

Corrosion characteristics in concrete environment of hot dip galvanised steel and Zn alloy hot dip coated steel

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The modern civilisation is based on steel reinforced concrete structures. Thus, the deterioration of concrete presents a threat to the infrastructure of our society and it is caused mainly by the corrosion of steel rebars. Such deterioration requires huge expenditure to maintain and recover the concrete structures. And the cracking and spalling of concrete may lead to accidents resulting in injury or death. From the viewpoint of both economics and safety, the anticorrosion characteristics of rebars should be enhanced. Hot dip galvanised rebars have been used for this purpose in Euro-American countries, while they have not been used in Japan. For the latter, high anticorrosion epoxy coated rebars have dominated the market. But due to the high cost of these, the application of less expensive hot dip galvanised steels should be investigated. The authors investigated the anticorrosion characteristics in concrete of hot dip galvanised steel and Zn alloy hot dip coated steel in this study. The electrochemical behaviours of specimens in the simulated concrete solutions were analysed by cyclic voltammetry, optical microscopy and X-ray diffraction analysis, and the corrosion characteristics of those specimens and the potential of this application were discussed.

Keywords: Hot dip galvanized steel, Zn alloy coated steel, Steel reinforced concrete, Corrosion characteristic

Introduction

Recently, the deterioration of concrete structures supposed to be semipermanent has become a serious social problem.¹ Steel rebars in concrete are supposed to be anticorrosive due to the passive surface films formed in alkali concrete solutions. However, there are many pores in the concrete where water can gather. In particular, capillary crevices, one type of micropore in concrete, contain water, oxygen and chloride ions for chloride corrosion and carbon dioxide for neutralisation.² These components induce the corrosion of steel rebars in concrete. Investigations of the solution in capillary crevices (concrete solution) began only in the last half of the 1980s when extraction means for concrete solution were developed.³ The concrete solution was generally supersaturated with Ca(OH)₂ immediately after the mixture of cement and water. Then it reached equilibrium with NaOH and KOH and the pH changed from 12 to 14 with the amount of alkali and the extent of hydration in cement.⁴

Hot dip galvanised steels have been applied to concrete rebars in Euro-American countries. They are anticorrosive in neutral or weak alkali aqueous solutions, since they form zinc hydroxide protective films on this surface and become passive. However, they could corrode in strong alkali concrete with hydrogen evolution.⁵ On the other hand, they were evaluated as highly anticorrosive rebars in Euro-American countries, since they can delay the initiation of corrosion in comparison with non-hot dip galvanised steels. According to these reports,^{6,7} the dissolution of zinc occurs first and the resulting compounds protect the substrate rebar. Although it is difficult to identify the compounds, a report confirmed CaHZn as one such protective compound.⁸ Another paper⁹⁻¹¹ reported that formation of calcium hydroxyzincate depends on pH and that there are also other coexistent compounds such as ZnO or Zn(OH)₂. In an investigation of microbially influenced corrosion of non-coated and hot dip galvanised steel, the dissolution of Zn from the hot dip galvanised sample has been shown to inhibit the microbially influenced corrosion action of *T. Ferrooxidans*.¹²

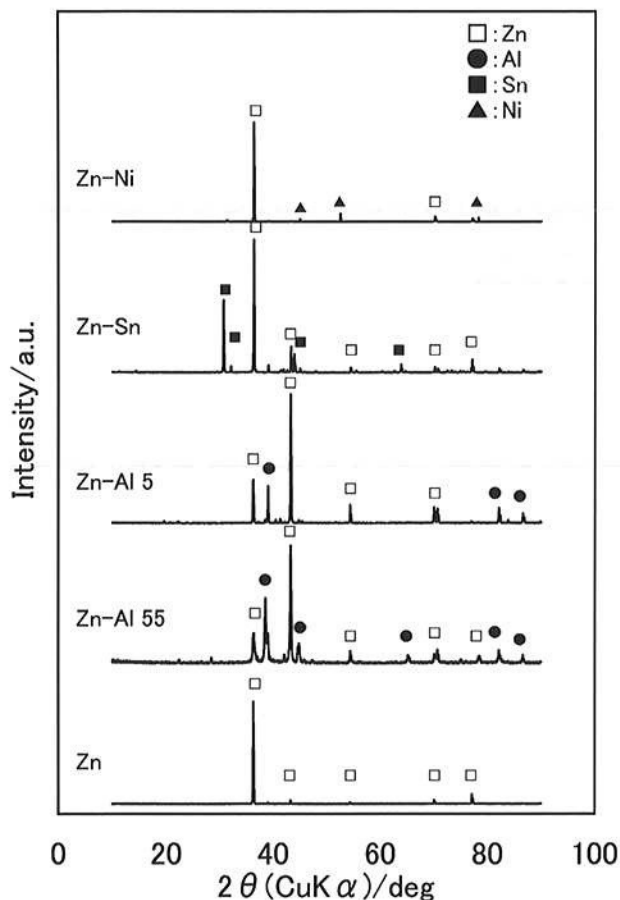
All of these investigations suggest that compounds play an important role in the mechanism of corrosion prevention. The authors have investigated cyclic voltammetry behaviour in the solutions, 'concrete solution' suction filtrated from cement paste (the solution before solidification) and also discussed the corrosion behaviour for hot dip galvanised steel and various Zn alloy hot dip coated steels.

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1 X-ray diffraction analysis of radical materials

Experimental

Hot dip galvanised steel, Zn–Ni coated steel, Zn–Sn coated steel, Zn–5%Al–Mg coated steel and Zn–55%Al coated steel were used as specimens in this experiment. All of these specimens were made by hot dip processes, and produced by an outside supplier. On the other hand, component analyses, X-ray analyses and cyclic voltammetry were carried out by the authors. Zn–Al plated steels were made using a commercial bath, while Zn–Ni and Zn–Sn were made from the supplier's special experimental baths. Substrates for all these zinc plated specimens were JIS SS400 steel. They were pretreated by a combination of flux treatment, acid pickling and water washing and then immersed into the baths for a time sufficient to create the desired coating thickness. The compositions of each specimen are shown in Table 1. Figure 1 shows the X-ray diffraction results of each specimen. The average thickness of zinc or Zn alloy layers was 60 μm . For usual practical purposes, the thickness would have been often much larger (e.g.m 200 μm). However, the authors requested that the thickness was restricted to 50–70 μm for the comparative experiments in this case. All of these specimens were

Table 1 Chemical composition of hot dip coatings

Plating	Zn	Sn	Al	Ni	Mg	Si
Zn–Ni	94.7	–	0.3	1.8	–	0.1
Zn–Sn	78.5	16.6	0.4	–	–	2.2
Zn–Al5	82.8	–	10.2	–	2.3	0.1
Zn–Al55	43.4	–	55.0	–	–	1.6

cut to small plates (10 \times 10 mm), degreased and used as working electrodes.

The corrosion behaviours for all of these specimens were investigated using cyclic voltammetry. For the investigation on corrosion behaviour, the lead wire was connected to one side of each specimen embedded into epoxy resin. Specimens were polished and used as the working electrode in an electrochemical cell. Platinum was used as the counter electrode and silver/silver chloride electrode as the reference. All of the potentials mentioned below are described based against this reference electrode.

The three electrodes were immersed into test solutions and terminals for all three electrodes were connected to a potentiostat (Hokuto HA-501G). Using a function generator (Hokuto HB-105), the potential was scanned and the potential-logarithmic current density curves were measured automatically by personal computer; the cyclic voltammograms were made using MS Excel. All cyclic voltammograms were measured in test solutions deaerated by argon gas for 600 s. The potentials were scanned from the rest potential to –1650 mV where hydrogen evolution was produced actively and then scanned back in the noble direction until it reached 1500 mV.

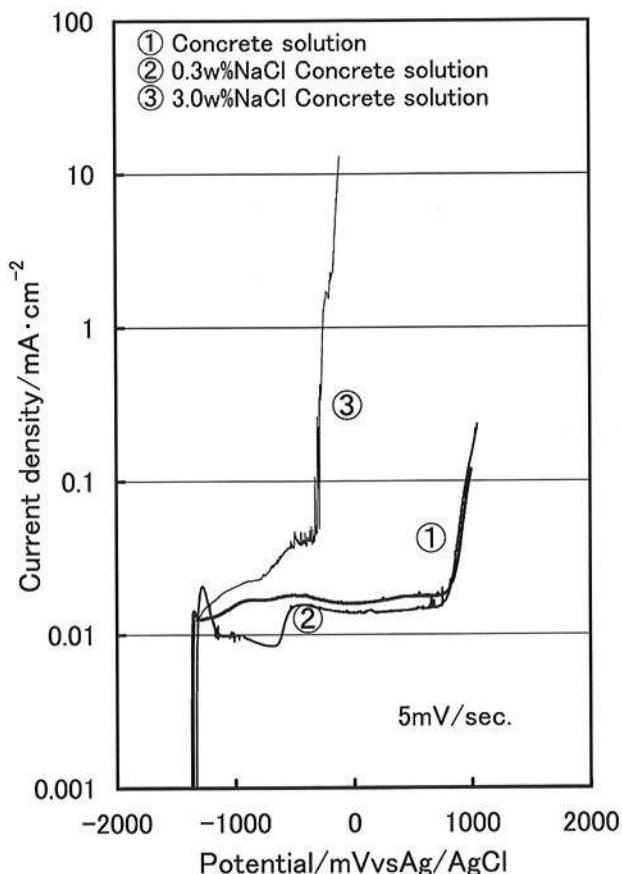
The test solution was made from the cement paste by aspiration–suction before complete solidification, and is called 'concrete solution' in this paper. The compositions of both solutions are 0.0120Ca–0.0035Na–0.077K–0.0001Cr–0.00000012Al (mol L^{–1}).

X-ray diffraction analysis (XRD, Phillips PW3050) was used for the identification of compounds on the surfaces of specimens. Cu K α X-ray was used as a probe and the results were shown as figures using MS Excel.

Results and discussion

Figure 2 shows the anodic polarisation curve for hot dip galvanised steels in concrete solution including chlorides. For all of these specimens, small current peaks were recognised at about –1100 mV. These peaks correspond to the dissolution of zinc and the subsequent formation of corrosion products.^{10,11} For the specimen in the concrete solution without chlorides (curve 1 in Fig. 2), the current remained almost constant until the potential reached +900 mV. Then the current increased drastically, which could be attributed to oxygen formation. For the specimen in the concrete solution including 0.3 wt-% chloride (curve 2 in Fig. 2), a small peak at about –400 mV was recognised in addition to that at about –1100 mV. For the specimen in the concrete solution including 3 wt-% chloride (curve 3 in Fig. 2), the current at potentials nobler than –1100 mV, increased gradually with the potential, and increased drastically at –200 mV. The increase could be attributed to the dissolution of corrosion product formed at –1100 mV.

Figure 3 shows the results of XRD for the specimens corresponding to curves 1 and 3 in Fig. 2. For the former, CaZn₂(OH)₆·2H₂O was observed on the surface, while Zn₅(OH)₈Cl₂·2H₂O was identified on the surface for the latter. Comparing Fig. 2 with Fig. 3, one can conclude that the compound formed on the specimen's surface at –1100 mV was the complex hydroxide composed of zinc and calcium. The authors can also conclude that these complex compounds had higher anticorrosion



2 Anode polarisation curve of galvanised steels in concrete solutions containing no addition, 0.3 and 3.0 wt-% chlorides respectively

characteristics, since the current density was kept almost constant in 0.3 wt-% NaCl solution. On the other hand, the surface compound formed in 3.0 wt-% NaCl solution was mostly $Zn_5(OH)_8Cl_2 \cdot 2H_2O$ when the potential was polarised in the noble direction. The compounds dissolved at about -400 mV and this could lead to continuous corrosion.

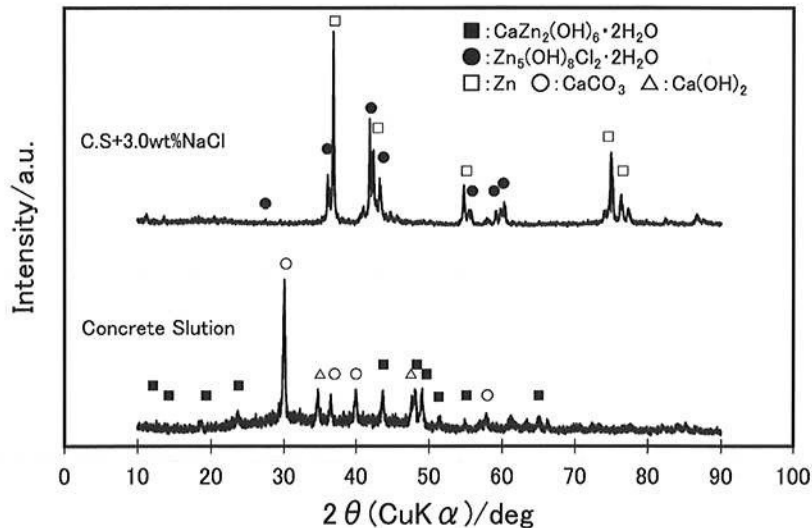
Figure 4 shows the polarisation curve of Zn-Ni alloy coated steels in concrete solution. As for those curves in both non-chloride and 0.3 wt-% solutions, the total shapes of the curves were almost the same, even though the current densities for the latter were slightly higher than those for the former. These curves had two anodic current peaks at -1100 and -500 mV respectively. The former corresponds to the dissolution of zinc and the subsequent formation of Zn-Ca compound, while the latter current peak was small and did not lead to the continuous dissolution of nickel, nor to any drastic change of surface profiles. Corrosion compounds were not observed for any specimens after the polarisation tests. For the specimen in the concrete solution containing 3.0 wt-% NaCl, the anode current density increased drastically at -900 mV. The increase of the current density could be attributed to the change of Zn-Cl-Ca compound to Zn-Cl compound through the dissolution of the calcium component, as shown also in curve 3 in Fig. 2. The comparison of Fig. 4 with Fig. 2 indicates that the change of corrosion compound formed on the specimen's surface occurred at a less noble potential in

the solution with 3.0 wt-% NaCl. This suggests that the nickel component made the surface film more unstable.

Figure 5 shows the polarisation curves of Zn-Sn alloy coated steels in concrete solutions. For the specimens in concrete solution without NaCl and with 0.3 wt-% NaCl, the curves' shapes and tendency were almost the same, even though the current was generally higher for the latter than for the former. Two anodic current peaks were observed at -1100 and -1000 mV respectively. The peak at -1100 mV corresponds to the formation of Zn-Ca compound formed on the specimen's surfaces, as shown also in Figs. 2 and 4. However, the peak at -1000 mV is still unknown. Since the peak was very small, it would have not affected the film formation remarkably. For the specimen in concrete solution with 3.0 wt-% NaCl solution, the anodic current increased drastically at -900 mV. The current increase could be attributed to the change of Zn-Cl-Ca compound to Zn-Cl compound, as shown in Fig. 4. The corrosion resistance decreased also for Zn-Sn alloy film, as with Zn-Ni film, drastically, when the sodium chloride content was 3.0 wt-%.

Figure 6 shows the anodic polarisation curves for Zn-5%Al-Mg coated steels in concrete solution. These specimens had two anodic current peaks at -1200 and -800 mV. The less noble peak at -1200 mV could be attributed to the dissolution of zinc and the formation of Zn-Ca-Cl compounds. However, the current increase was not so marked. It suggests that the amount of corrosion compounds formed on the specimen's surfaces was not so large. Therefore, the authors cannot anticipate much corrosion protection capability for this Zn-Al-Mg alloy coated specimen in comparison with pure zinc, Zn-Sn and Zn-Ni coated specimens. On the other hand, the noble peak at -800 mV could be attributed to the dissolution of the aluminium component. In fact, the corrosion compound was observed on the specimen's surface after the polarisation test. Generally speaking, a Zn-5%Al-Mg coated steel has very high corrosion resistance in atmospheric environments, since the aluminium component forms a passive film. However, for the alloy plated specimen in a strong alkali concrete environment (pH=13), the aluminium component dissolved selectively and the plated steel continued to corrode without the formation of corrosion compound. For the specimen in the concrete solution with 3.0 wt-% NaCl, the current increased drastically at about -800 mV. The authors assume that this increase could be attributed to the anodic dissolution of the aluminium component and the substrate. The surface condition of the specimen after the anodic polarisation confirmed this assumption. From all of these results in Fig. 6, it can be concluded that Zn-5%Al-Mg alloy coated steels are very unstable in concrete solution.

Figure 7 shows the anodic polarisation curve for Zn-55%Al alloy plated steels in concrete solutions. For the specimen in the concrete solution without NaCl solution, a characteristic anodic current peak was observed at -800 mV. The tendency was much the same with the Zn-5%Al-Mg alloy coated specimen. However, the anodic peak in Fig. 7 was more marked than that in Fig. 6. The peak could be attributed to the dissolution of aluminium in this figure. Since the aluminium content was larger in Fig. 7 than that in Fig. 6, the current peak at -800 mV became more marked. However, the

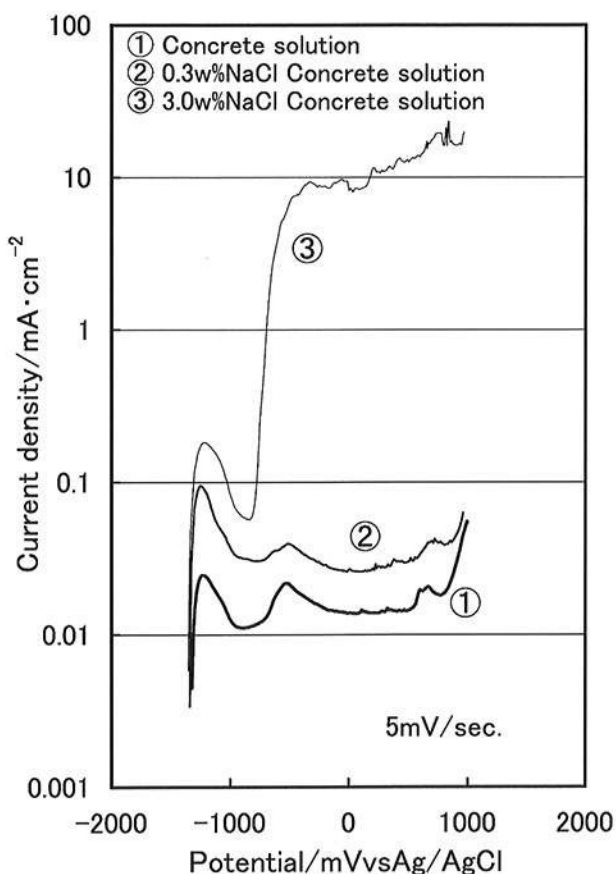


3 X-ray diffraction analysis of hot dip galvanised steels after anode polarisation in solutions containing no addition and 3.0 wt-% chlorides

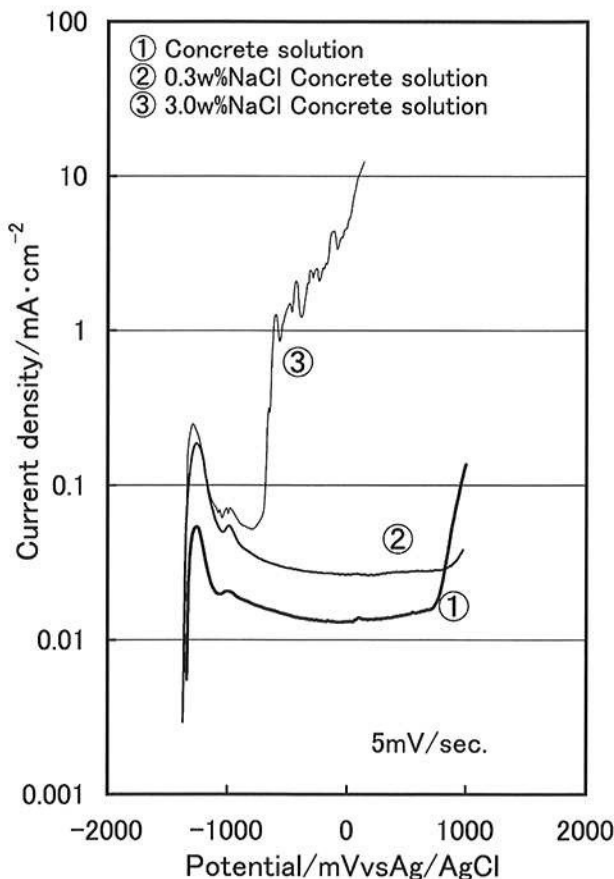
corrosion compound did not prevent the subsequent corrosion at all in the concrete solution with 0.3 wt-%NaCl and the current continued to increase with the anodic polarisation, as shown in curve 2 in Fig. 7. For the specimen in the concrete solution with 3.0 wt-%NaCl, the tendency was almost the same. From all of these results in Fig. 7, it can be concluded that the increase in aluminium content in zinc coated film made the corrosion resistance worse in concrete solution.

Conclusions

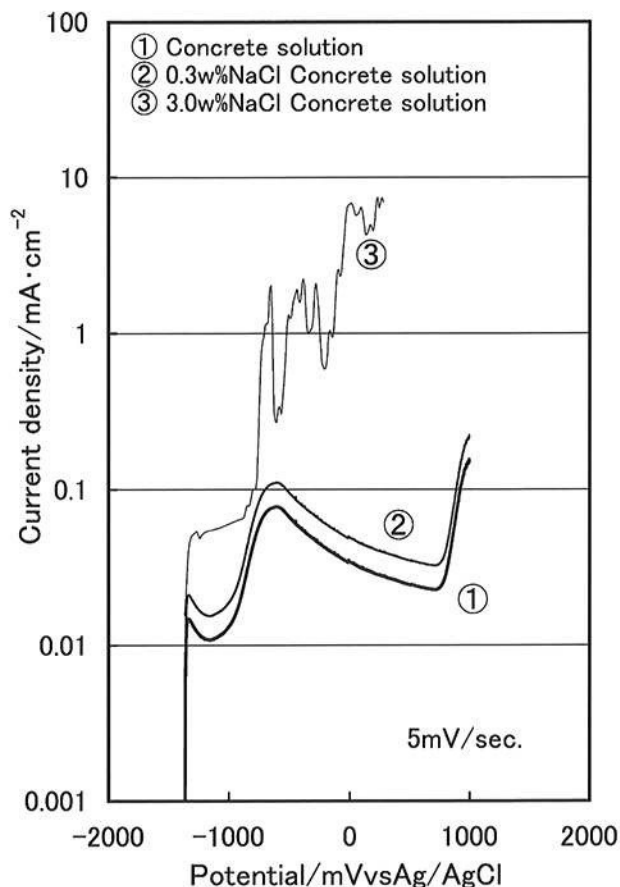
The corrosion resistance of hot dip coated steels using pure zinc and Zn alloy coatings in concrete solution was measured, using an anodic polarisation method, surface observation and X-ray diffraction analysis. The zinc component in the surface film dissolved first and formed a Zn–Ca corrosion compound in concrete solution. In the concrete solution with NaCl, it formed a Zn–Ca–Cl



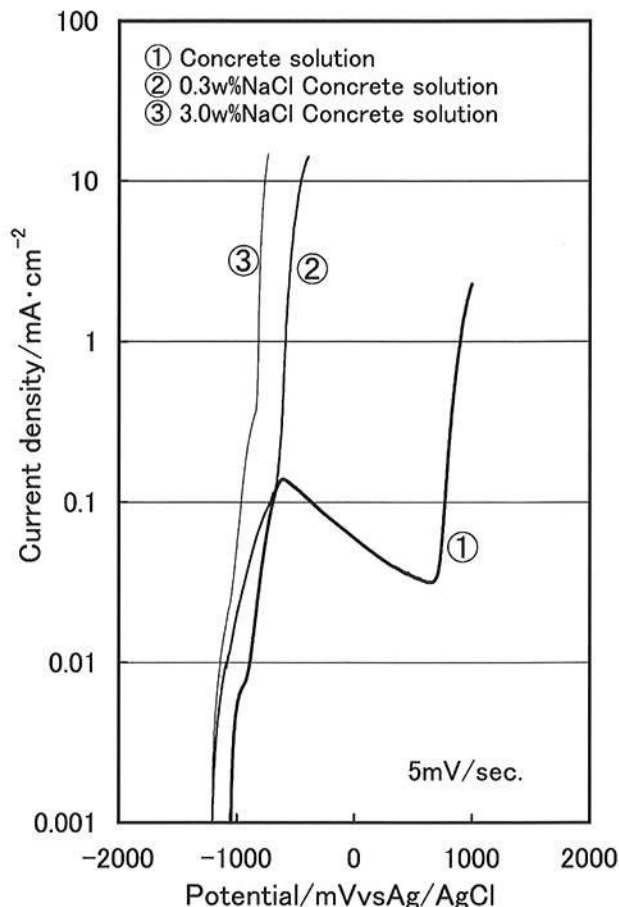
4 Anode polarisation curve of Zn–Ni alloy hot dip coated steels in concrete solutions containing no addition, 0.3 and 3.0 wt-% chlorides respectively



5 Anode polarisation curve of Zn–Sn alloy hot dip coated steels in concrete solutions containing no addition, 0.3 and 3.0 wt-% chlorides respectively



6 Anode polarisation curve of Zn-5%Al-Mg alloy hot dip coated steels in concrete solutions containing no addition, 0.3 and 3.0 wt-% chlorides respectively



7 Anode polarisation curve of Zn-55%Al-Mg alloy hot dip coated steels in concrete solutions containing no addition, 0.3 and 3.0 wt-% chlorides respectively

compound. Since these compounds reduce the corrosion rate after their formation, they have high corrosion resistance from the view point of substrate protection. With the increase in chloride, the calcium content in the surface compound decreased and as a result, the deceleration effect of the compounds for corrosion decreased. Zn-Al, Zn-Ni and Zn-Sn alloy coated steels showed different polarisation behaviours in a strong alkali concrete environment. For Zn-Al alloy, the aluminium component dissolved selectively and continuously. It did not form any Zn-Ca-Cl compounds and the corrosion resistance decreased drastically. For Zn-Ni and Zn-Sn alloy coated steels, the corrosion deceleration effect of the compounds formed on the steel surfaces decreased in comparison with the pure zinc hot dip coated steel. However, it showed relatively good corrosion resistance as a whole. The detailed structure of the corrosion products still remains presumptive. However, the authors have shown that the formation of the corrosion products plays an important role as a barrier effect to inhibit further corrosion. Further investigation of the corrosion products will be important follow-up research for the authors in the future.

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