Deterioration mechanism of hot-dip Al coating in a coastal-atmospheric environment

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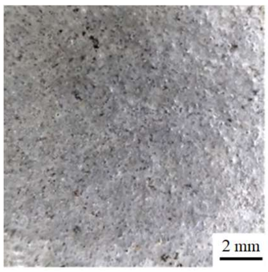
1. Introduction Hot-dip coating is of considerable significance in protecting steel to improve the durability of the structure and reduce the cast[1]. Until now, the Zn and Al-based hot-dip coatings have been studied a lot by scholars. Their anti-corrosion effects on steel members were usually clarified according to their microstructural characterization, oxidation kinetics[2], etc. As we knew, Al coating owns a better corrosion resistance than Zn coating in a coastal environment as its outmost oxide layer can play an excellent physical shielding effect. However, the protective effect of hot-dip Al coating was not invariable in the actual steel structure. In some previous studies, it shows that Al and Al-rich alloy coatings cannot afford the cathodic protection effectively in the ordinary atmospheres where own low or medium chloride contamination.

In this study, the object is a hot-dip Al coated steel bridge, which serviced over 25 years in a coastal atmospheric environment. In several structure components, the outmost Al layer has started to be dissolved, as shown in Fig.1. Three types of deteriorated hot-dip Al coating were discussed to clarify the corrosion progress and deterioration mechanism, according to corresponding SEM-EDS and EPMA element analysis.

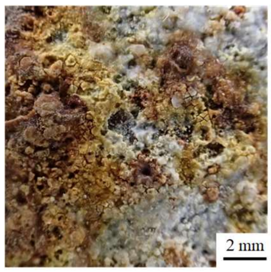
2. Test method The object of this study is an oil terminal constructed 25 years ago, that located in the coast of Kagoshima, Japan (Lat. 31°29'N, Long. 130°32'E). The main steel structure of this oil terminal is a trestle bridge constructed by rolled H-shape trusses, that all steel components were coated by hot-dip Al coating. Generally, the skyward surface would be affected by rain washing larger than the groundward surface of a steel component in the same atmospheric environment, which leads to the deposited salt of the skyward surface that should be smaller than that of groundward. The aged coating in this bridge is consistent with this phenomenon. There is no evident deterioration occurred in most of the skyward surface of trusses. In contrast, several groundward surfaces of trusses own a large amount of rust and oxide, as shown in Fig.2.

According to visual estimation, three locations A, B, and C in the 45° trusses with various degrees of the aged coating were set as targets. The corresponding samples denoted as A, B, and C. Herein, location A is the skyward surface, and B, C are the groundward surface in the truss webs. Core samples were taken from the trestle bridge by the borehole (inner diameter: 25mm). The samples for SEM observation and elemental analysis were fabricated by embedding the cores in phenolic resin, hardening, and polishing with alumina suspension (particle size: 3 μm). The element of Fe, Al, Mg, Cl, Ca, O were mapped by EPMA-1600.

Fig.1 Structural trusses with hot-dip Al coating in a trestle bridge after service for 25 years.

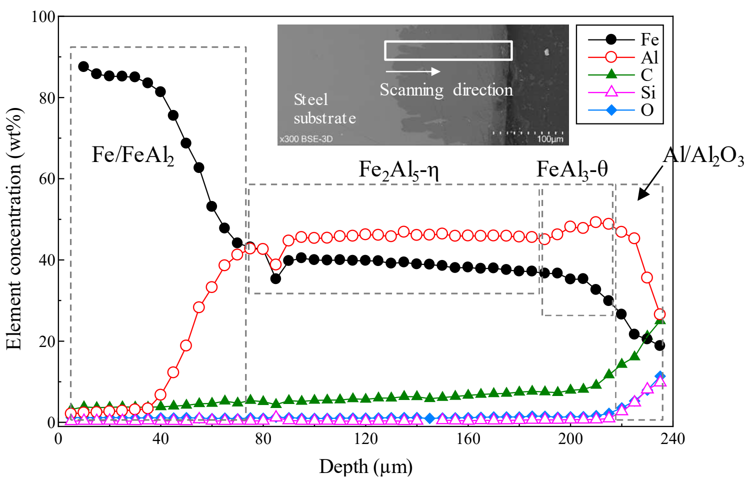


(a) Skyward surface without evident deterioration

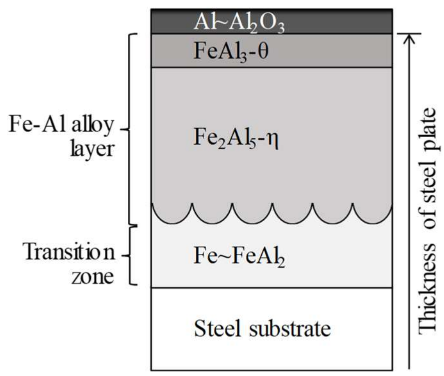


(b) Groundward surface with rust and oxide

Fig.2 Digital photos of aging Al coating surfaces in trusses before borehole.



(a) Element concentration by SEM-EDX at the cut-edge of coating



(b) Schematic diagram of Al coating layers

Fig.3 Sample A: skyward surface (with rain-wash effect) shows no evident deterioration.

Keywords: Hot-dip Al coatings, corrosion, deterioration mechanism, coastal-atmospheric environment.
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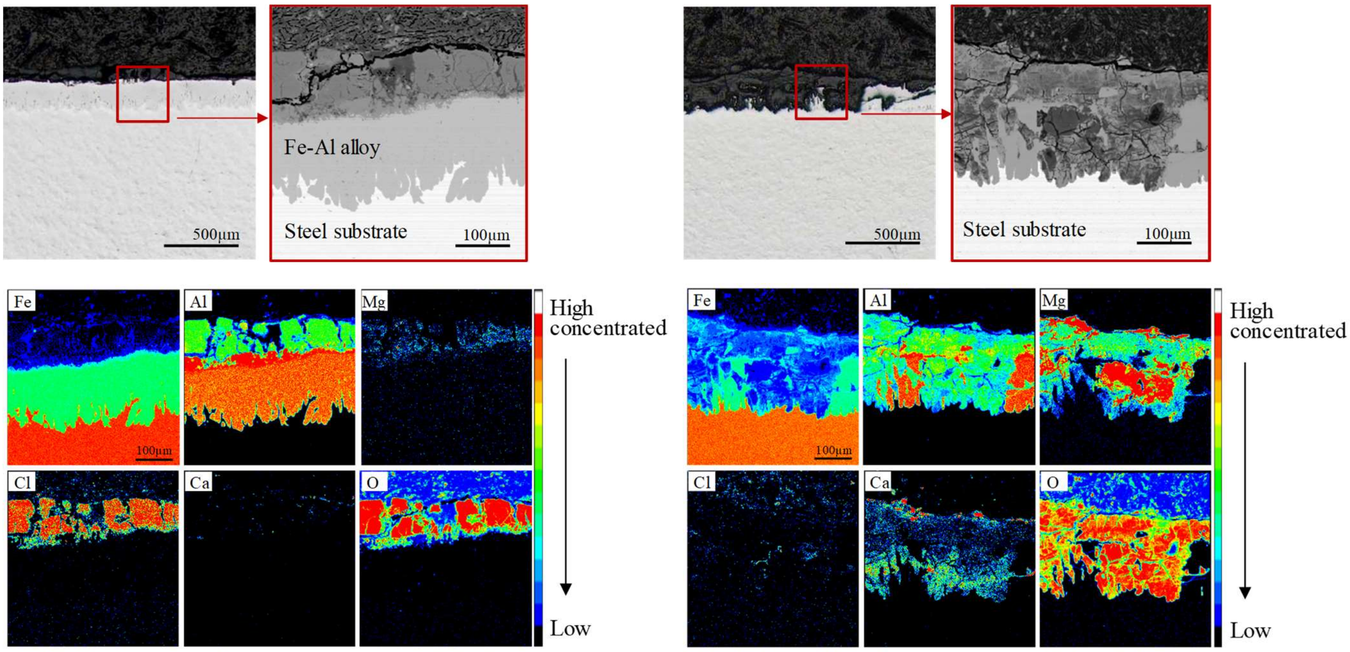

(a) Sample B: half-degraded (b) Sample C: full-degraded

Fig.4 BSE image and EPMA elemental analysis on the groundward surfaces (without rain-wash effect).

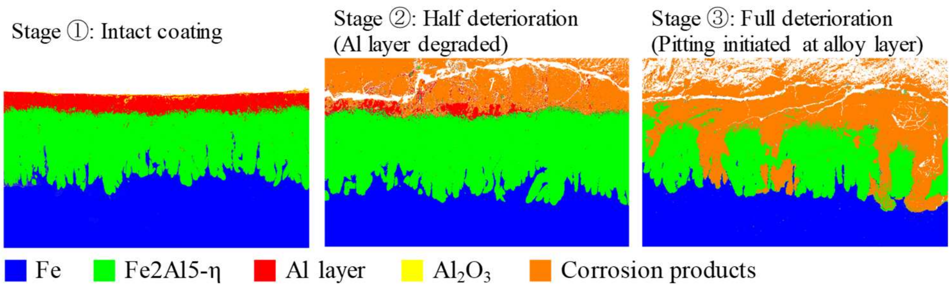

Fig.5 Phase distribution map of Al coating in three deterioration stages.

3. Test results Fig.3(a) shows the element concentration at the cut-edge of Al coating when sample A used for SEM-EDX detection. Corresponding BSE image shows the Al coating is still complete, which is composed of an outer Al topcoat and an inner Fe–Al intermetallic layer (AKA alloy layer). The overall thickness of the entire coating was about 200 μm, while the outermost Al layer should have lost part of its thickness. A schematic diagram of complete hot-dip Al coating was speculated from element concentration, as shown in Fig.3(b). It revealed that the Fe–Al alloy layer was composed of an outer minor $FeAl_3$ layer and an inner major Fe_2Al_5 layer. The transition zone existed between the steel and alloy layer, and the steel substrate shows a tongue-like morphology. Fig.4 shows the elemental analysis on the cut-edges of sample B and C, which were groundward surfaces without rain-washing effect, and both of them shows the outermost Al layer has been consumed. In Fig.4(a), sample B shows part of Fe–Al alloy layer can be identified easily, whereas Fig.4(b) shows only little remaining Fe–Al intermetallic layer that near the steel substance can be observed, the majority of the region has occurred deterioration. EPMA mapping comparison between samples B and C clarified that the effect of chloride and oxide would be blocked entirely by Fe–Al intermetallic layer, as long as the pitting corrosion didn't occur. However, sample C subjected a high risk of corrosion, as the main part of its coating has been destroyed, and the chloride had penetrated steel substrate, although the residual Al-Fe intermetallic layer still providing the sacrificial anodic protection for steel.

Above all, the phase distribution map of three deterioration stages was speculated, as shown in Fig.5. Stage ① shows the intact coating: it should be a long-term state and represents a consuming process of Al oxide and Al layer. Stage ② is named as the half-deterioration: the Al layer has almost disappeared, and the alloy layer still provides good cathodic protection. Stage ③ could be considered as full-deterioration: the pitting progress would largely accelerate the transform from ② to ③. After the pitting occurred, the residual alloy still has a contribution to steel protection lead to a faster consuming of coating and the pitting expansion in width.

4. Summary 1) Hot-dip Al coating deterioration would be largely affected by rain washing, and most of the skyward surface shows complete coating after 25 years of coastal-atmospheric exposure, which is composed of an outer Al topcoat and an inner Fe–Al intermetallic layer. 2) The durability of the groundward coating would be reduced due to deposited salt, and the phase distribution map of three deterioration stages has been speculated in this study.

References 1) G. Vlourlias, N. Pistofidis, D. Chaliampalias: A comparative study of the structure and the corrosion behavior of zinc coatings deposited with various methods, Surface & Coatings Technology, 200(2-3): 6594-6600, 2006. 2) WJ. Cheng, CJ. Wang: Growth of intermetallic layer in the aluminide mild steel during hot-dipping, Surface & Coatings Technology, 204(6-7): 824-828, 2009.

