Technical Report

New Corrosion Resistant Coated Steel “ZEXEED™”

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Abstract

Nippon Steel Corporation developed and launched new corrosion resistant Zn-Al-Mg alloy coated steel sheets “ZEXEED™” for the first time in 20 years. During the development time, we focused on not only the corrosion resistance inherent in the coating, but also that under an actual use environment. ZEXEED has approximately double the corrosion resistance of that of JIS G 3323 (conventional Zn-Al-Mg alloy coated steel sheets), or 10 times that of JIS G 3302 (commodity type Zn coated steel sheets) under the cyclic corrosion test (JASO mode) environment. It is expected to be widely used in social facilities in severe corrosion environments, and thus extend their life span.

1. Introduction

In the building and civil engineering material market, the hot-dip galvanized coating method is widely adopted to provide corrosion resistance to steel materials more economically. In order to provide higher corrosion resistance to a coating layer which directly extends the life span of steel materials, hot-dip Zn-Al-Mg alloy coated steel sheets (JIS G 3323) containing alloy elements such as Al and Mg are widely used. Since 2000, Nippon Steel Corporation has marketed “ZAM™”[1)], “SuperDyma™” (hereafter referred to as SD)[2)], and the total accumulated amount of sales of the products both in Japan and abroad has exceeded about 15 million tons. In October 2021, Nippon Steel launched the sales of new hot-dip Zn-Al-Mg alloy coated steel sheets named “ZEXEED™” for the first time in about 20 years.

In the report “The desirable maintenance and renewal of future social infrastructures” released in 2013 by the Ministry of Land, Infrastructure, Transport and Tourism, it is stated that many of the domestic social infrastructures (road bridges, tunnels, river facilities, sewage systems, and harbor facilities) were constructed after the period of high economic growth, and within the subsequent 20 years to come, the percentage of facilities in which 50 years have passed since their construction will increase at an accelerating rate. Additionally, the extent of deterioration of facilities through aging cannot be defined uniformly only by the year of their construction, but varies depending on the location or maintenance circumstances. However, it is stated in the report that, for convenience, the criterion for aging is set at “50 years after construction”. Furthermore, in the following year of 2014, the “Infrastructure life span extension plan of the Ministry of Land, Infrastructure, Transport and Tourism (Action plan)” was decided. Since then, technologies which are characterized by a marked difference in life cycle cost (LCC) and low maintenance management cost are gaining a lot of attention. In this field, conventionally, the hot-dip galvanizing technique represented by JIS H 8641 (post galvanized coatings or hot dip galvanized coatings) is widely employed. However, hot-dip galvanized steel sheets that are applied to many of the social infrastructures do not have sufficient corrosion resistance to endure a long periods of exposure, and as a result, demands for high corrosion resistance have continued to increase recently. Taking such a social background into consideration, a new high corrosion resistant coated steel sheet “ZEXEED” has been developed. It can contribute to the process and labor savings in response to the decrease of the working population in developed countries, reduce the life cycle cost (LCC), and also provide measures to combat aging social infrastructures.

To estimate the accurate life span of products and facilities, it is necessary to understand the exact level of corrosion resistance of the target coating layer. In order to achieve this, conducting exposure tests under actual usage situations is paramount. However, it is impractical to conduct long-term exposure tests that last several years to confirm the life span. Furthermore, the life span of hot-dip coated steel sheets depends not only on the usage conditions, location environment, and maintenance status, but also on product configuration i.e. the number of bending, cutting, and joint parts such as bolts and welding on the pre-coated steel sheets. Practically, it is necessary to predict the expectations of life span through short-term accelerated corrosion tests and a variety of hypotheses based on exposure tests.

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Considering the various social needs stemming from products and facilities, in the case of the development of “ZEXEED”, the methods used for predicting the life span of the coating layer have been comprehensively reviewed and revised. For the exact life span prediction, the following three points are particularly crucial: (1) Evaluation of the correlation between the exposure corrosive environment and accelerated corrosion test, (2) Exact evaluation of the corrosion resistance inherent to the coating layer, and (3) Assessment of corrosion resistance deterioration in the processed part.

The evaluation of corrosion resistance based on the corrosivity categories has been standardized recently, and high corrosion resistant coated steel sheets have been increasingly applied in many industrial fields. Thus, there have been many studies on the relationship between the corrosion resistance and corrosion factors such as sea-salt particle density, temperature, and so forth in the actual exposure sites. For instance, in the International Organization for Standardization (ISO), the corrosivity level for atmospheric corrosion is classified into six categories,[3] as shown in **Table 1**, from C1 (Very low) to CX (Extremely high) based on the corrosion weight losses or corrosion rates of carbon steel and zinc. For the evaluation of the life span of the coated steel sheets, it is necessary to understand the corrosion resistance based on these corrosivity categories. In Japan, since the corrosion environment in sea coastal areas becomes more severe due to the higher amount of salt deposition depending on the distance from the sea. In addition, the lower the latitude, the higher the temperature tends to become; therefore, the more severe the corrosion environment becomes. Meanwhile, although the salt spray test (SST) has been widely used as a conventional corrosion acceleration test, from the aspect of accuracy, evaluation by using a cyclic corrosion test (CCT) that simulates the corrosive state under the actual exposure environment is preferable.

Secondly, to predict the future state of the steel sheets through exposure tests, evaluation of the corrosion resistance of the coating layer through accelerated corrosion tests is necessary, wherein the following two points should be ascertained: corrosion rate of coating layer thickness based on the evaluation of the corrosion weight loss and the corrosion protection duration by corrosion products. Since the main corrosion protection duration of a coated steel sheet is determined by these two points, both an appropriate corrosion product removal method (pickling) for the former, and the duration of retention of corrosion products on a coated steel sheet for the latter, are essential for the accurate evaluation of durations.

Lastly, the coated steel sheets such as ZAM, SD, and “ZEXEED” belong to the pre-coated steel sheet category which are coated in a hot dip continuous galvanizing line, and then processed. Therefore, they should be dealt with separately from post-coating wherein coating is applied after processing steel sheets. Processing means cutting, bending, and jointing with bolts or welding. In these processed parts in the pre-coated steel sheet, corrosion resistance deteriorates inevitably in the coating layer due to processing. However, since the deterioration greatly depends upon the compositions and/or the phase structure of the coating layer, it is possible to maintain the high corrosion resistance of pre-coated steel sheets sufficiently by applying the appropriate processing,

Table 1 Classification of Environments

Category	Corrosivity
C1	Very low
C2	Low
C3	Medium
C4	High
C5	Very high
CX	Extreme

Hereafter, we introduce the corrosion resistance of “ZEXEED” which is about two times higher than that of the conventional JIS G 3323 (hot dip Zn-Al-Mg alloy coated steel sheet), and about ten times higher than that of JIS G 3302 (hot dip Zn coated steel sheet). Also introduced hereafter are the corrosion resistance evaluation methods of hot dip Zn-Al-Mg alloy coated steel sheets required for the life span prediction of future products and facilities, and countermeasures for the processed parts.

2. Main Discourse

2.1 Domestic corrosion environment and accelerated corrosion test

According to the Atmospheric Exposure Test Handbook published by the Japan Weathering Test Center,[4] the environments of many of the major locations in Japan surrounded by sea on all sides belong to Category 3 as of 2004. In the Okinawa district, the environments are Category 4, which are considered to become Category 5 or X depending on the distance from the coast.

As an accelerated corrosion test, the salt spray test (SST) specified in ISO 9227 has been used conventionally. Although SST is suitable for quality control, considering it lacks correlation with the corrosion in an atmospheric exposure environment, CCT has recently been used for the evaluation of life span in the actual environment.[5] The JASO cycle test (M609)[6] specified by the Japan Automobile Standard Organization (JASO) is most widely used as CCT having high reproducibility, and is the accelerated corrosion test suitable for confirming corrosion resistance widely. It should be noted that when confirming its correlation with the exposure test, a JASO test of a long duration is more severe than SST[7]. For instance, one report states that the corrosion appearance of a bare steel sheet tested by a JASO 45 cycle test is close to that after about one year’s atmospheric exposure in Okinawa. Additionally, another report states that, based on the corrosion rate of Zn in a JASO test, the JASO 30 cycle is considered to be equivalent to about three years’ exposure in Okinawa.[8] The corrosion resistance of “ZEXEED” is evaluated based on the corrosion weight loss of the coating layer that mainly consists of Zn, and therefore, the JASO 30 cycle is used as the exposure forecast standard.

2.2 Evaluation of corrosion resistance of coating layer

Figure 1 shows the changes in corrosion weight loss of various Zn coatings measured by Nippon Steel. This corrosion weight loss was measured after removing the corrosion products by immersing in the 30 vol.% chromic acid (VI) solution at an ordinary temperature (23°C) for fifteen minutes. The conventional methods to chemically remove the corrosion products of zinc and/or zinc alloy are proposed in JIS Z 2371[9] and ISO 8407[10], in which the existence of Zn weight loss in the pristine coating layer is caused by immersing in a solution such as boiled 30 vol.% chromic acid (VI) solution or other acids. According to Nippon Steel’s reports, Zn weight loss in the pristine coating layer is confirmed in JIS G 3323 and/or “ZEXEED”. Furthermore, the larger the corrosion weight loss becomes, the greater the errors, resulting in a lack of accuracy in a long-term corrosion test. Therefore, we have judged that the method is not applicable to the latest hot dip Zn-Al-Mg alloy coating. Additionally,

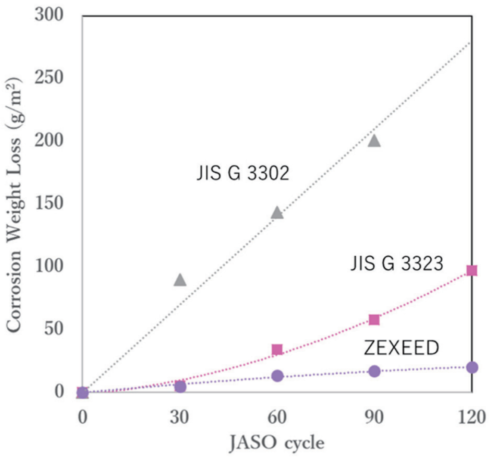

Fig. 1 Changes in corrosion weight loss of Zn coatings

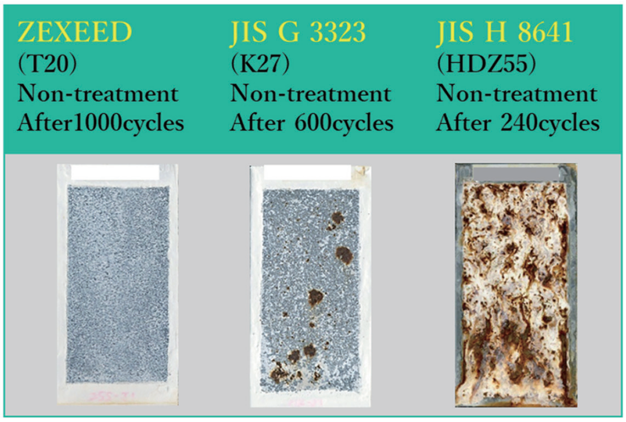

Fig. 2 Appearance of coated steel sheets in CCT (JASO)

the methods with other types of acid specified in the standards have the problem of being unable to remove corrosion products of chlorides and sulfate containing Al and Mg in an atmospheric corrosion environment. However, the method of immersing in 30 vol.% chromic acid (VI) solution at an ordinary temperature of 23°C minimizes the damage to the coating (reduction of Zn weight loss in the pristine coating layer and after the corrosion test), and provides an appropriate chemical reaction rate and exhibits excellent removal of corrosion products. Furthermore, from the changes in corrosion weight loss in Fig. 1, the corrosion weight loss of "ZEXEED" reaches 10 g/m^2 at the JASO 50 cycle, about 1/2 of that of JIS G 3323, and about 1/10 of that of JIS G 3302, and that the difference continues to increase after that. Based on the aforementioned assumption in converting the JASO test to years of exposure in Okinawa, it is considered that the clear difference of corrosion resistance from that of JIS G 3323 is confirmed to start at the JASO 50 cycle, i.e. after about five years' of exposure in Okinawa. Furthermore, for forecasting a life span based on the transition of the corrosion weight loss, the following calculation method to estimate the durable years of Zn coating is used.[11]

<Durable years>

= "Zn coating weight (g/m^2)" ÷ "corrosion rate (g/m^2/year)" × 0.9

According to this indictor, the life span of "ZEXEED" with a coating weight mark of T20 (≈100 g/m^2 or more per side) becomes about 450 cycles (equivalent to about 45 years in Okinawa). Practically, even when the amount of the corrosion weight loss reaches the coating weight, since the corrosion products protect the base steel for a certain duration, red rust is not formed immediately after that. **Figure 2** shows the appearance of the corroded "ZEXEED" sheet after a JASO test, and red rust has not been formed on the coated surface even after JASO 1 000 cycles. This is considered due to the corrosion products' stabilizing effect caused by Mg[1, 2] that both JIS G 3323 and "ZEXEED" contain. "ZEXEED" that contains Mg in an amount larger than that of JIS G 3323 stabilizes basic zinc chlorides for a period longer than that of JIS G 3323, and suppresses their transformation to oxidized chlorides, which accompanies volume-expansion, resulting in breakouts of corrosion products that weaken the coating protection performance.

2.3 Corrosion resistance in processed part

Since JIS G 3323 and "ZEXEED" are pre-coated steel sheets, they are processed after hot dip coating, and the coating layers would be damaged by cracks and/or by welding heat depending on the processing form. Major forms of damage are: cracks on the coating layer developed by bending and/or by drawing, exposure of base steel on the cut edge surface caused by cutting and/or punching, different metal contact corrosion in bolt joining, and reduction of thickness and/or degeneration of the coating layer by welding. It is possible for a pre-coated steel sheet to restore its corrosion resistance close to its inherent level by understanding its performance in the processed parts, and by applying appropriate measures.

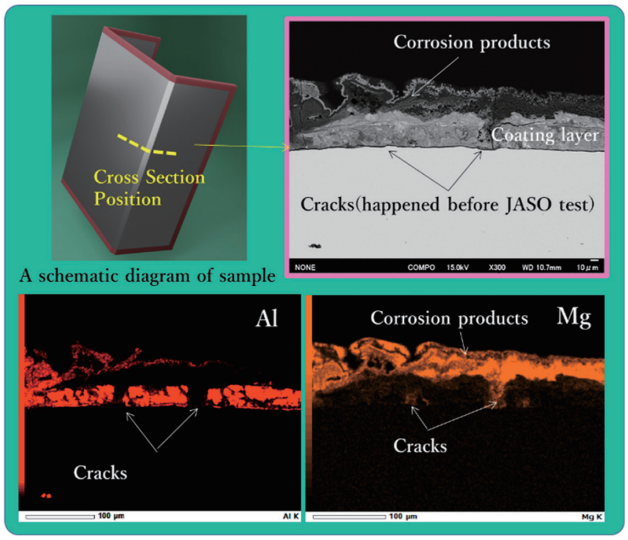

Fig. 3 SEM-EDS images of 90-degree-bending part in ZEXEED (After JASO 600 cycles)

Due to the difference between plastic deformability of the hot dip Zn-Al-Mg alloy coating layer and that of the steel in contact, cracks are developed in the coating layer during the steel processing. **Figure 3** shows the result of the observation after JASO 600 cycles of the section (element analysis) of the bent part of "ZEXEED" with roll forming processed. The base steel exposed in the surface between the coating layer cracks caused by 90° bending is protected by the sacrificial corrosion prevention reaction of the coating layer, and covered by corrosion products completely. The covering corrosion products deter the progress of corrosion, wherein Mg that plays a vital role is confirmed.

In addition, on the cut end face having a base steel exposure area larger than that of the crack in the processed part, both the superior

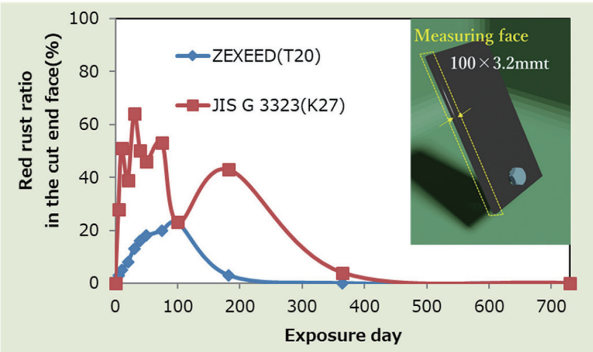

Fig. 4 The transition graph indicating red rust of 3.2 mm-ZEXEED cut end face in Futtsu, Japan

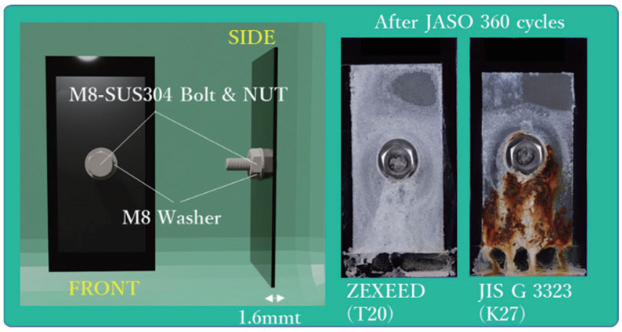

Fig. 5 Appearances of SUS joined body (After JASO 360 cycles)

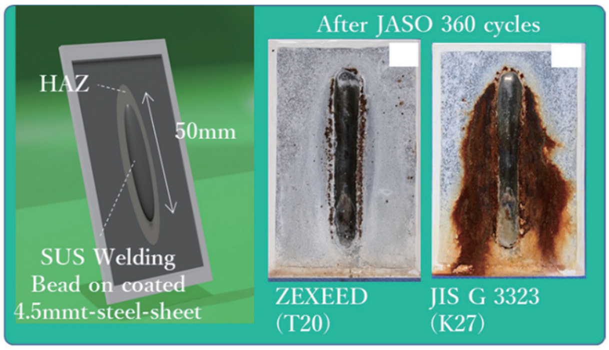

Fig. 6 Appearances of SUS bead (NSSW SF-309SD) surroundings (After JASO 360 cycles)

sacrificial corrosion prevention property of pre-coated steel sheets and the great planar surface corrosion resistance that realize the low corrosion rate in the peripheral area of the sacrificial corrosion section are compatibly required. As **Fig. 4** shows, on the cut end face of "ZEXEED", red rust is less noticeable than on the JIS G 3323 cut edge surface. This is attributed to the effect of Mg contained in the corrosion products that covers the base steel exposed face at the early stage.

In the case of mechanically joining coated steel sheets with a bolt, in order to maintain the high corrosion resistant pre-coated steel sheets, use of a bolt having equally high corrosion resistance is desirable. When a SUS bolt is used, different metal contact corrosion takes place in the surrounding area in contact with the coated steel sheet. In "ZEXEED" also, this phenomenon is unavoidable since "ZEXEED" is a sheet covered by a coating that consists of metal atoms. However, as **Fig. 5** shows, the red rust protection effect of "ZEXEED" is confirmed to be superior to that of JIS G 3323 even in the periphery of the bolt joining part.

When arc welding is used as a joining method, not only the weld bead part coating layer, but also the coating layer in the heat affected zone (HAZ) is damaged. It is possible to maintain the excellent corrosion resistance of "ZEXEED" in the weld part and its peripheral part by applying, as a means to protect the corrosion resistance in the welded part, the stainless system seamless flux cored welding wire NSSW SF-309SD (flux cored welding wire for welding SuperDyma™ and ZAM™[12]) to "ZEXEED" (**Fig. 6**). As other methods to repair the weld part, the use of various zinc-rich paints is also possible. Thus, even in large-scale structures where welding is used, high corrosion resistance is expected by employing pre-coated steel sheets.

3. Conclusion

Demand for energy saving, life cycle cost (LCC) reduction, and maintenance-free performance is growing in anticipation of new renewable energies for the carbon-neutral society, and on account of changes in social structure due to the global dispersion of new Corona virus. To cope with such demand, extension of the life span of construction materials that constitute social infrastructures is required, and as a part of this, high corrosion resistance is required for hot dip galvanized steel sheets. In recent years, for designing infrastructure facilities, products, and equipment, development is implemented taking into consideration their usage environments and forms. In the development of "ZEXEED", implementation of accelerated tests in a condition close to the exposure environment and the evaluation of the corrosion state were prioritized as most important, and corrosion resistance superior to any of the existing hot dip Zn-Al-Mg alloy coatings was realized. We also considered that the maintenance of high corrosion resistance in actual usage form, which is a problem of pre-coated steel sheets, was simultaneously important. Therefore, we not only simply confirmed the level of the coating layer corrosion resistance, but we also verified that high corrosion resistance is maintained in any of the various processes applied to our products. Through "ZEXEED" that has been developed with priority placed on meeting the various social needs first, we are keen to contribute to the creation of a variety of products that have been unrealized in the past, and/or to the construction and maintenance of social infrastructures in the regions with severely corrosive environments.

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