Corrosion resistance of hot-dip Zn-6%Al-3%Mg alloy coated steel sheet used in automotive parts

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ABSTRACT

For the purpose of applying hot-dip Zn-6%Al-3%Mg alloy coated steel sheet ("Zn-Al-Mg") to automotive parts, we compared and investigated the corrosion resistance of Zn-Al-Mg and ordinary materials treated using a conventional rustproofing method ("post-Zn-coated material") exposed to accelerated corrosion test environments. We also collected automotive parts made from Zn-Al-Mg from vehicles that had been driven for three to five years in Canada to examine corrosion resistance capabilities when exposed to actual vehicle environment conditions. We found that Zn-Al-Mg exhibited better corrosion resistance than post-Zn-coated material, even at portions where the steel substrate was exposed (along cut edges and in bent or spot-welded portions). Such Portions of the Zn-Al-Mg were observed as being covered by fine and dense Zn corrosion products containing Mg, which suppresses cathode reactions (dissolved oxygen reduction reactions). As a result, elution of the coating layer around such portions was suppressed and favorable corrosion resistance maintained. The flat and bent portions of automotive parts made of Zn-Al-Mg collected from actual vehicles were covered by fine and smooth corrosion products, with only little corrosion being observed. It was thus confirmed that Zn-Al-Mg also exhibits excellent corrosion resistance in an actual vehicle environment.

RIASSUNTO

Con lo scopo di applicare il rivestimento "Zn-Al-Mg" sui laminati di acciaio per componenti di autoveicoli, mediante "immersione a caldo" nel bagno della lega Zn-6%Al-3Mg, gli Autori hanno studiato la resistenza a corrosione del rivestimento "Zn-Al-Mg" confrontandola con quella dei materiali comuni trattati con metodi convenzionali di protezione alla corrosione (rivestimento di Zn) esposti a test ambientali di corrosione accelerata. Sono state anche prelevate parti ricoperte con Zn-Al-Mg da veicoli guidati da 3 a 5 anni in Canada, con lo scopo di valutare le prestazioni di resistenza alla corrosione quando sono esposte alle condizioni ambientali di esercizio. Gli autori hanno trovato che il rivestimento Zn-Al-Mg mostra migliore resistenza a corrosione rispetto a quello solo Zn, anche in zone dove il substrato di acciaio era esposto (lungo gli orli tagliati, in parti piegate o saldate a punti). Le parti ZnAlMg apparivano coperte da prodotti di corrosione di Zn fini e dense contenenti Mg, che sopprime le reazioni del catodo (reazioni della riduzione dello ossigeno dissolto).Come risultato, la perdita del rivestimento attorno a queste zone è stata soppressa e la favorevole resistenza a corrosione appare mantenuta. Le parti piatte e piegate dell'auto realizzate con Zn-Al-Mg, prese dai veicoli esistenti, erano coperte da prodotti di corrosione fini e lisci con scarsa corrosione. Si può quindi confermare che il rivestimento Zn-Al-Mg mostra anche una eccellente resistenza alla corrosione nell'ambiente degli attuali veicoli.

KEYWORDS

Hot-dip Zn-6%Al-3%Mg alloy coated steel sheet, accelerated corrosion test, actual vehicle environment, corrosion resistance, corrosion products.

INTRODUCTION

The metal parts used in an automotive engine compartment and the underbody require exceptionally high corrosion resistance. Among the rustproofing techniques used in fabricating such parts is the treatment of punched and shaped steel sheets with electro-zinc plating, and the use of chromate film. The advantage of this rustproofing method is that it covers the entire surface with plating, including cut edges and/or bent and otherwise processed portions, thereby yielding the corrosion resistance required. However, this electro-chemical processing is cumbersome, and applying the chromate film poses particular problems due to the discharge of waste liquid. Thus, there is a demand for alternative rustproofing methods.

Zn-Al-Mg has recently been developed [1,2] and is increasingly being applied in construction materials for various purposes. In this study, we also examined the possibility of exploiting the high corrosion resistance of Zn-Al-Mg for automotive parts. Fig. 1 shows images of automotive parts fabricated using a conventional rustproofing method and using Zn-Al-Mg, respectively. The fabrication of parts using Zn-Al-Mg having corrosion resistance matching that of parts fabricated using conventional rustproofing methods will make it possible to omit the treatment processes after press forming (electro-zinc plating and applying post-treatment), and thus lead to a significant cost reduction and resolve the problem of waste solution. However, the use of Zn-Al-Mg will expose the steel substrate along the cut edges and in the processed portions, where cracks may form in the coating layer. This poses a risk of corrosion resistance at such portions possibly not being as good as that of automotive parts fabricated using conventional rustproofing methods. To examine this issue, we manufactured several test specimens of various shapes using a conventional rustproofing method and Zn-Al-Mg, and then compared the corrosion resistance of these specimens based on accelerated corrosion tests.

So far, there have been no studies conducted on the corrosion resistance of Zn-Al-Mg as investigated in actual vehicle environments. In this study, we collected automotive parts made of Zn-Al-Mg from vehicles that had been driven in Canada, and investigated the corrosion conditions.

This paper also reports these results.

EXPERIMENTAL PROCEDURE

Accelerated corrosion test

We fabricated test specimens having the three basic shapes shown in Fig. 2 by using Zn-Al-Mg and materials subject to a conventional rustproofing method ("post-Zn-coated material"), and then compared the corrosion resistance of said specimens. The Zn-Al-Mg produced in a continuous hot dipping line, with a coating of 80 g/m2 per side and with a chromium-free treatment was used as specimen. For the post-Zn-coated material specimens, cold-rolled steel sheet was processed into the shape shown in Fig. 2, and then electro-zinc plating was applied with a target coating weight of 100 g/m2 per side, followed by a film of trivalent chromate being applied.

In order to evaluate the corrosion resistance along the cut edges, we used test specimens with a thickness of 2.3 mm cut with a shear into a size of 70 × 150 mm. To evaluate the corrosion resistance of the processed portions, we used test specimens with a thickness of 0.8 mm processed by cylindrical drawing (shoulder radius: 5 mm, die radius: 5 mm, blank diameter: 100 mm, punch diameter: 50 mm, stroke speed: 60 mm/min). We put and spot-welded two pieces of steel sheet 0.8- mm thick (electrode:

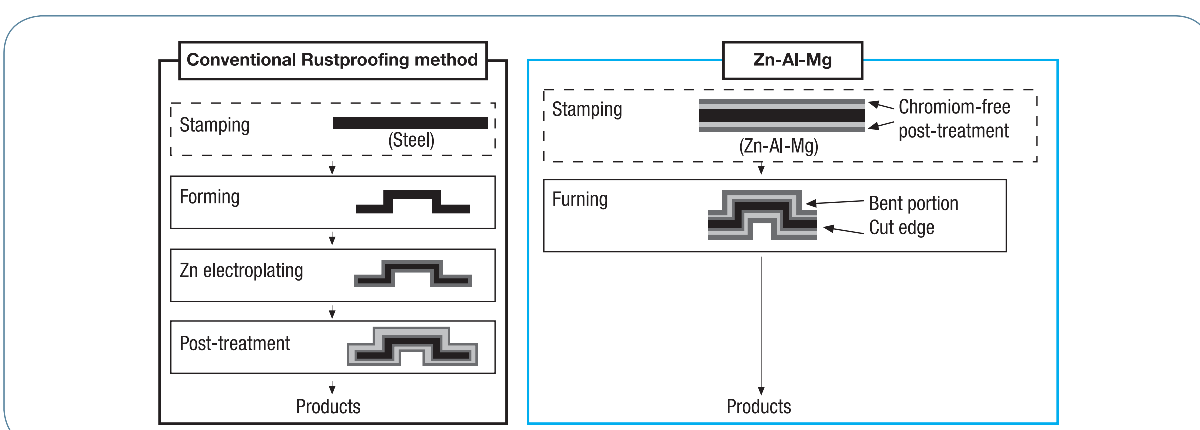


Fig. 1: Images of fabricating automotive parts.

Cu-Cr alloy, electrode shape: 6DR, welding force: 1.96 kN, welding current: 8.5 kA, welding time: 0.2 sec), and then evaluated the corrosion resistance of the surface side in contact with the spot-welding electrodes.

We employed the JIS H 8502 combined-cycle corrosion test ("CCT") for our accelerated corrosion testing consisting of the following cycles: two hours of salt spray (at 35°, 5% NaCl), four hours of drying (at 60°, R.H. of 30%), and two hours of humid (at 50°, R.H. of 95%).

We observed the test specimens after the CCT by using a SEM, and examined corrosion products formed on the test specimens using an EPMA and a micro-XRD (X-ray tube:Cr, 40kV, 100mA). In order to study the rustproofing mechanism along the cut edges, we also masked the specimens with silicone resin so that only the fractured sections of the cut edges were exposed for measurement (1 mm × 15 mm), and then measured the cathodic polarization curves of the cut edges.

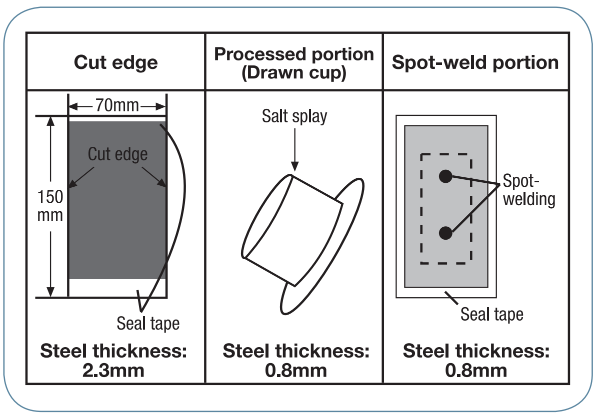
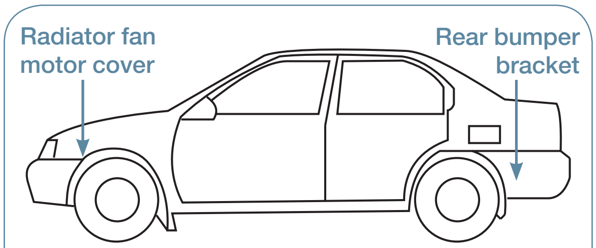


Fig. 2: Corrosion test specimens.



Type	Driving area	Driving term	Driving distance
A	Quebec city	About 3 years	45,503km
B	Montreal	About 5 years	70,105km

Fig. 3: Mounting positions of collected automotive parts and driving logs of vehicles.

Investigation of corrosion resistance of actual vehicle parts

Fig.3 shows the mounting positions of the collected automotive parts and the vehicle driving logs.

A radiator fan motor cover made of Zn-Al-Mg (1.0 mm thick) was collected from the engine compartment of vehicle A; a rear bumper bracket made of Zn-Al-Mg (0.6 mm thick) was collected from the underbody part of vehicle B. In addition, a radiator fan motor cover made of post-Zn-coated material (1.2 mm thick) mounted on vehicle B was collected for use in a comparison study.

We also examined of initial coating weight per side by observing the cross sections of portions where corrosion did not occur. Our measurements indicated coatings of approximately 100 g/m^2 for the radiator fan motor cover made of Zn-Al-Mg, approximately 60 g/m^2 for the rear bumper bracket made of Zn-Al-Mg, and approximately 100 g/m2 for the radiator fan motor cover made of post-Zn-coated material. We cut out small sample pieces from the collected parts and examined their corrosion conditions and corrosion products by using SEM, EPMA.

RESULTS AND DISCUSSION

Evaluation of corrosion resistance in accelerated corrosion test

(1) Flat portions

Fig.4 shows the surface appearance of the test specimens used in evaluating the cut edges after the CCT. We evaluated the center of each test specimen as a flat portion and found some red rust mixed with white rust in 60 cycles of CCT for post-Zn-coated material. Then, the red rust expanded and fully covered the surfaces of the test specimens after 180 cycles of CCT. In contrast, only white rust was formed on the Zn-Al-Mg coated steel sheet specimens even after 180 cycles of CCT, clearly indicating that Zn-Al-Mg has superior corrosion resistance in the flat portions. Fig.5 shows the cross-sectional structures of Zn-Al-Mg and post-Zn-coated material specimens after 40 cycles of CCT, as well as the surface morphologies of corrosion products formed on the surfaces of both types of specimens. In the post-Zn-coated material specimens, the whole of coating layer was already corroded, with rough porous corrosion products formed on the surface. Conversely, little corrosion was observed on the coating layer of the Zn-Al-Mg specimens, with the surface layer covered by fine and dense corrosion products. It is known that these fine and dense zinc corrosion products contain Mg and/or Al, which contributes to the excellent corrosion resistance of Zn-Al-Mg [2-5].

(2) Cut edges

Fig.6 shows the appearance of the cut edges of test specimens shown in Fig. 5. On the post-Zn-coated specimens, the cut edges are covered by Zn plating and thus only white rust can be seen up to 60 cycles of CCT. Red rust later appears among the white rust at 120 cycles of CCT. The surface of cut edges is fully covered by red rust at 180 cycles of CCT. For the Zn-Al-Mg specimens, on the other hand, the formation of red rust is observed very quickly (after CCT 10 cycles) on the fractured section of the cut edges, because the steel substrate is exposed. This status continues for a while, until red rust finally begins to spread again (180 cycles of CCT). These changes were observed in the appearance of the cut edges of Zn-Al-Mg specimens during CCT.

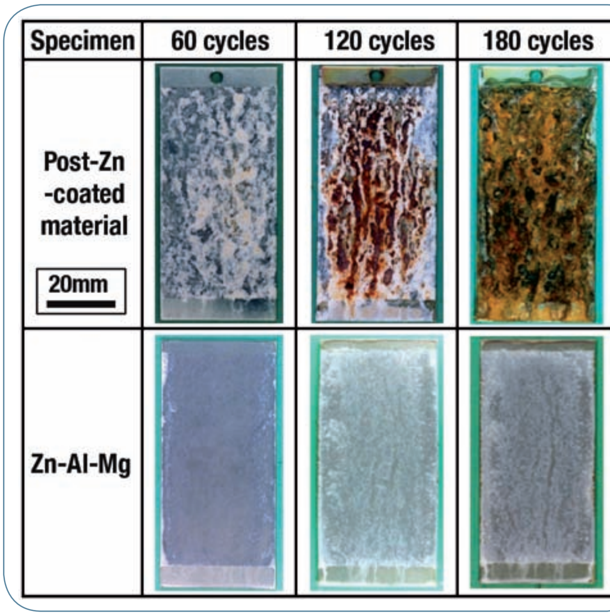


Fig. 4: Surface appearance of test specimens after CCT.

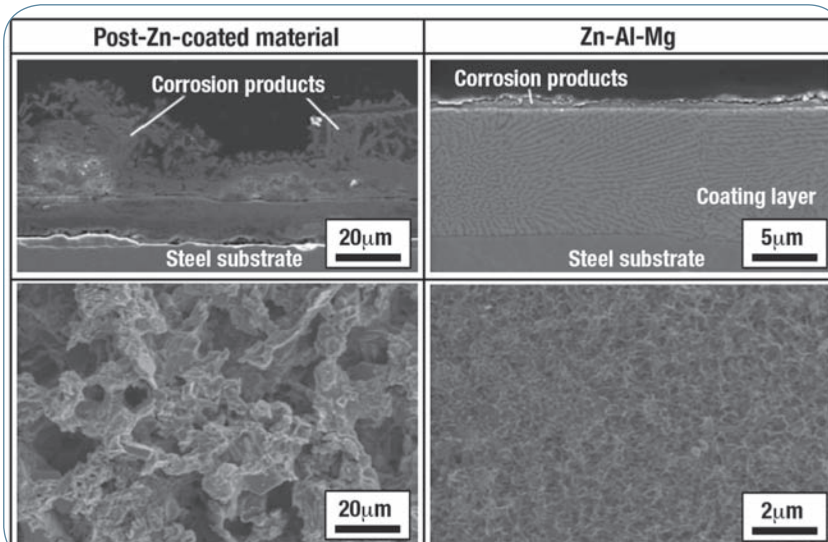


Fig. 5: Cross-sectional structures and surface morphologies of corrosion products formed on Zn-Al-Mg and post-Zn-coated material specimens after 40 cycles of CCT.

Fig.7 shows an example of the cross-sectional structures of the cut edges of the post-Zn-coated material and Zn-Al-Mg specimens after 180 cycles of CCT. A clear difference can be seen in the corrosion depth of steel substrate along the cut edges: there is approximately 0.4 mm of corrosion on the steel substrate of the post-Zn-coated material, whereas little corrosion of the steel substrate is seen along the cut edges of the Zn-Al-Mg specimens. We thus conducted an electrochemical measurement of the cut edges and examined the corrosion products, in order to study the causes of the observed difference in corrosion resistance.

Fig.8 shows the cathodic polarization curves of the fractured sections of the cut edges before the corrosion tests, as well as after 20 and 40 cycles of CCT. For the post-Zn-coated material specimens, cathode reactions (dissolved oxygen reduction reaction) are well suppressed along the cut edges before the corrosion tests due to the electro-zinc plating and chromate film. However, as the number of CCT cycles increases, corrosion along the cut edges advances and the cathode current density increases dramatically. In contrast, the Zn-Al-Mg specimens exhibit higher rest potential than the post-Zn-coated material specimens because the steel substrate is exposed along the cut edges, and a relatively large cathode current density before the corrosion tests. Conversely, as the number of CCT cycles increases, the cathode current density drops.

Fig.9 shows the surface morphologies of the corrosion products formed on the fractured sections of the cut edges of the post-Zn-coated material and

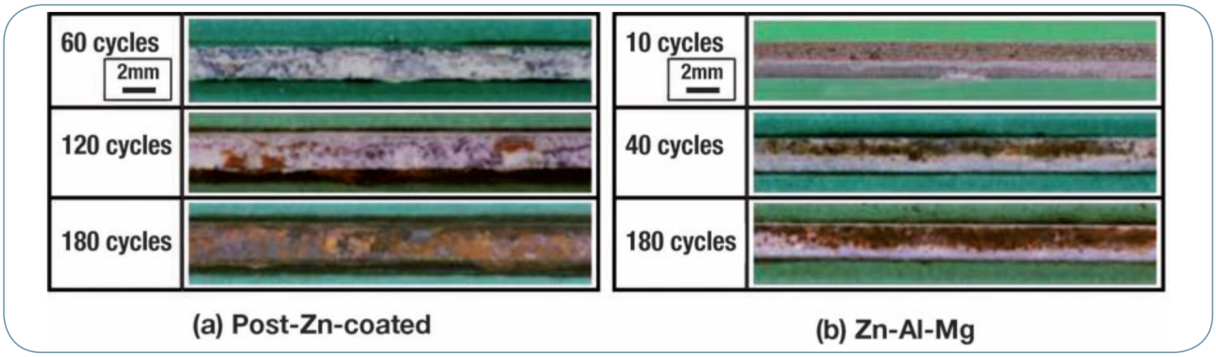


Fig. 6: Appearance of cut edges after CCT.

Zn-Al-Mg after 40 cycles of CCT. Fig.10 shows diffraction patterns of those corrosion products measured by using a micro-XRD. Rough granular porous corrosion products mainly composed of ZnO are formed on the cut edge of post-Zn-coated material specimens, whereas fine and dense corrosion products including $Zn_5(OH)_8Cl_2{\cdot}H_2O$ and ZnO are formed on the cut edge of Zn-Al-Mg specimens. Fig.11 shows the results of an EPMA analysis for the cross sections of the cut edges of the Zn-Al-Mg specimens after 40 cycles of CCT.

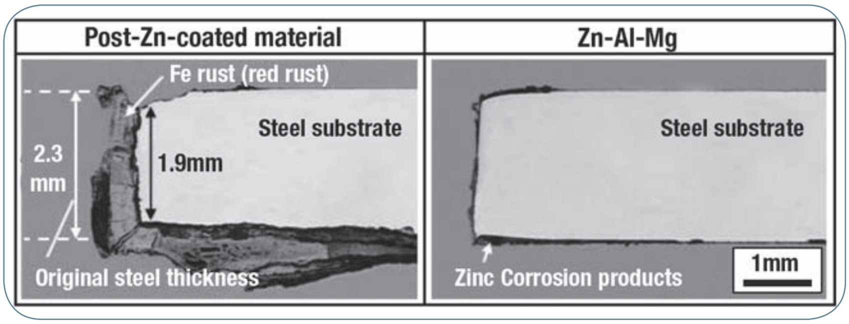


Fig. 7: Cross-sectional structures of cut edges after 180 cycles of CCT.

Zinc corrosion products containing Mg were observed as covering over the Fe rust (red rust) formed on the cut edges. Based on the observations above, we consider the reason why the cut edges of the Zn-Al-Mg specimens exhibit excellent corrosion resistance even though the steel substrate is exposed to be as follows: As corrosion advances, Zn and Mg eluted from the coating layer due to a galvanic action form fine Zn corrosion products on the cut edges, thereby suppressing cathode current density in the cut edges. As a result, elution of the coating layer around the cut edges

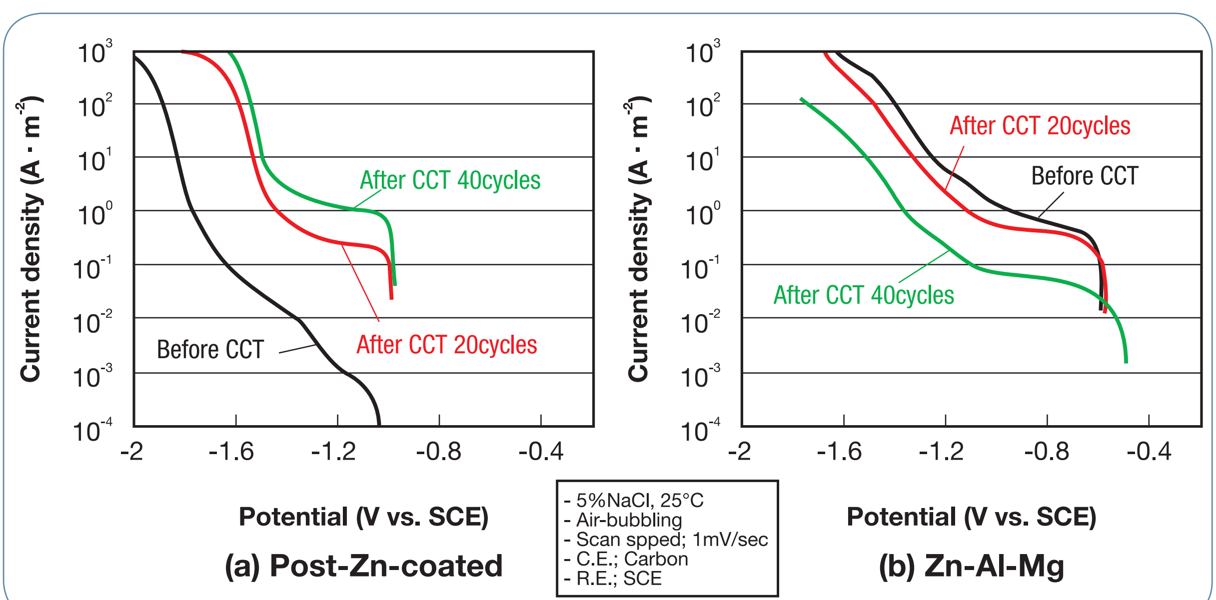


Fig. 8: Cathodic polarization curves of cut edges before corrosion test, as well as after 20 and 40 cycles of CCT.

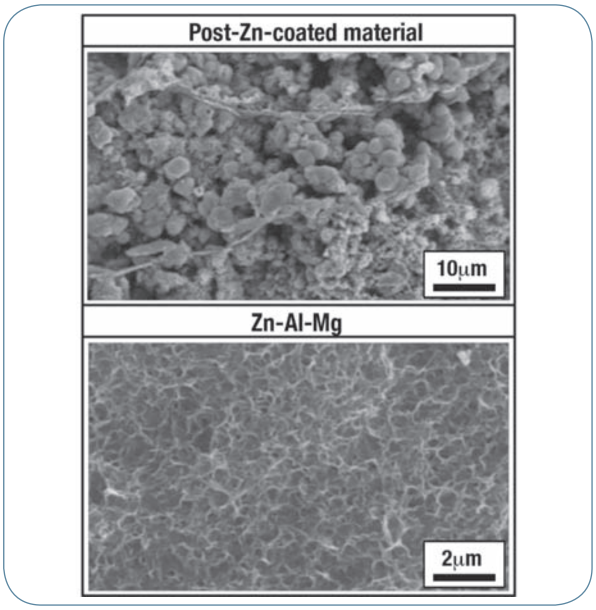


Fig. 9: Surface morphologies of corrosion products formed on the cut edges after 40 cycles of CCT.

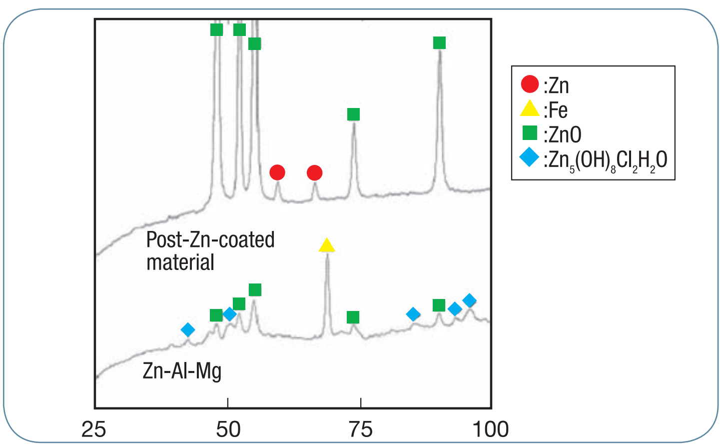


Fig. 10: X-ray diffraction patterns of corrosion products formed on the cut edges after 40 cycles of CCT.

was suppressed, leading to favorable corrosion resistance of the cut edges. Various past studies reported that Zn-Al-Mg exhibits excellent corrosion resistance in the flat portions because the formation of ZnO, which is considered to be porous and have little anticorrosive effect [6-9], is inhibited, and fine Zn corrosion products containing Mg and Al cover the coating layer [2-5]. The effect of the corrosion prevention mechanism similar to the flat portions can be seen also along the cut edges, where the steel substrate is exposed.

(3) Processed portions and spot-welded portions

Fig.12 shows the appearance of cup-shaped fabricated material after 180 cycles of CCT. Whereas the entire cup-shaped surface is covered by red rust for post-Zn-coated material, only little red rust is formed on the processed portion of Zn-Al-Mg specimens. Fig.13 shows the results of an EPMA analysis for the cross sections of the processed portion (cup shoulder) of the Zn-Al-Mg specimens after 40 cycles of CCT. Zinc corrosion products containing Mg and Al cover portions of the coating layer where cracks formed, thereby protecting the steel substrate and the coating layer of surroundings.

The Zn-Al-Mg specimens show some formation of red rust in the spot-welded portions, but little corrosion of the steel substrate is seen at such portions.

From the accelerated corrosion test results described above, it is confirmed that Zn-Al-Mg exhibits better corrosion resistance than post-Zn-coated material, even in portions where the steel substrate is exposed, such as cut edges, processed portions and spot-welded portions.

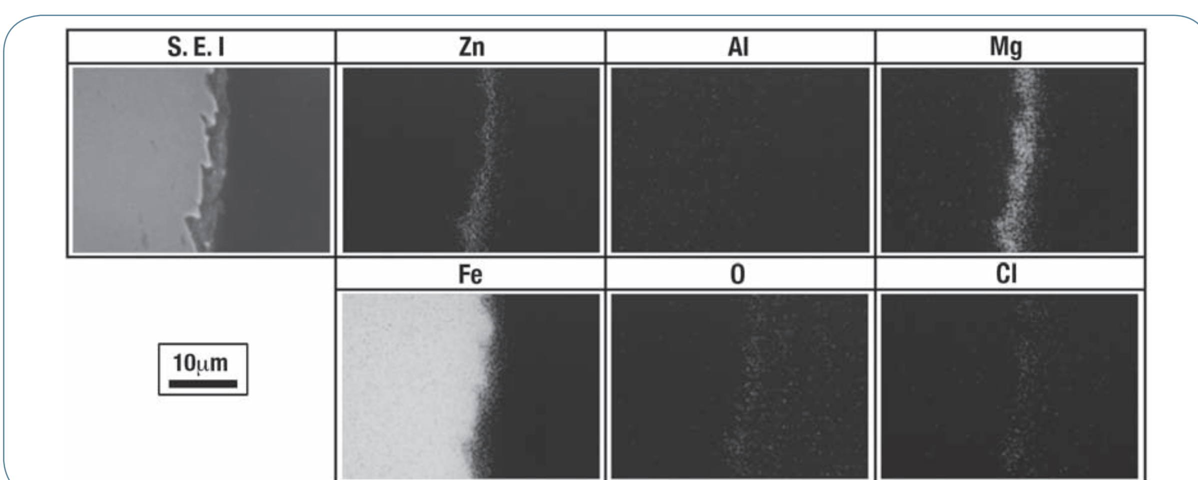


Fig. 11: EPMA analysis for cross section of cut edge of Zn-Al-Mg after 40 cycles of CCT.

Investigation of corrosion resistance of actual vehicle parts

Fig.14 shows the appearance of the automotive parts collected. The white rust is formed on each part, but no red rust is observed. Fig.15 shows the cross-sectional structures of the coating layers of each part. The coating layer of the radiator fan motor cover made of post-Zn-coated material, which we collected for comparison purposes, had completely corroded. In contrast, the radiator fan motor cover made of Zn-Al-Mg only showed a thin layer of corrosion product on the surface of flat portions; little corrosion was observed in the coating layer itself. Moreover, in the flat portions of the rear bumper bracket made of Zn-Al-Mg (collected from the same vehicle as the post-Zn-coated radiator fan motor cover), there was only about 4 μm of corrosion on the coating layer. The underbody where the rear bumper bracket is mounted is considered to be exposed to a more severe environment than the engine compartment where the radiator fan motor cover is mounted. Fig.16 shows the results of an EPMA analysis for the cross sections of the bent portions of the rear bumper bracket made of Zn-Al-Mg. Dense zinc corrosion products containing Mg and Al cover the surface of the coating, including portions where cracks formed in the coating.

From the results described above, it is confirmed that Zn-Al-Mg exhibits excellent corrosion resistance in an actual vehicle environment. Zn-Al-Mg is expected to exhibit excellent corrosion resistance, even used as automotive parts with portions where the steel substrate is exposed, such as the cut edges of 2.3mm thickness and spot-welded portions.

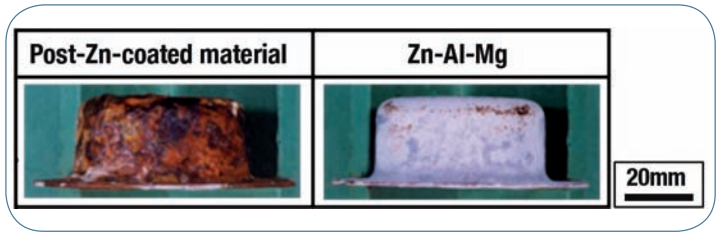


Fig. 12: Appearance of cup drawn specimens after 180 cycles of CCT.

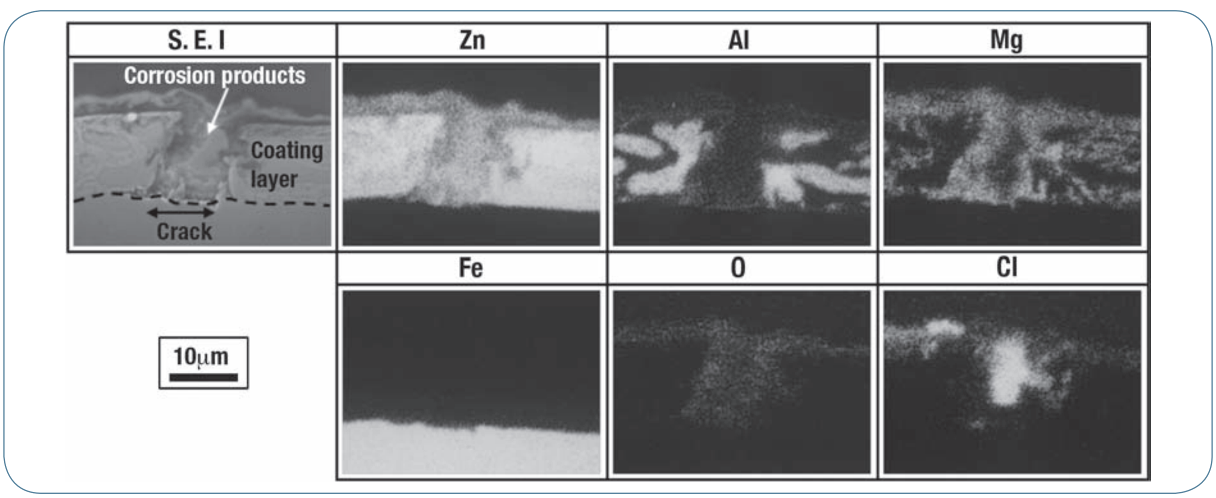


Fig. 13: EPMA analysis for cross sections of processed portion (cup shoulder) of Zn-Al-Mg specimens after 40 cycles of CCT.

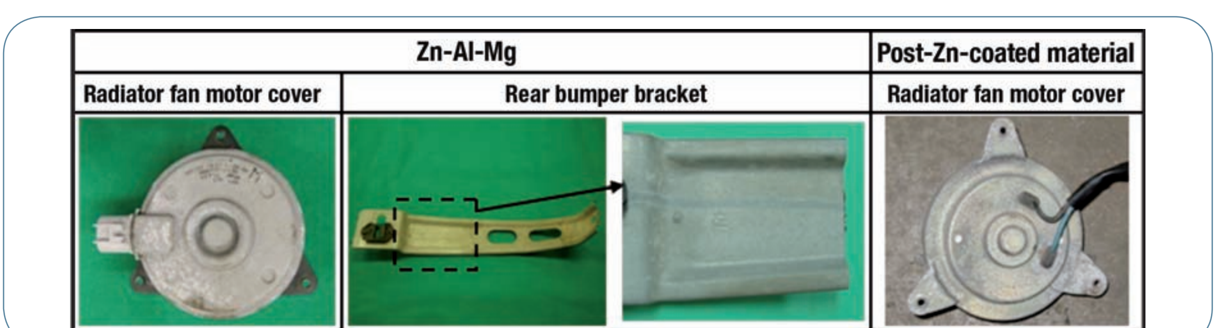


Fig. 14: Appearance of collected automotive parts.

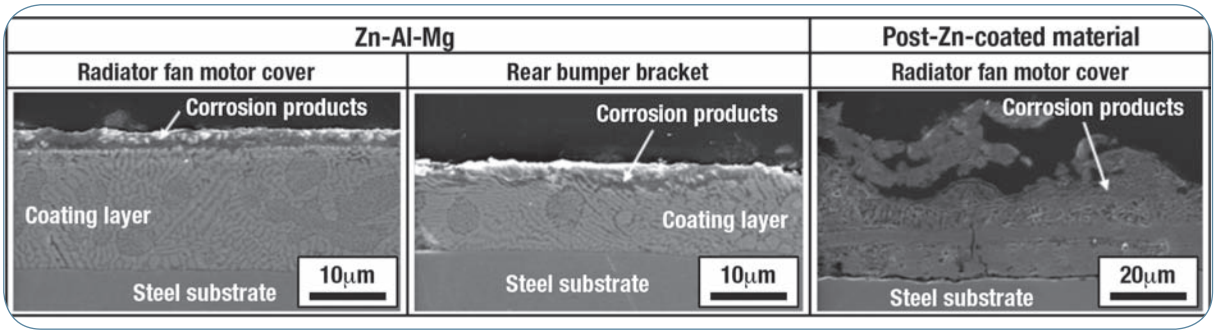


Fig. 15: Cross-sectional structures of coating layers on automotive parts.

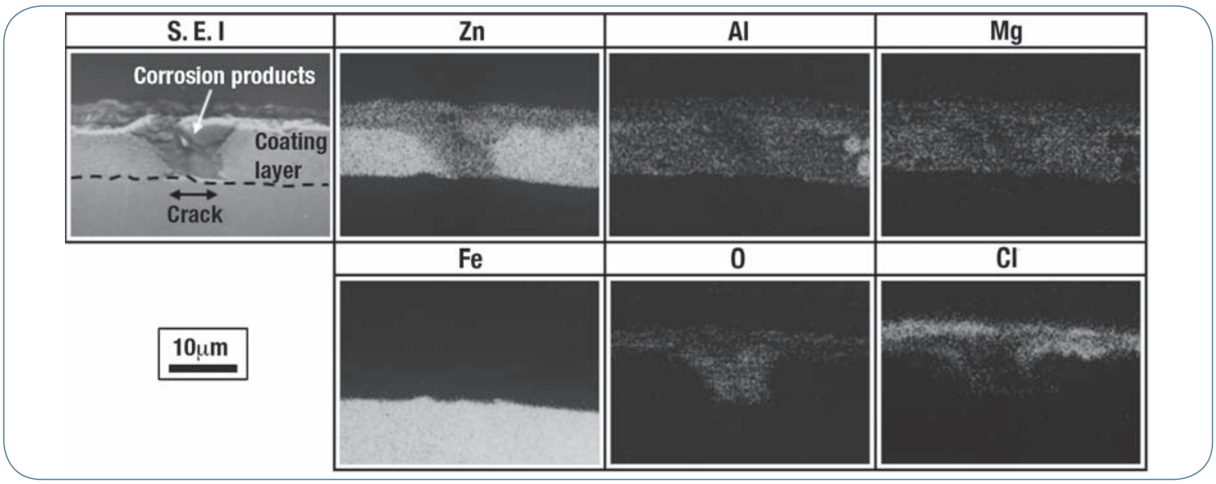


Fig. 16: EPMA analysis of corrosion products on the bent portions of the rear bumper bracket made of Zn-Al-Mg.

CONCLUSION

In this study, we compared the corrosion resistance of post-Zn-coated material and Zn-Al-Mg in accelerated corrosion test conditions, investigated the corrosion resistance of automotive parts made of Zn-Al-Mg in actual vehicle environment, and obtained the following results:

- In the accelerated corrosion tests, the Zn-Al-Mg specimens exhibited better corrosion resistance than the post-Zn-coated material specimens, even in portions where the steel substrate was exposed, such as cut edges, processed portions and spot-welded portions.
- Zn and Mg eluted from the coating layer due to a galvanic action formed fine Zinc corrosion products on the cut edges of Zn-Al-Mg, leading to reduced cathode current density in those portions. It was considered that the reduced cathode current density in turn suppressed elution of the coating layer around the cut edges, thus maintaining favorite corrosion resistance.
- In an actual vehicle environment, Zn-Al-Mg exhibited favorite corrosion resistance. Dense zinc corrosion products containing Mg and Al covered the surface of the coating, including portions where cracks formed in the coating.
- It was considered that Zn-Al-Mg is expected to exhibit excellent corrosion resistance, even used as automotive parts with portions where the steel substrate is exposed, such as the cut edges of 2.3 mm thickness and spot-welded portions.

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