Technical Report

UDC 669.14.058:669.586.5

# Development of Zn Coated Steel Pipe Corresponding to Environment

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## Abstract

In general, for the flux hot dip Zn coating, distilled Zn containing Pb and Cd etc. has been used. However, because Pb and Cd are the substances of concern for example in RoHS, the reduction of them has been demanded recently. Then it was developed the Zn coated steel pipe using the purest Zn less the substances of concern. The most of the properties and operations with the purest Zn are as same as the distilled Zn, and corrosion resistance and peeling resistance with the purest Zn are better than with the distilled Zn.

#### 1. Introduction

Hot-dip galvanized steel pipes are relatively inexpensive and have good corrosion resistance, especially in the case of immersed zinc-coated steel pipes obtained by the flux method. This type of hot-dip galvanized steel pipe is therefore widely used for products such as water and gas piping, electrical conduits, and steel structures. When steel pipe is zinc coated using the flux method, distilled zinc containing Pb, Cd and the like has generally been used. However, since Pb and Cd are among the environmentally hazardous substances specified in the Directive on the Restriction of Hazardous Substances (RoHS), etc., in recent years there has been a growing need to reduce the use of Pb and Cd, with a view to promoting green procurement measures. Against this backdrop, Nippon Steel & Sumitomo Metal Corporation studied the possibility of developing an environmentally friendly zinc coated steel pipe using pure Zn that is almost free of the above-mentioned environmentally hazardous substances. There was concern, however, that the presence or absence of Pb and other elements could negatively affect such factors as the viscosity,<sup>1)</sup> reactivity,<sup>2,3)</sup> and wettability<sup>4)</sup> of molten zinc. Therefore, laboratory tests were conducted to verify the effect of using pure Zn instead of distilled Zn, that is, how this would affect product performance, production efficiency, and the factors mentioned immediately above. Furthermore this report describes the development of a new zinc-coated pipe that has been put into practical use

Table 1	Chemical	compositions	of bath (	(wt%)
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	Pb	Fe	Cd	Zn
Distilled Zn	1.26	0.042	0.089	bal.
Purest Zn	0.0005	0.002	< 0.001	bal.

## 2. Method of Coating in Laboratory

## 2.1 Compositions of zinc coating baths

**Table 1** shows the compositions of coating baths used in the laboratory tests. The distilled zinc bath was added with Pb to saturation.**2.2 Study of coating performance** 

The pipe blank used for coating in the laboratory was a 100A pipe (outside diameter 114.3 mm, thickness 4.5 mm) obtained by electric-welding a hot-rolled low-carbon steel plate. The coating process applied was alkali degreasing  $\rightarrow$  rinsing  $\rightarrow$  pickling  $\rightarrow$  rinsing  $\rightarrow$  liquid flux treatment  $\rightarrow$  drying  $\rightarrow$  zinc coating  $\rightarrow$  water cooling  $\rightarrow$  drying. Factors studied included pipe appearance, coating weight, composition and structure, and pipe corrosion resistance and expandability (flanging of pipe ends). Measurements were conducted using a uniformity test (JIS H 0401) and salt spray test (SST).

#### 2.3 Study of steel pot wastage

When a steel pot is used as a coating bath, the pot wastage rate may change when pure Zn is used instead of distilled Zn. In addition, since a thinned steel tank is repaired by welding, it is necessary to evaluate the wastage of the weld zone. Therefore, using a 30 mm (W)  $\times$  200 mm (L)  $\times$  4.5 mm (T) plate that was made from the same

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material as a steel pot and provided with a weld bead about 100 mm in length at the center of the plate (the rightmost specimen in Fig. 11), the author and colleagues studied the behavior of pot wastage by immersing the plate in a coating bath.

## 3. Experimental Results

#### 3.1 Appearance of coated pipe (Fig. 1)

No marked difference in pipe appearance was observed even after distilled Zn was replaced with pure Zn.

#### 3.2 Coating weight and composition (Fig. 2)

Although Pb concentration in the coating decreased after distilled Zn was replaced with pure Zn, the coating weight and Fe content in the coating remained nearly the same as long as the immersion time was kept unchanged.

#### 3.3 Uniformity test (Fig. 3)

Distilled Zn and pure Zn made no significant difference in the uniformity of coating thickness: both met the JIS.

#### 3.4 Coating cross section structure (Fig. 4)

Cross sections of the coatings were subjected to element map-



Fig. 1 View of coated pipe

ping by an electron probe microanalyzer (EPMA). In the distilled Zn coating, many Pb particles dispersed in the solidified part of the Zn were observed. In contrast, such a dispersion of Pb particles was not observed in the pure Zn coating, indicating that the pure Zn coating was highly uniform. As described later, the decrease in amounts of Pb and other impurities through the use of pure Zn is considered to account for improvements in corrosion resistance and coated pipe formability.

#### 3.5 Corrosion resistance (Fig. 5)

The pure Zn coating on the pipe was nearly equal in corrosion resistance to the distilled Zn coating, and the former was slightly superior in resistance to white rust, red rust and blackening. The reason for this is considered to be that, in a distilled Zn coating, corrosion is promoted by a local cell reaction between impurities (Pb, etc.) dispersed in the coating (as shown in Fig. 4) and the Zn, whereas a pure Zn coating is free from a local cell reaction.

## 3.6 Formability (Fig. 6)

It was found that, during pipe flaring, the pure Zn coating peeled a little less than the distilled Zn coating, on both the inside and the outside. To study the reason for this, cross sections of the coatings on flared pipe were observed (**Fig. 7**). It was found that flaring causes cracks in the coating perpendicular to the base metal, and that many of the cracks penetrate through the distilled Zn coating, although a  $\eta$ -solidified Zn layer on the pure Zn coating strides over many of the cracks. It seemed, therefore, that the pure Zn coating was more ductile than the distilled Zn coating. To verify this, the



Fig. 3 Uniformity test by CuSO<sub>4</sub> aqueous solution



Fig. 2 Chemical analysis of coating (seconds are dipping time in bath)

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Fig. 4 EPMA element mapping on cross section of coating



Fig. 6 View of flared pipe

Vickers hardness of each of the coatings was measured. It was found that both the  $\eta$ -solidified Zn layer and the alloy layer of the pure Zn coating were softer than those of the distilled Zn coating (see **Fig. 8**). In addition, specimens prepared from solidified ingots of both types of Zn were subjected to tensile tests. As shown in **Fig. 9**, pure Zn was found to be more ductile than distilled Zn. This is considered to be due to the fact that pure Zn is free of Pb and other impurities dispersed in distilled Zn.

## 3.7 Steel pot wastage (Figs. 10 and 11)

It was found that pure Zn caused less wastage of the coating pot steel than distilled Zn. Figure 10 shows the rate of wastage per day of the steel plate. Distilled Zn showed a tendency for the rate of wastage of the steel plate near the bath surface level to become especially greater at high bath temperatures.



Fig. 5 Views after SST corrosion test



Fig. 7 SEM (scanning electron microscope) image on the cross section of flared coating \* Intermetallic compound



Fig. 8 Vickers hardness of coating

## 4. Summation of Experimental Results and Development of Commercial Production

As described above, in laboratory tests, the pure Zn coating was comparable or superior to the distilled Zn coating, especially in terms of corrosion resistance and formability. Therefore, the author and colleagues started commercial production of a practical pure Zn coating in 2010. **Figure 12** shows the main aspects of the perfor-



Fig. 10 Dissolution rate of bath steel

mance of the newly developed Zn-coated pipe. As in the laboratory tests, the pure Zn coating displays a performance equal or superior to that of a conventional distilled Zn coating.

## 5. Conclusion

In view of the growing severity of environmental needs, the author and collaborators developed a new hot-dip galvanized steel pipe that replaces conventional distilled Zn with pure Zn that is almost free of Pb and other environmentally hazardous substances. It was found that the use of pure Zn was advantageous in terms of coating corrosion resistance, coated pipe formability, and resistance to pot wastage, and that it did not cause any remarkable decline in pipe performance. The enhancement of these aspects of pipe performance is considered to be due mainly to the reduction of Pb and other impurities in Zn coating.



Fig. 11 Dissolved steels in Zn bath



Fig. 12 Main results of commercial products

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