

Zinc Alloy Coated Steel Wire with High Corrosion Resistance

Satoshi SUGIMARU*¹
Naoshi HIKITA*³
Atsuhiko YOSHIE*⁴

Satoru TANAKA*²
Hiroshi OHBA*³
Seiki NISHIDA*⁵

Abstract

To improve the corrosion resistance of Zn coating and Zn-Al alloy coating for steel wires, Zn-Al-Mg alloy has been developed. In this study Mg was added in Zn-Al alloy of double hot-dip process, and we found that 2mass% Mg was desirable for manufacturing. Zn-11mass% Al-2mass% Mg coating of which thickness is 200g/m² remains 60% after 3,000 hours salt spraying test. We developed “High corrosion resistance Zn alloy coated steel wire with high friction” coated by newly developed Zn-11%Al-2%Mg alloy. A net made by “High corrosion resistance Zn alloy coated steel wire with high friction” reveals high friction that prevents a man from slipping on the riparian.

1. Introduction

Zn coating has been used since long ago for anti-corrosion treatment of steel wires. Al is added to Zn to improve the corrosion resistance of Zn coating. Zn-5mass%Al (mass% is hereinafter simply stated as %), and Zn-10%Al containing more AL to improve the corrosion resistance, are often used¹⁻⁶⁾. Flux is usually used in Zn coating, but no flux suited for Zn-Al alloy direct coating of steel wires in industrial manufacture is available. For this reason, a double hot-dip process in which Zn-coated steel wires are recoated in a Zn-Al alloy bath is often used.

As an attempt to further improve the corrosion resistance of Zn-Al alloy coating, Mg is added⁷⁻⁹⁾. In this study, Mg was added to a Zn-Al alloy bath in a double hot-dip process to produce steel wires coated with Zn-Al-Mg alloy to examine the property of the alloy coat. As a result, it was found that it is possible to easily produce Zn-Al-Mg alloy coated steel wires and that the corrosion resistance of this alloy was much higher than that of Zn-Al alloy coat. Making use of the high corrosion resistance of this alloy coat, the authors commercially produced coated steel wires having high friction, i.e., steel wires whose surface is covered with a rough, unsmooth alloy coat. This new type of steel wires is widely used as wire netting for revetment, minimizing the danger of slipping of people who step on

the banks revetted with it.

2. Development of High Corrosion-Resistant Coat Components

2.1 Test method

2.1.1 Alloy coating

For this experiment, the authors used specimens of an annealed low-carbon steel wire, having a diameter of 4 mm and coated with Zn at a rate of approx. 300 g/m², and having an Fe-Zn layer of 12 μm. The components of the low-carbon steel are listed in **Table 1**. This Zn-coated steel wire specimen was dipped for further coating in a 450°C Zn-Al-Mg alloy bath for 10 seconds and was taken out of the bath vertically. The specimen was then air-cooled and, upon solidification completion, was water-cooled. For comparison, a steel wire specimen coated with a Zn-10%Al alloy in a Zn-10%Al alloy bath was prepared by a similar process.

2.1.2 Microstructure observation of coat layer

The specimen showing its section perpendicular to its longitudi-

Table 1 Chemical compositions of the steel (mass%)

C	Si	Mn	P	S
0.036	0.3	0.27	0.02	0.01

*1 Osaka Sales Office
*2 Niigata Sales Office
*3 Kimitsu Works

*4 Steel Research Laboratories
*5 Kimitsu R&D Laboratories

nal axis was set in resin, and the section was mirror-finished by grinding. Secondary electron images (hereinafter, SEI) of the section were photographed by EPMA. Zn, Al, Mg and Fe were mapped with an electron beam of 3 μm in diameter, used as a probe.

2.1.3 Evaluation of corrosion resistance

A cut length of the specimen, approximately 120 mm long, was degreased, and had its weight measured by an electronic balance down to 1 mg. The both ends of the cut length were then sealed such that the part to be examined was 100 mm. The sample thus prepared was subjected to a salt spray test (hereinafter, SST) performed under conditions shown in Table 2 in accordance with JIS. After SST, the sample was immersed in a solution shown in Table 3 for 5 minutes, and consequent corrosion products were removed in running water. After removal of the corrosion products, the sample was weighed again. Weight decrement was determined by the difference between the weights before and after SST.

For the removal of the corrosion products, the authors did not follow a method generally performed with a 200g/l CrO₃ aqueous solution at 80°C, because even an uncorroded part of the coat is melted out in this case of Zn-Al-Mg coat. Nor did they follow a method performed with an ammonium bichromate aqueous solution because this method, although capable of slowly removing corrosion products only, requires an extended time during which ammonia is produced.

2.2 Experiment results and discussions

2.2.1 Structure of coat

2.2.1.1 Structural change due to Mg addition

Fig. 1 shows the appearance of steel wires coated in an alloy bath of Zn-10%Al, Zn-11%Al-1%Mg, and Zn-11%Al-3%Mg, respectively. The wires coated in an Mg-added alloy bath have a similar glossy appearance to that of the wire coated in a Zn-10%Al alloy bath.

Table 2 Salt spraying test conditions

Concentration of salt	4.8-5.15%
pH	6.8-6.9
Spraying quantity	1.7-1.8 l/min
Temperature	35°C

Table 3 Conditions to remove corrosion products

Solution	300g CrO ₃ in water solution 1 liter
Temperature	Room temperature (25°C)
Dipping time	5 minutes

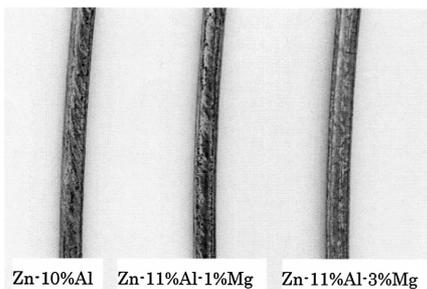


Fig. 1 Appearance of coated wires

Fig. 2 shows SEI and element distributions in the coated wire sections. In the photographs of the Zn-10%Al sections, the region that appears black is a layer where much Al are contained and where α-phase crystallization took place initially in the process of solidification and crystals grew as granular crystals. The region that appears white in the photographs is a layer in which the remainder in liquid phase solidified to α-phase and β-phase Zn eutectic crystals at eutectic temperatures. At a eutectoid temperature, the α-phase crystals develop into a structure where Zn and Al are separated. This Zn-10%Al coated wire is well workable. In the alloy of the Fe-Zn phase that was originally present in the coat, Al concentration is increased up to about 30 percent, because the intermetallic compound is changed from Fe-Zn to Fe-Al, and Zn is solidified into Fe₄Al₁₃. The intermetallic compound formed by Zn-Al coating is workable better than that formed by Fe-Zn coating¹⁾. The high Al concentration region where the initial α-phase crystals are solidified and are thereafter transformed is hereinafter referred to as an α-layer.

When 1%Mg is added to the Zn-Al bath, the consequent solid solution is a set of three layers, consisting of a coarse layer in which visually black Al concentration is high, a coarse region where visually white Zn concentration is high, and a fine layer. The region where visually white Zn concentration is high is of β phase (Zn) which is further crystallized in succession to the initial α phase, and becomes coarse as crystals grow. Probably, the solidification is completed when the liquid phase remaining after the crystallization of α and β ends in a ternary eutectic (Zn/Al/MgZn₂). The crystallized α phase is probably transformed at a eutectic temperature as in Zn-10%Al.

When 3%Mg is added, the consequent solid solution is a set of three layers, consisting of a coarse α layer in which visually black Al concentration is high, a coarse region consisting of Zn and Mg that appear gray, and a fine layer. In the visually gray region, crystallization might have taken place in an early stage of solidification

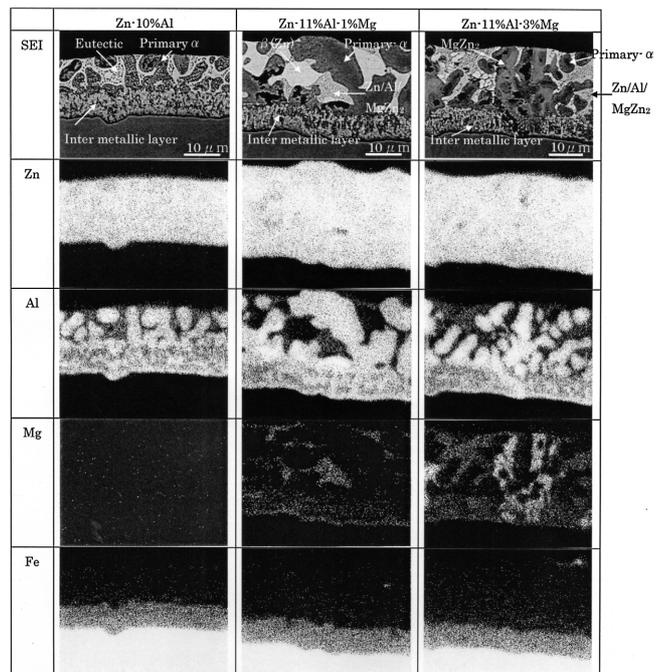


Fig. 2 SEI and chemical elements image of the samples

and crystal growth might have succeeded to it, to result in $MgZn_2$ as presumed from the results of the chemical composition analysis and from the phase of the intermetallic compound in the Zn-Mg binary condition images. Further presumably, the remainder in a liquid phase after the crystallization of α and $MgZn_2$ becomes a ternary eutectic (Zn/Al/ $MgZn_2$) to complete the solidification. No Mg was found in the α layer where Zn might have been crystallized out of the α phase at a eutectic temperature after completion of the solidification. In the case where 1%Mg is added, Mg exists in $MgZn_2$ in the ternary eutectic. In the case of 3%Mg, Mg exists in the $MgZn_2$ in the ternary eutectic and in the coarse $MgZn_2$ crystal produced in an early stage of solidification.

Fig. 3 shows the percentages of the α layer (primary- α in the figure), the β layer (Zn) (β (Zn) in the figure) that crystallized and grew coarse in an early stage of solidification or $MgZn_2$ (Zn/Al/ $MgZn_2$ in the figure), determined in the coat, excluding the part that was the Fe-Zn intermetallic compound in the Zn-coated wires in the SEI photographs. In the region which was in an Fe-Zn intermetallic compound phase in the original coated wire, Mg is presumed from our analytical results to be present in the solid solution at a nearly same concentration as in the coating bath.

2.2.1.2 Structural changes by cooling method

Fig. 4 shows the structures of the Zn-10%Al and Zn-11%Al-3%Mg coated wires, water-cooled before solidification completion (hereinafter called "water-cooled wires") and air-cooled, solidified, and then water-cooled (hereinafter called "air-cooled wires"). In the Zn-10%Al coated wire, when water-cooled, crystals in α phase abounding in Al initially grow as columnar crystals, whereas, when air-cooled, they grow as granular crystals. In either of these cases,

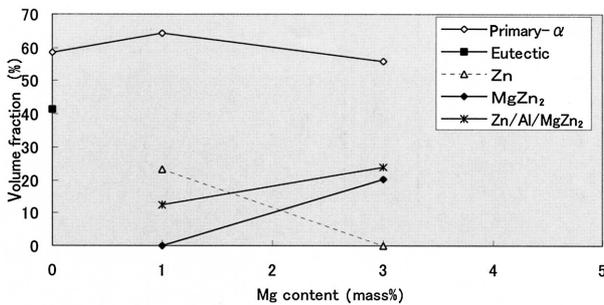


Fig. 3 Influence of Mg to volume fraction of phase in coating metal

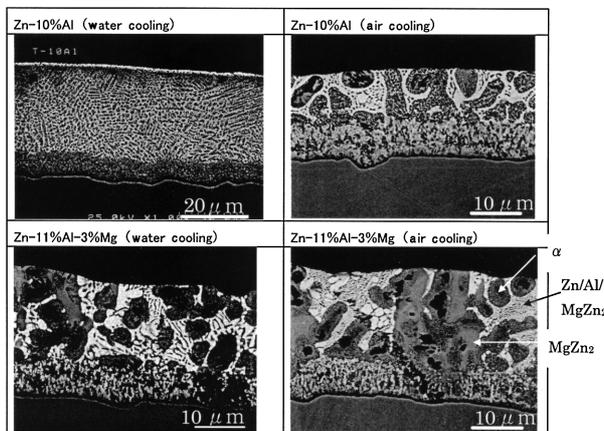


Fig. 4 Cross-sectional structure of coated wires (EPMA-SEI)

the remaining solid solution is Zn and α phase at a eutectic temperature, and the α phase undergoes transformation at a eutectoid temperature.

In the cases where Mg is added, the α layer of the water-cooled wire is granular and is smaller than that of the air-cooled wire. $MgZn_2$ shows the same result as α layer. It presumably means that no temperature gradient at which $MgZn_2$ and initial crystals in α phase grow as columnar crystals existed in this cooling. But the temperature of the solid solution in liquid phase declined to the eutectic temperature or lower and the eutectic reaction progressed before the start of the growth of granular crystals, to result in the spread of the eutectic region.

2.2.2 Difference in corrosion resistance of coat dependent on its composition

Fig. 5 shows the results of our evaluation by 250-hour SST of the corrosion resistance of wire coats having a varied composition. Zn-coated and Zn-10%Al-coated wire samples were water-cooled at a temperature near the solidification temperature immediately after the samples were taken out of the coating bath. The water-cooled Zn-10%Al coated sample corroded more, showing a lower corrosion resistance, than the sample having the same Zn-10%Al composition but air-cooled. This result agrees with the finding by Ochiai et al.¹⁾

Addition of Mg decreases weight reduction by corrosion and increases corrosion resistance. Comparison of the weight reductions by corrosion between the 1%Mg and 3%Mg added samples shows little difference. The addition of Mg improves corrosion resistance probably by formation of $MgZn_2$. Even the corrosion resistance of the Zn-11%Al-1%Mg coat, where large coarse $MgZn_2$ crystals in an early stage of solidification are not seen, shows little difference from that of the Zn-11%Al-3%Mg, and this fact is thought to be indicative that even fine $MgZn_2$ produced by ternary eutectic crystallization has a sufficient corrosion-resistant effect, independent of its form.

2.2.3 Zn-11%Al-2%Mg
The difference of the effect of Mg upon corrosion resistance by 1% and 3% is small as discussed above. Then, the authors prepared steel wire samples 2.3mm-coated with Zn-11%Al-2%Mg, using an Mg addition by 2% for the purpose of decreasing the weight of large coarse $MgZn_2$ crystals that are presumed to be produced at an early stage of solidification, and applied somewhat stronger air cooling for the purpose of increasing the weight of eutectic $MgZn_2$.

Fig. 6 shows structural element images of this wire. The α layer (Primary- α in this figure) contains fine particles but scarcely contains large coarse $MgZn_2$, a product of crystallization probably in an early stage of solidification. Nor it contains coarse Zn, another product of crystallization probably in an early stage of solidification.

The weight of this sample was measured in the same way as the measurement of the slowly air-cooled 1%Mg- and 3%Mg-added samples, and compared the results of the former with those of the

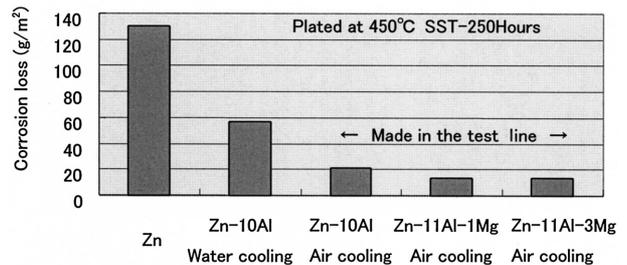


Fig. 5 Corrosion loss of coated wires

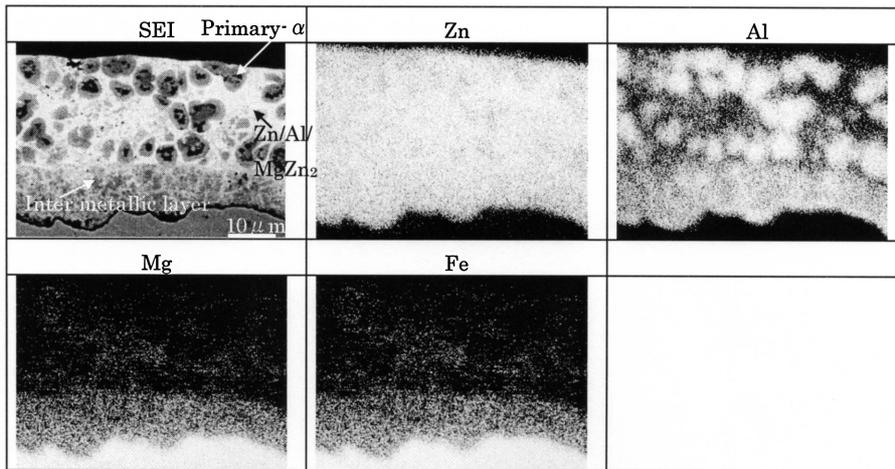


Fig. 6 SEI and chemical element image of the Zn-11%Al-2%Mg coated samples

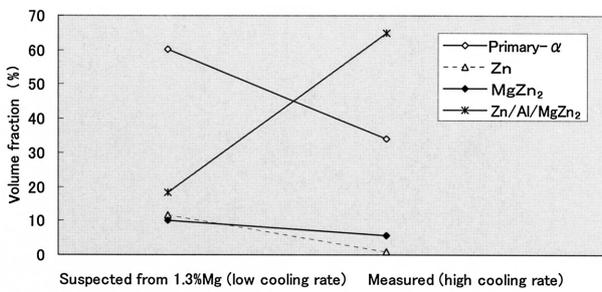


Fig. 7 Influence of cooling to volume fraction of phase in coating metal

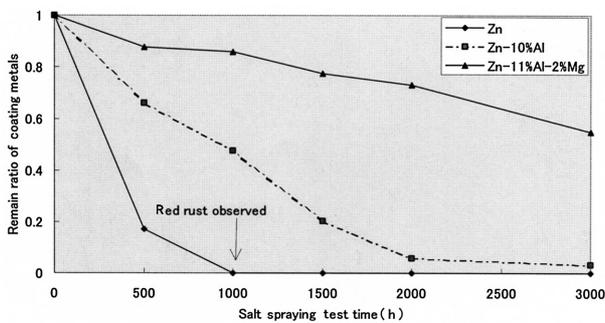


Fig. 8 Remain ratio of coating metals after salt spray test

latter estimated from the results of the 1% and 3% additions of Mg, as shown in Fig. 7. The structure mostly comprises an α layer and eutectic, and the α layer is slightly less than that in the slowly air-cooled sample, probably denoting its partial change to eutectic.

This wire sample was subjected to an SST for up to 3000 hours. After the SST, corrosion product was removed, and the ratio of the remainder of the coat (= coat weight minus corrosion loss) to the original coat weight was determined as shown in Fig. 8. The coat weight consisted of Zn and Zn-10%Al at about 300 g/m² and Zn-11%Al-2%Mg at 200 g/m². As seen from this figure, the Zn of the coat fully changed to corrosion product in 1000 hours, leaving no layer of the original coat. The Zn-10%Al also mostly changed to corrosion product in 2000 hours, leaving almost no layer of the original coat. By contrast, the Zn-11%Al-2%Mg lost its weight only by

0.4 of the original coat even in 3000 hours, leaving 0.6 of the original coat as seen from the figure.

3. Development of High-Friction Coated Wire

3.1 Coated wire having coat surface roughness

Coated steel wires were developed whose coat surface has fine irregularities so that the wires, when used as wire netting, provide a non-slip surface for people who step on them. The corrosion resistance of the coated steel wire having irregular, rough coat surface is nearly halved when exposed to salt spraying, but the use of a Zn-Al-Mg alloy for the wire coating improved the wire's corrosion resistance to a level higher than the corrosion resistance of Zn-10%Al alloy coated steel wires having a smooth surface. Fig. 9 shows an appearance and the measured roughness of the coated wire having the surface irregularities. The advantages of the coated steel wire having minute surface roughness include the non-necessity of resin application to it for increasing wire net friction, as well as wire workability for making wire nets in usual way.

3.2 Evaluation of wire net anti-slip characteristic

A procedure for evaluating the friction coefficient of steel wires

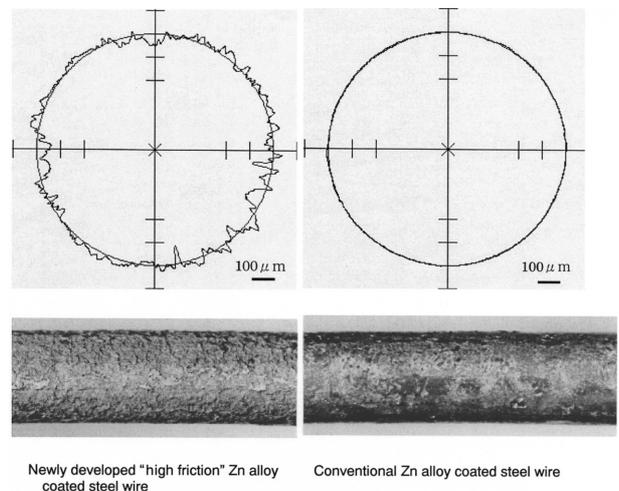


Fig. 9 Appearance and roughness of newly developed high friction Zn alloy coated steel wire and conventional Zn coated steel wire

is specified by Public Works Research Center⁹⁾, Japan. The slipperiness of wire nets when people actually walk on them greatly depends on the types of shoes they wear and the wetness of wire nets. A procedure for evaluating the personal perception of the slipperiness of a wire netting when actually walking on it is reported by the Public Works Research Center¹⁰⁾. The personal slipperiness perception is not well recognizable on a flat surface, and valuation on a slope is important.

Fig. 10 shows the experiment result of personal slipperiness perception on wire nets by 100 persons, male and female, aged teens to sixties, and the result of measurement of the friction coefficient of the nets, reported by the Public Works Research Center. A majority of them felt the newly developed wire less slippery.

3.3 Application example

The Zn alloy coated steel wire having a high friction as stated above is applicable to both types of the river bank protection wire netting shown in Fig. 11 and is especially effective when used as the top stretch of the slope type wire netting.

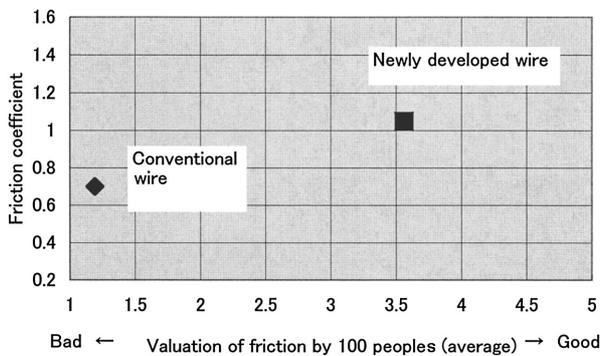


Fig. 10 Valuation of friction by 100 peoples

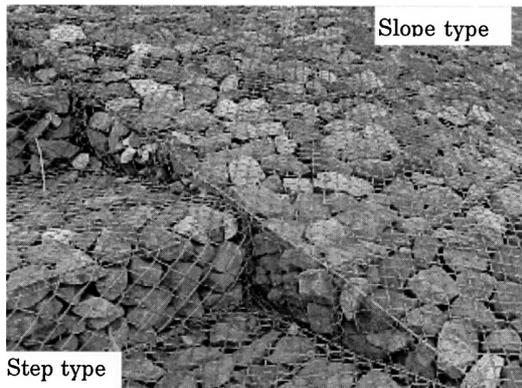


Fig. 11 Type of the riparian works

4. Conclusion

A new type of steel wire coated with Zn-11%Al-Mg alloy was developed having a higher corrosion resistance than conventional Zn-10%Al coated steel wire. By our research it was found that the newly developed wire has the following characteristics.

- (1) Zn-11%Al-1~3Mg alloy coating is available by a double-hot dip process.
- (2) In the chemical composition of the alloy containing 1-3% Mg, the presence or non-presence of large coarse MgZn₂ crystals which are considered to be produced in an early stage of solidification had no effect on the corrosion resistance of the alloy in 250-hour SST.
- (3) The presence of large coarse MgZn₂ tended to lower workability.
- (4) Zn-11%Al-2%Mg coated wire, prepared with a view to reducing the formation of large coarse MgZn₂ crystals, exhibited an excellent corrosion resistance.
- (5) The authors developed a high-friction steel wire having the high corrosion resistance property of Zn-11%Al-2%Mg coated wire. The newly developed wire, when applied to the top of wire net basket, showed a good anti-slip effect to support safety of people walking on it.

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