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Hot-dipped Al-Mg-Si Coating Steel - Its Structure, Electrochemical and Mechanical Properties -

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Hot-dipped Al-Mg-Si coatings to alternate Zn and Zn alloy coatings for steel were examined on metallographic structure, corrosion resistance, sacrificial ability, formation and growth of inter-metallic compounds, and mechanical properties. Near the eutectic composition of quasi-binary system of Al-Mg_2Si, very fine eutectic structure of α-Al and Mg_2Si was obtained and it showed excellent corrosion resistivity and sacrificial ability for a steel in sodium chloride solutions. Formation and growth of Al-Fe inter-metallic compounds at the interface of substrate steel and coated layer was suppressed by addition of Si. The inter-metallic compounds layer was usually brittle, however, the coating layer did not peel off as long as the thickness of the inter-metallic compounds layer was small enough. During sacrificial protection of a steel, amount of hydrogen into the steel was more than ten times smaller than that of Zn coated steel, suggesting to prevent hydrogen embrittlement. Al-Mg-Si coating is expected to apply for several kinds of high strength steels.

Keywords : *Hot-dipped coating, Al-Mg-Si alloy, corrosion resistance, sacrificial protection, inter-metallic compounds, high strength steel, hydrogen embrittlement*

1. Introduction

Zinc and zinc alloy coatings for steel has been widely used, because of its high corrosion resistance and excellent sacrificial ability for underlying steel. In recent years consumption of zinc, not only for galvanized steel but also for other usage, rapidly increased especially in China. Clarke Number of zinc is known as 0.004% and it is smaller than that of nickel and copper as 0.04%. It is also reported that the reserve-production ratio of zinc is about 22years.[1)] So we can not say for zinc as an abundant resource material.

To alternate zinc for steel coating, my research group started to use aluminum alloys and this is supported by the ministry of education and science for five years project.[2)] The final goal of this project is that to develop a new aluminum based hot-dipped alloy coating which has almost same level to zinc and zinc alloy coatings of corrosion resistivity and sacrificial ability, to apply the coating for high strength steels and not to change present hot dip processes drastically. This paper reports the results of the project for recent two and half years for fundamental researches.

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2. Search for optimum alloy composition

It is well known that aluminum and Al-Si coated steel have excellent corrosion resistivity and high temperature oxidation, however, their ability for sacrificial action is not enough to protect underlying steel. Magnesium was considered as an alloying element to add sacrificial ability, and from metallurgical reason will be described latter, silicone was also added. By simultaneous vacuum evaporation of magnesium and aluminum or magnesium and Al-Si mother alloy, evaporated coatings having wide composition range were obtained and electrochemical properties, such as polarization curves and galvanic couple currents were measured.

From preliminary experiments,[3)] it was found that increasing the magnesium content lowered the corrosion potential and increased sacrificial ability. Fig. 1 shows effect of silicone content on the polarization curves of Al-10%Mg-x%Si (in mass%) alloys in 0.5 M Na_2SO_4 + 0.1 M NaCl solution. It is seen from the polarization curves that the corrosion potential ranged in -1.1 to -1.3 V (vs Ag/AgCl electrode, SSE) and passive currents ranged in 0.1 to 1 μA/cm^2. The corrosion potential was shifted more negative and passive current was increased by increasing silicone content. The passive current increased above -0.6 V.

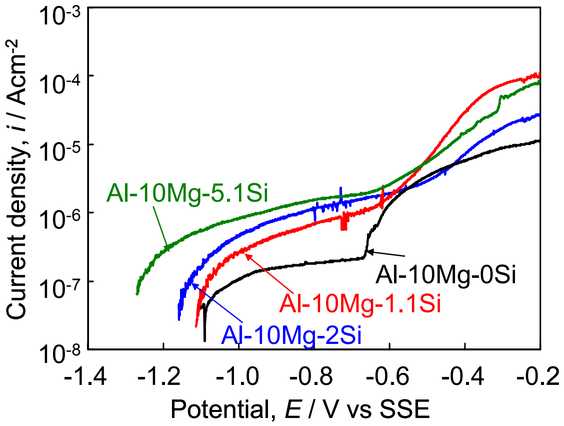

Fig. 1. Anodic polarization curves of Al-10Mg-×Si coated steels in 0.5M Na_2SO_4+0.1M NaCl.

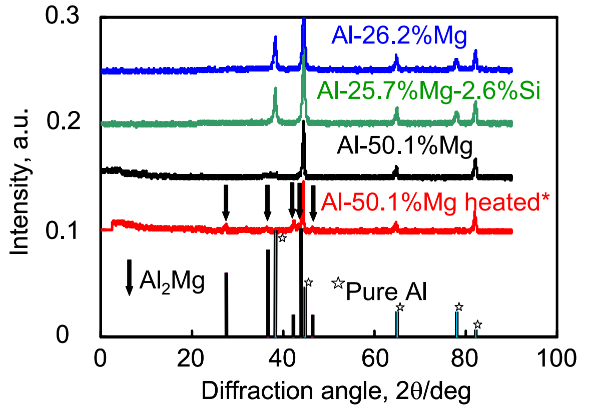

Fig. 2. XRD results of as deposited and heat treated Al-Mg and Al-Mg-Si alloys.

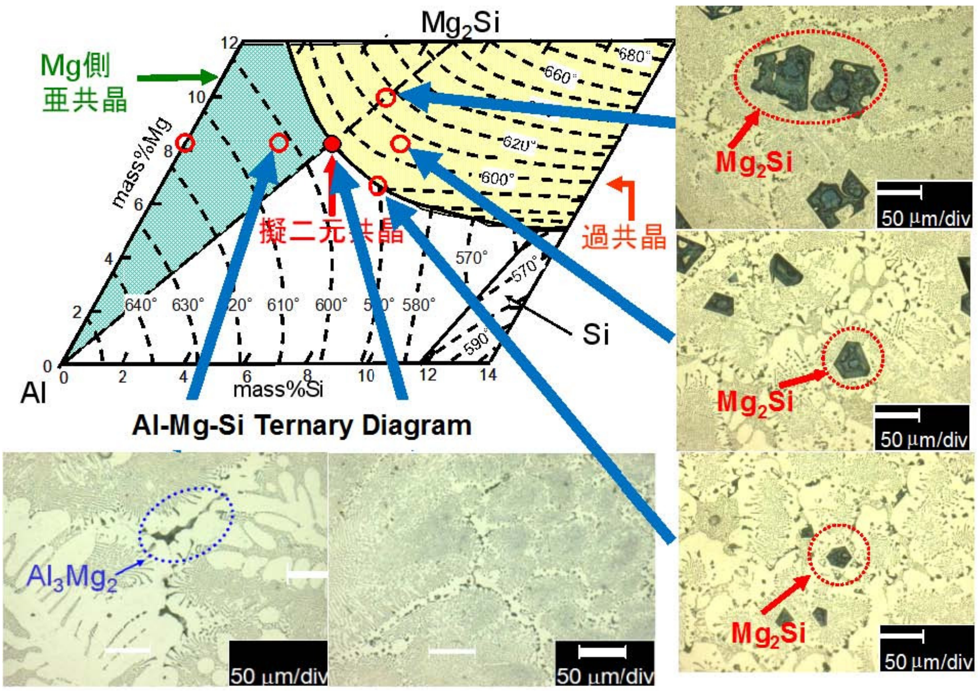

Fig. 3. Al-Mg-Si ternary phase diagram and typical micro-structures. At the eutectic composition of quasi-eutectic system of Al-Mg_2Si, almost all the phases composed of fine eutectic structure.

Pitting corrosion or localized dissolution of evaporated coating was hardly observed after the polarization measurements.

Results of X-ray diffraction (XRD) analysis for evaporated coatings are shown in Fig. 2. It is interesting that all the evaporated coatings, even high magnesium content alloys, show only the peaks belonging to *α*-Al, and Al-Mg compounds peaks appear after heat treatment. This suggests that the evaporated coating has homogeneous structure like amorphous alloys so pitting corrosion or localized corrosion hardly observed.

Based on the results of polarization measurements and corrosion tests, primary precipitated massive Al_3Mg_2 and Mg_2Si preferentially dissolved and result localized corrosion, and eutectic fine structure of *α*-Al and Mg_2Si dissolved homogeneously. Phase diagram of Al-Mg-Si system and typical micro-structures are shown in Fig. 3. At the quasi-eutectic composition of Al-Mg_2Si system, almost all the phase composed of fine eutectic structure. Anodic polarization curves of casted and hot-dip coated steel almost similar shown in Fig. 1, however, they showed rapid current increase above -0.6 to -0.5 V indicating start of localized corrosion.[4)]

After X-cut corrosion tests of evaporate coated steel and hot-dip coated steel in 0.5 M Na_2SO_4 + 0.1 M NaCl solution for 20 h and 1 week, no red rust was observed on the steel surface. Galvanic couple corrosion test for bare steel and evaporate coated steel, area ratio was 1:10, in the same solution for 1 week resulted no red rust on the steel surface indicating complete sacrificial action. Stable sacrificial current was observed and the coating dissolved almost uniformly.

3. Effect of Micro-structure on corrosion resistance and sacrificial action

In a casted alloy and hot-dip coated layer, primary precipitated massive Al_3Mg_2 and Mg_2Si preferentially dissolved and they caused localized corrosion.[4)] Furthermore, hot-dipping bath contains considerable amount of iron which dissolved into the melt bath during dipping. Iron precipitates in the coating layer as Al_3Fe or Al-Fe alloy which acts as cathode site for corrosion reaction. Around these precipitates, aluminum depletion leads to precipitate massive Al_3Mg_2 and Mg_2Si. After the corrosion test, Al_3Fe or Al-Fe alloy remained in the coating and preferential dissolution was observed around these precipitates. It was confirmed that all the phases such that Al_3Mg_2, Mg_2Si, Al_3Fe and also quasi-eutectic structure, should be as fine as possible to prevent localized corrosion of coating layer. This indicates importance for controlling the micro-structure of coating layer.

As a test for sacrificial action of quasi-eutectic alloy coating, Al-8.2%Mg-4.8%Si was used for X-cut test and galvanic couple test in a solution of 0.5 M Na_2SO_4 + 0.1 M NaCl for 1 week. No red rust observed on the bare steel surface and the galvanic couple current continued between 60 to 90 $\mu A/cm^2$ for the steel. Zinc has excellent ability to supply large anodic current to protect a wide surface area of steel such like a sacrificial anode for cathodic protection of structural materials, however, Al-Mg-Si alloy coating has enough ability to protect underlying steel when the coating scratched or it has native defects. Moreover, the corrosion potential of zinc coated steel under sacrificial action is usually below -1.0 V where hydrogen evolution and entry into the underlying steel will occur. On the other hand, that potential for Al-Mg-Si alloy coated steel usually ranged between -0.6 to -0.75 V. Since the amount of hydrogen into a steel is controlled by the electrode potential, so that for Al-Mg-Si alloy coated steel can be expected several orders of magnitude smaller than zinc coated steel. Using a zinc coated and Al-Mg-Si coated steels with a scratch in wet and dry cyclic corrosion condition, amount of hydrogen permeation current against the corrosion potential is shown in Fig. 4. The alloy composition of evaporated coating used is Al-12%Mg-3%Si, a little bit different from the quasi-eutectic composition and the corrosion potential is much negative than usual, even so the amount of hydrogen entered is five times smaller than that of zinc coated steel.[5)] This suggests that Al-Mg-Si coating can be used for high strength steels without risk or more safely use for hydrogen embrittlement.

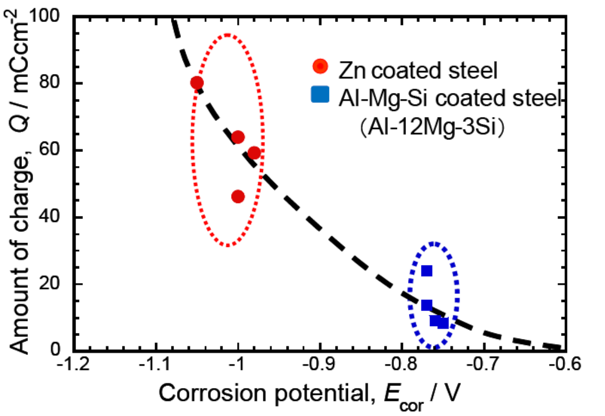

Fig. 4. Amount of hydrogen entered into substrate steel during wet and dry corrosion cycle. Both coated steels scratched 1 mm width and 0.2 µL of 0.1 N NaCl solution was placed on the scratch.

4. Control of reaction layers at the substrate and coating layer

It is well known that Al-Fe inter-metallic compounds or Al-Fe alloy layer formed and developed rapidly and these layers are usually loose the mechanical ductility of coated layer and causes flaking of the coated layer. It is also known that addition of silicone decreases the alloy layer growth by forming Al-Si-Fe layer prior to the alloy layer formation. Similar effect was observed for hot-dip Al-Mg-Si alloy coating. Reaction layer thickness with time is shown in Fig. 5, where pure iron was dipped into pure aluminum bath and Al-8.2%Mg-4.8%Si bath at 973 and 923 K for 2 to 60s. In case of Al-Mg-Si alloy, the reaction layer thickness largely suppressed and lowered the growth rate.[6)]

Temperature of the melted alloy bath, time for immersion and cooling rate of coated steel are also important factors for the structure of the coating layer. Fig. 6 shows

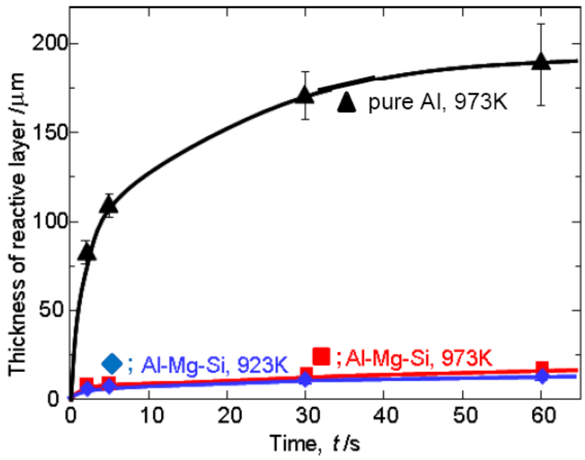

Fig. 5. Thickness of the reaction layer formed on pure Al and Al-Mg-Si coating

a typical example of the effect of cooling rate on the structure. In case of fast cooling rate, massive Mg_2Si and needle-shaped Al-Fe compound disappeared and they dispersed as fine particles.

5. Mechanical properties and flaking mechanisms

Crack growth and flaking of coated layer on a steel is important characteristics for mechanical forming coated steel. The author's group developed methods for continuous observation of deforming process under optical microscope (OM) and scanning electron microscope (SEM).

SEM observation for bending Al-8%Si hot-dip coated steel is shown in Fig. 7 where white triangles (Δ) indicate preexisted cracks in the reaction layer and black triangles (▲) indicate newly formed cracks by deformation.[7] By deformation of bending, number and width of cracks increased, however, these does not act as an origin of crack of coated layer. For the Al-8%Si coated steel, no apparent crack was observed after 180 degree bending.

Fig. 8 shows the result of OM observation for Al-Mg-Si hot-dip coated steel.[7] In this case no preexist crack observed in the reaction layer. At the lateral strain of 4.6%, vertical cracks observed in the reaction layer then several cracks were coupled by a lateral crack. Flaking stats from this coupled crack when the lateral cracks coupled much more and opened widely. It is also confirmed that no cracks in the coating layer originated from the vertical cracks in the reaction layer even when the later crack opened widely.

Crack initiation for both directions depended upon the thickness of the reaction layer, as shown in Fig. 9. For the initiation of horizontal cracks which will result flaking or peel off of coating layer, reducing the reaction layer thickness increases the strain to start horizontal crack initiation. In other words, decreasing the thickness of the

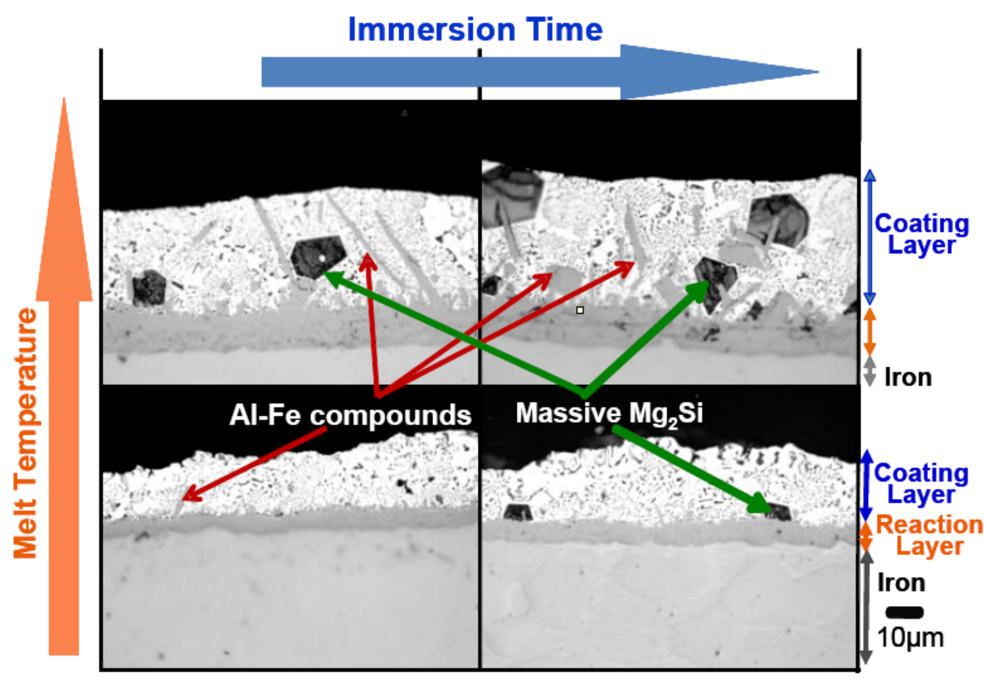

Fig. 6. Effect of melt temperature and immersion time on the morphology of coating layer

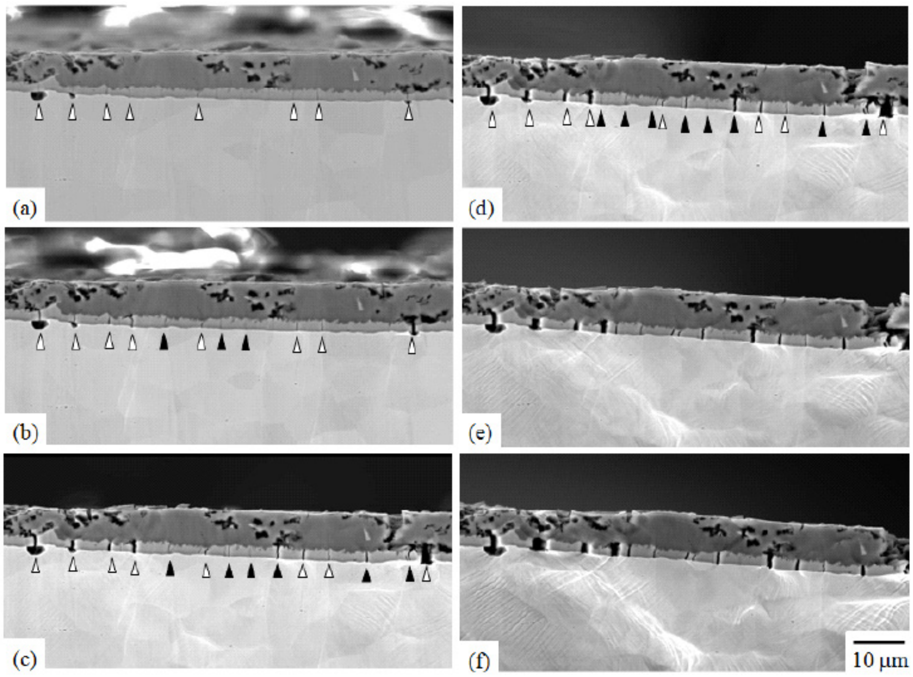

Fig. 7. Cracks formation and propagation in Al-Fe reaction layer. (a) before bending, Δ indicates preexist crack, (b) bending angle θ = 4.2º, (c) θ = 12.7º, (d) θ = 25.0º, (e) θ = 40.6º, and (f) θ = 67.4º. (SEM observation)

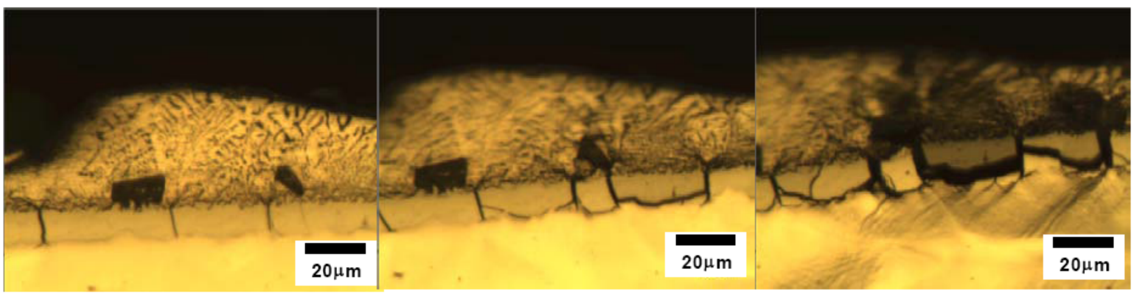

Fig. 8. In the initial stage of deformation, vertical cracks start in the Al-Fe layer, then they joined by new horizontal cracks. Lateral strains are 4.6%, 5.6% and 11.2%. (Optical microscope observation)

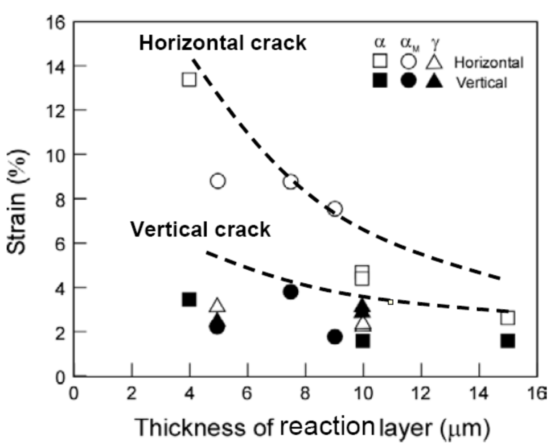

Fig. 9. Dependence of reaction layer thickness on the starting strain of vertical and horizontal (lateral) crack

reaction layer improves the flaking resistivity.

6. Application to high strength steels and continuous coating line

One of main goal of this project is application of Al-Mg-Si coating to high strength steels. Some alloying elements in high strength steel is known to make difficult for galvanizing of zinc, so similar difficulty may occur for hot-dip coating process of Al-Mg-Si alloy coating. Investigation on this subject is going on in author's group. As mentioned before, suppression of hydrogen entry into the substrate steel during sacrificial action of Al-Mg-Si alloy coated steel should be one of superior advantages of this coating over zinc coating.

Another main goal of this project is that the production process for Al-Mg-Si coating should not change drastically from present continuous galvanizing line. Slight modified process is considered and the process should involve the heat treatment of high strength steels to simplify the production. Production process is too complicated to investigate and to analyze by a research group belonging to universities, collaboration with steel makers will develop new fields.

7. Concluding remarks

New hot-dip coatings of Al-Mg-Si alloy is investigating to alternate zinc and zinc alloy coatings. This is expected to have equivalent level of corrosion resistance and sacrificial ability for underlying steel. Al-8.2%Mg-4.8%Si alloy is one of candidate for this purpose and its moderate sacrificial action prevents hydrogen entry into the substrate steel much smaller than that of zinc coated steels. The investigation just started so there remains many problems to be solved. Environmental demand for auto-vehicles enforces to product lighter auto-bodies, amount of aluminum used for auto-body will increase much more. Steels have to be used mixed with aluminum parts, in this case, aluminum alloy coating will solve the problems on conversion coatings or joining with aluminum.

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