Effects of Chromate Coating on Solder Wettability of Electrogalvanized Steel Sheet

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Two types of chromate coatings were investigated to assess solder wettability of electrogalvanized steel in this study, namely coatings by a plain chromate (CrO_3) solution and a CrO_3 solution containing triethanolamine. While the plain chromate solution provided poor solder wettability, the coatings by CrO_3 -triethanolamine solutions showed remarkably improved solder wettability.

It can be considered that the addition of triethanolamine prevents the formation of an insoluble zinc-chromate complex compound and facilitates the contact between zinc layer and the solder.

1 INTRODUCTION

Sn and Pb-Sn plated steel sheets have been widely used as solderable outer-packaging materials for electric appliances. However, recently short-circuiting due to growth of Sn whiskers and negative influences of Pb on the environment associated with conventional solderable sheets have become increasingly serious problems. Therefore, solderable electrogalvanized steel has been developed in replacement of Sn and Pb-Sn plated steel¹⁻³.

In general, the surface of electrogalvanized steel is coated with a chromate post-treatment layer for corrosion resistance^{4,5}. A chromate layer deteriorates solderability, since Cr is a difficult to solder⁶. Then, it is required to devise a chromate coating in which both corrosion resistance and solderability can be simultaneously satisfied.

In this report, we examined a triethanolamine ($(\text{CH}_2\text{CH}_2\text{OH})_3\text{N}$: 2,2',2''-Nitrilotriethanol) added chromic acid (CrO_3 :chromium (vi) oxide) solution as

a chromate post-treatment solution. Triethanolamine is a rust-preventive agent and is used as an element of solder fluxes for Al, Ag and Zn^{7,8}.

2 EXPERIMENTAL

2.1 Specimens

As a base steel, cold rolled steel sheets with thickness of 0.5mm and surface roughness (Ra) of $0.52 \mu\text{m}$ used in this study. Table 1 shows the chemical composition of the steel.

Table 1 Chemical composition of base steel. (mass%)

C	Mn	P	S	Fe
0.05	0.34	0.013	0.015	bal.

As shown in Table 2, the sheets were degreased in a NaOH solution at 60 °C rinsed in water, and pickled in a H_2SO_4 solution at 25 °C. After a rinse in water again, the sheets were galvanized with coating weight of 10 gm^{-2} .

As the chromate post-treatment solution, two types of chromic acid solutions were prepared. One was a CrO_3 solution (plain chromate solution), and the other was a CrO_3 -triethanolamine solution. The galvanized sheets were rinsed in water and dipped into the chromic acid solutions for 2 seconds.

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Table 2 Processes and conditions for Zn-electroplating.

Processes	Solutions	Conditions
1. Degreasing	NaOH : 20 g l ⁻¹	Temp. : 60 °C Current Density : 5 Adm ⁻² Time : 10 sec
2. Pickling	H ₂ SO ₄ : 70 g l ⁻¹	Temp. : 25 °C Immersing Time : 10 sec
3. Zn-electroplating	ZnSO ₄ ·7H ₂ O : 250 g l ⁻¹ (NH ₄) ₂ SO ₄ : 30 g l ⁻¹	pH : 2.5 ~ 3 Temp. : 45 °C Current Density : 20 Adm ⁻² Coating Weight : 10 gm ⁻²

Fig. 1 Schematic description of cross-section of specimens.
(a) coating by plain chromate (CrO₃) solution
(b) coating by CrO₃-triethanolamine solution

After that, the specimens were rinsed in water for 10 seconds and then dried. Figure 1 showed a schematic description of cross-section of the chromated specimens.

2.2 Solder wettability

Solder wettability was evaluated by wetting time of the specimens in solder by means of Meniscograph Tester (SOLDER CHECKER, MODEL SAT-2000 by RHESCA Co., Ltd.)^{9,10)}.

The specimens were immersed into a molten solder bath (JIS 3282 H60A : Sn-40mass%Pb alloy at 250 °C at a speed of 2 mmsec⁻¹, then held at the depth of 2 mm from the bath surface for 10 seconds, then removed from the bath. The time until the force acting upward recovered to neutral was defined as wetting time.

2.3 Corrosion resistance

To evaluate corrosion resistance of the chromated specimens, a salt spray test (JIS Z 2371) was carried out for 1 cycle (8 hours spray and 16 hours no spray).

And the degree of red rust occurrence was rated in 10 grades (from the best 10 to the worst 1) based on rating-number by JIS Z 2371.

2.4 Surface analyses

Zn coating weight and Cr content in the chromate layers were measured by a fluorescent X-ray analysis (X-ray Spectrometer : Rigaku ; RIX3000).

Amount of Cr deposited on the zinc surface was expressed by the atomic concentration measured by XPS (X-ray Photoelectron Spectroscopy : PERKIN ELMER ; PHI 5100 ESCA SYSTEM).

The depth profiles of Zn and Cr concentrations were determined by GDS (Grow Discharge Lamp Spectrometer : Shimadzu Co., Ltd. ; GDLS-5017).

3 RESULTS AND DISCUSSION

3.1 Dilute chromic acid solution

3.1.1 Coating by plain chromate (CrO₃) solution

At first, the solder wettability was investigated at a very dilute CrO₃ range below 10 × 10⁻² g l⁻¹. Figure 2 shows solder wettability of coating by a plain chromate solution as a function of chromium (vi) oxide concentration in the post-treatment solution.

Before soldering, two kinds of solder fluxes were applied on the specimens. One was a mildly activated rosin flux (RMA flux, none chloride) and the other was an activated rosin flux (RA flux, chloride : 0.14%)¹¹⁾. When the RMA flux was used, the solder wettability extremely deteriorated and the wetting time rapidly reached the measurement limit of 10 seconds at a CrO₃ concentration of 1 × 10⁻² g l⁻¹. Gradual deterioration of the wettability with increasing chromium oxide concentration was observed for the RA flux.

Fig. 2 Effect of CrO₃ concentration in post-treatment solution on solder wettability.

Fig. 3 Cr concentration in coated layer as a function of CrO_3 concentration in post-treatment solution.

Plain chromate solutions resulted in poor solder wettability even in very low CrO_3 concentrations. Figure 3 shows the chromium concentration on the zinc surface measured by XPS. The chromium existing on the zinc surface increased with increasing chromium oxide concentration in the post-treatment solution. Thus, it can be considered that the deterioration of the solder wettability was largely due to the amount of chromium deposited on the zinc layer.

3.1.2 Coating by CrO_3 -triethanolamine solution

Instead of plain chromate solutions, CrO_3 -triethanolamine solutions were examined as the chromate treatment to improve the solder wettability.

Figure 4 shows the solder wettability of coating by CrO_3 -triethanolamine solutions as a function of triethanolamine concentration in the post-treatment solution. The additions of triethanolamine to the $10 \times 10^{-2} \text{ gl}^{-1}$ CrO_3 solution were from 0 to 20 gl^{-1} . The RMA flux which exhibited a dependence of effectiveness on chromium oxide concentration as shown in Fig. 2 was used for the measurements. The wetting time of the coating is less than 2 seconds for the triethanolamine concentration higher than 3 gl^{-1} . Thus, coatings by CrO_3 solutions containing triethanolamine can remarkably improve the solder wettability of electrogalvanized steel.

Zn and Cr concentration depth-profiles of the coated layers by GDS are shown in Fig. 5. In the case of the coating layer by a plain chromate solution, a sharp peak of the chromium concentration was

Fig. 4 Effect of triethanolamine addition to post-treatment solution on solder wettability.

Fig. 5 Zn and Cr concentration profiles of coated layer measured by GDS. Coating was performed by (a) plain chromate solution and (b) CrO_3 -triethanolamine solutions, respectively.

clearly observed in the vicinity of the surface of the Zn plating. This Cr concentration indicates the formation of insoluble zinc-chromate complex compounds¹²⁾ by a chemical reaction between chromic acid and zinc.

On the contrary, in the case of the coating layers produced by CrO_3 -triethanolamine solutions, the peak height of chromium gradually decreases with increasing triethanolamine concentration due to suppression of zinc-chromate complex compound formation.

Based on these results, it is speculated that a zinc-chromate complex compound can be readily formed by a plain chromate solution and hinders solder infiltration toward the zinc layer. Poor solder wettability can be attributed mainly to the compound

formation. Additions of triethanolamine to a chromate solution suppress a reaction of zinc and chromate and compound growth, resulting in largely improved solder wettability.

3.2 Post-treatment for practical applications

(Use of concentrated chromic acid solution)

A small amount of chromium about $1 \times 10^{-3} \text{ gm}^{-2}$ or less on the electrogalvanized steel sheet, which can not be detected by fluorescent X-ray analyses, significantly deteriorates solder wettability. It is practically known that the thicker the chromate coating, the better the corrosion resistance. Thus, the effects of the chromate coating by a CrO_3 -triethanolamine solution on solder wettability and corrosion resistance were investigated for chromium amounts from 0 to $10 \times 10^{-3} \text{ gm}^{-2}$ as shown in Fig. 6. The specimens were coated by concentrated chromic acid solutions with a #3 bar coater. The amount of the addition of triethanolamine was 20 gl^{-1} .

Although the solder wettability of the coating by the CrO_3 -triethanolamine solution deteriorated gradually with increasing chromium amount in the chromate layer, the wetting time was less than 2 seconds up to a chromium amount of $3 \times 10^{-3} \text{ gm}^{-2}$. Chromated specimens with chromium amount more than $3 \times 10^{-3} \text{ gm}^{-2}$ exhibited excellent corrosion resistance.

It was considered that an insoluble zinc-chromate complex compound formed by a chemical reaction between chromic acid and zinc in a plain chromate solution, rapidly grows and covers zinc surface, preventing the contact between zinc layer and the solder during soldering.

On the other hand, in CrO_3 -triethanolamine solutions, triethanolamine absorbed to zinc layer and chromium oxide can be considered to inhibit the direct chemical reaction between chromic acid and zinc, leading to suppression of zinc-chromate complex compound formation. This may facilitate the contact between zinc layer and the solder during soldering. Concerning the corrosion resistance, it can be assumed that sufficient amount of unreacted chromium oxide exists in the post treatment layer. Thus, when the chromated specimens were exposed to a corrosion environment, Cr^{6+} oxide ions with a high redox potential exhibit a protective action,

Fig. 6 Solder wettability and corrosion resistance as a function of Cr coating weight. (a) coating by plain chromate solution (b) coating by CrO_3 -triethanolamine solution (coated with a #3 bar coater)

so-called self-healing^{13,14}, to the zinc surface, making a significant improvement of solder wettability and corrosion resistance simultaneously.

4 CONCLUSIONS

A chromate coating by a plain chromate solution extremely deteriorated even at a very low CrO_3 concentration.

On the other hand, chromate coatings by CrO_3 -triethanolamine solutions showed remarkably improved solder wettability.

It can be considered that triethanolamine added to chromic acid solutions prevented an insoluble zinc-chromate complex compound formation.

As a result, the contact between the zinc and the solder was enhanced during soldering, resulting in significant improvement of the solder wettability.

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