

Development of Trivalent Chromium Passivation for Zn Plating with High Corrosion Resistance after Heating

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ABSTRACT

Trivalent chromium passivation is used after zinc plating for enhancing corrosion resistance of parts. In the passivating process, the amount of dissolved metal ions (for example zinc and iron) in the passivation solution increases the longer the solution is used. This results in a reduced corrosion resistance at elevated temperatures. Adding a top coat after this process improves the corrosion resistance but has an increased cost. To combat this, we strove to clarify the mechanism of decreased corrosion resistance and to develop a trivalent chromium passivation with a higher corrosion resistance at elevated temperatures.

At first, we found that in parts produced from an older solution, the passivation layer has cracks which are not seen in parts from a fresh/new solution. These cracks grow when heated at temperatures over 120 degrees Celsius.

Next we researched the reason for cracks to occur and found that the main difference between an old and new solution's layer is the amount metal deposits in it. These metal ions deposit into the passivation as hydroxides, and the larger the quantity in this layer the more the layer contracts by heating, meaning the newer the solution the less the layer contracts.

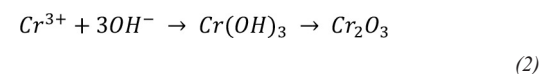
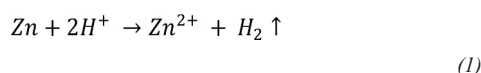
So, we investigated developing a new solution to improve the corrosion resistance after heating through the reduction of metal ion deposits in the passivation layer. We achieved this reduction by adding organic carboxylic acid to chelate the dissolved metal ions. The carboxylic acid prevents excess depositing of these ions in the passivation layer. Using this developed solution, cracks disappeared and the corrosion resistance after heating was improved.

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INTRODUCTION

Zinc plating is applied for parts that need corrosion resistance with low price. Generally, Trivalent chromium passivation is applied with zinc plating at same time to prevent the zinc corrosion (white rust). Sometimes, the specifications for these coatings (zinc plating + passivation) includes corrosion resistance after heating at 120 degrees Celsius for 24 hours. It is difficult to meet this requirement using only these coatings.

The main chemical reaction of the trivalent chromium passivation has two steps. At first, zinc dissolves and pH goes up. Then the metal ions (for example chromium) deposit as the passivation layer.



Therefore, in the production line, metal ions such as zinc and iron are increasing in the passivation solution by dissolving from the parts' surface. Zinc is dissolved from plating surface, and iron is dissolved from the base metal surface at non-plated areas such as inner face of pipes. The trivalent chromium solution in which these metal ions are dissolved over time is referred to in this report as the "long run" solution. Figure 1 shows the neutral salt spray test result (72 hours) of samples passivated in fresh/new solution and in long run solution after heating at 120 degrees Celsius for 24 hours. The zinc concentration is 8.9 g/L and iron concentration is 26 mg/L in the long run solution. The result for the part passivated in new solution is good (no rust), but the result for the part passivated in

the long run solution is not good (white rust). Thus the deterioration of the corrosion resistance after high temperature exposure may be effected by the dissolved ions.

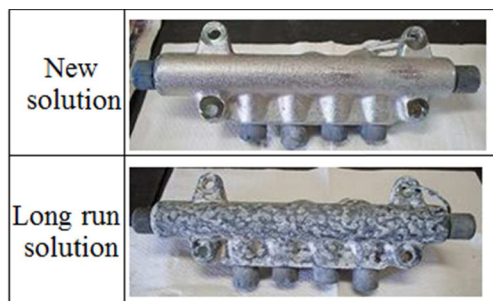


Fig. 1. Corrosion resistance after heating

Adding a top coat after this process improves the corrosion resistance but has an increased cost. To combat this, we strove to develop a trivalent chromium passivation with a higher corrosion resistance at elevated temperatures.

INVESTIGATION DETAIL

Mechanism of the Corrosion Resistance Reduction after Heating

We investigate the reason for the corrosion resistance reduction after heating before developing new passivation. Test samples (steel plates and steel pipes) are passivated by the condition shown in Table 1 after zinc plating (about 10 micrometer). Some of the samples are then heated to 120 degrees Celsius for 24 hours.

Table 1. Test condition for analyzing the long-run effect

	New solution	Long run solution
Cr^{3+}	4.2 g/L	4.2 g/L
Dissolved ion	Zn^{2+} 0 g/L	20 g/L
	Fe^{3+} 0 mg/L	100 mg/L
Temperature	30°C	
pH	2.0	
Time	40 sec	

The test samples with and without heating were then evaluated using the following methods.

- Neutral salt spray test for 72 hours
- Surface observation by scanning electron microscopy, SEM
- Cross-sectional observation by Transmission electron microscopy, TEM
- In-depth composition analysis by X-ray photoelectron spectroscopy, XPS

The NSS test result is shown in Figure 2. Both samples treated in the new solution (with/without heating) have no white rust and good corrosion resistance. The sample treated in the long run solution without heating also has no white rust, but the sample with heating has

white rust. This shows that the corrosion resistance decreases after exposure to high temperatures. We verified the passivation's condition by SEM (see Figure 3). The new solution's passivations have no damage. The long run solution's part has small cracks, and these cracks grow by heating. The cracks growth is caused by the passivation's constriction with high temperature. The crack growth may cause the passivation to peel off from the zinc surface. Thus the corrosion resistance can be decreased by heating.

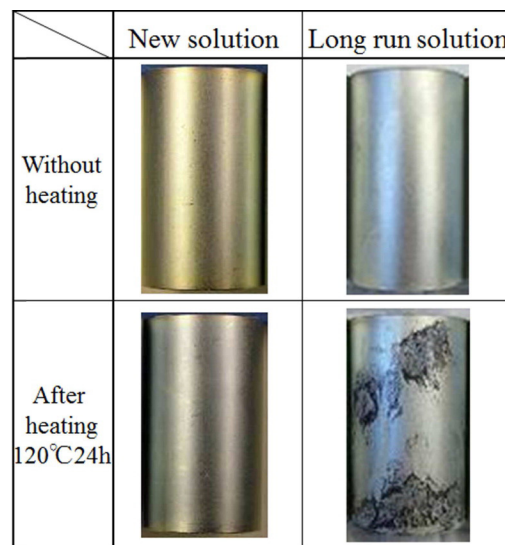


Fig. 2. Salt spray test result of the Cr^{3+} passivation layer with/without heating

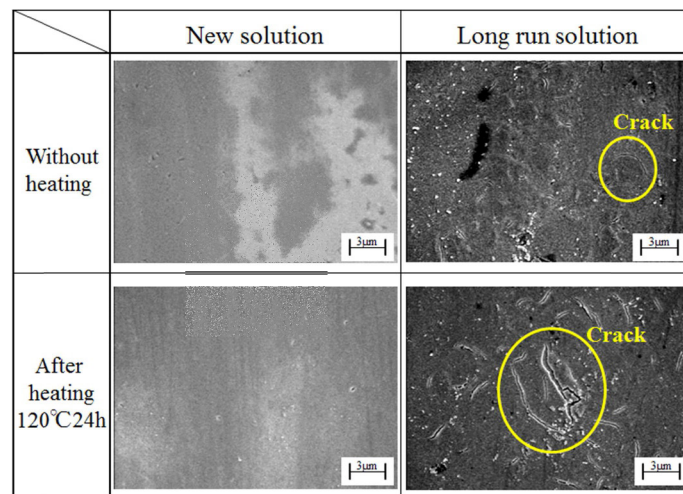


Fig. 3. SEM observation result of the Cr^{3+} passivation layer with/without heating

Next, we investigate the reason for the cracks. The trivalent chromium passivation is generated by deposit of the metal ions in the solution with elevated pH. In the long run solution, the dissolved ions (zinc and iron) concentration in the passivation layer is presumed to be higher than the new solution's. We investigated the passivations' makeup and the dissolved ions' distribution by cross-sectional TEM observation and by XPS analysis. Figure 4 shows the cross-sectional TEM observation result. The new solution's passivation can be seen as a uniform single layer, but the long run solution's passivation can be seen as a thicker double layer. XPS analysis was used to identify the double layer (shown in Figure 5). From the XPS result, the trivalent chromium passivation consists of a chromium layer and an