by vacuum-drying the AZC aqueous solution at 30 °C, were performed by using differential thermal analysis. The analyses were carried out twice, 25–1000 °C and 25–250 °C, in a mixture of N_2 and air, respectively, with a flow rate of 100 ml/min. The temperature increase rates were 10 °C/min and 5 °C/min, respectively.

2.3.2. Morphology and characterization of coatings

The morphology of the coatings on the plates was observed using scanning electron microscope (SEM), and the coatings on the plates were characterized by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR). The measurement conditions were as follows:

(1) SEM — JEOL Ltd. SEM (JSM-6460) was used to observe the coating morphology.
(2) XPS — Shimadzu Co. XPS system (ESCA-850) was used for the depth analysis of Zr(3d), Zn(2p), and O(1s). Excitation acceleration voltage: 8 kV, Ar etching (acceleration voltage 0.6 kV), sputtering rate: 53.5 nm/min (Si equivalent), X-ray sources: Mg Kα, sample size: 8 mm diameter.
(3) FT-IR — JASCO Corporation FT-IR (610 type) was used to obtain data about the structure of the coating film structure on the substrate.

2.3.3. Polarization measurement

Polarization measurements of the coating plates were carried out at room temperature in 5 wt.% NaCl aqueous solution using a potentiostat (Hokuto Denko Co., Ltd. HZ-3000) under an open system.

Other conditions were as follows:

Reference electrode: Ag/AgCl electrode (saturated KCl solution), counter electrode: Pt, measurement area: 1 cm^2, sweep rate: 1 mV/s.

Table 1
Treatment process and conditions.

	Process	Treatment	Condition
1	Degrease	CL-N364S[a](20 g/l)	Spray (60 °C,10 s)
2	Water rinse	Tap water	Spray (R.T.,10 s)
3	Roll squeeze	–	–
4	Drying	Blower	–
5	Coating	AZC solution(5 wt.% as Zr)	Bar coat
6	Curing	Oven	80–200 °C[b]

[a] Alkali type degrease (Nihon Parkerizing Co.,Ltd.).
[b] Peak temperature of the metal surface.

3. Results

3.1. Effect of curing temperature on corrosion resistance

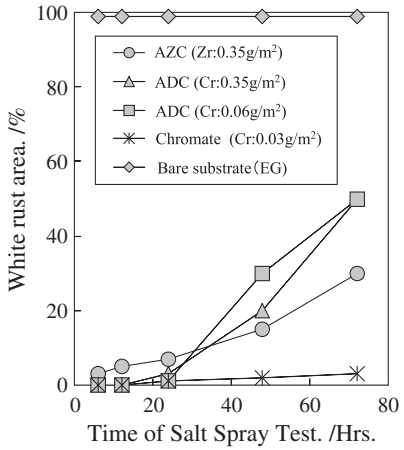
The corrosion resistance of AZC coating was shown in Fig. 1 along with the bare substrate (EG) and chromate coating. Ammonium dichromate (denoted as ADC) which is one of the raw materials of a chromate coating solution was adopted in order to simply compare with AZC as a raw material. On the almost whole surface of the bare substrate white rust was observed after just 3 h salt spray test. Ammonium dichromate (denoted as ADC) coatings showed the almost same good performance regardless of the coating weight. It was observed that the coating weight after 12 h salt spray test was reduced to be about 0.02 g/m^2 (as Cr) regardless of the initial coating weight (0.35 g/m^2 or 0.06 g/m^2), because the chromate except for the reaction layer at the surface of the substrate would be readily dissolved by brine spray.

On the other hand no decrease of AZC coating weight was observed after salt spray test. Therefore it is supposed that AZC coating could maintain good corrosion resistance. Typical commercialized chromate usually is consist of the chromic chromate (reduced chromate containing Cr^{3+}), silica, and inorganic acid such as nitric acid or phosphoric acid. Corrosion resistance of such a typical conventional chromate was also shown in Fig. 1. It can be seen that the high performance is sustainable because the coating film is not readily dissolved.

The corrosion resistance of AZC coatings, whose zirconium coating weight varied from 0.10 to 0.50 g/m^2, is described in Fig. 2. As can be seen from the figure, the AZC coating achieved excellent corrosion resistance above a zirconium coating weight of 0.30 g/m^2. Fig. 3 shows the corrosion resistance of the AZC coating with a zirconium coating weight of about 0.30 g/m^2 cured at temperatures of 80 °C, 120 °C, 160 °C, and 200 °C. It can be seen from these results that the curing temperature of the coating film affects the corrosion resistance. After an SST of 24 h, the film cured at 80 °C gave good performance, while the white rust area was under 5%. A little amount of white rust (20%) was observed in the film cured at 120 °C, and a significant amount of white rust (over 80%) was observed in the films cured at 160 °C and 200 °C.

3.2. Coating surface morphology

SEM images of the coating surfaces are shown in Fig. 4. A significant number of fissures in the coating surfaces cured at 160 °C and 200 °C were observed.



AZC: Ammonium Zirconium Carbonate
ADC: Ammonium Dichromate
Chromate: Conventional (Dry-in-place type)[10]

Fig. 1. Effect of zirconium coating weight on corrosion resistance (curing temperature: 80 °C).