1. Introduction
The good resistance of zinc and aluminum against corrosion and their relatively low price is the reason for their widespread use as a coating on steel.1) Zinc and aluminum protect steels through original barrier layer action of the coating, secondary barrier action of corrosion products layer, and galvanic action of coating layer with the exposed parts of underlying steel.2) Aluminum coating provides better protection than zinc coating since aluminum itself carrying protective oxide is attacked very slowly.3) However, under certain mild conditions the attack on aluminum is too slow to provide cathodic protection to steel and in such circumstances zinc coating is preferred.4) In view of the advantages and also the short-comings of individual zinc and aluminum coatings a new concept of combining the best properties of these traditional coatings has been developed by Bethlehem Steel, USA during the 1970s, better known as Al–Zn alloy coated steel (GL) with the composition 55mass%Al–1.6mass%Si–Zn.4)

GL has shown a superior anticorrosion performance than any other zinc or Al–Zn alloy coated steel in field exposure tests.5) However, there are limited laboratory investigations using accelerated test methods, which give quick information about the performance of coating in the desired environment. To further widen the knowledge about the corrosion performance of GL coated steel in marine environment, in this study, wet–dry cyclic test, which simulates marine atmospheric environment, has been used to evaluate the corrosion behavior of 55mass%Al–1.6mass%Si–Zn alloy.

2. Experimental
55mass%Al–1.6mass%Si–Zn alloy (GL alloy) sample was prepared from aluminum (99.99%), silicon (99.9%) and zinc (99.5%). They were melted at 883 K and cooled by pouring on a stainless steel plate so as to obtain similar structure and chemical composition to that on the GL coating on steel. The purpose of experimenting with bulk alloy sample instead of coated steel was to avoid the necessity of repeated preparation of the cell as the bulk sample could be polished and used repeatedly. For the monitoring of ac impedance and corrosion potential, a two-electrode cell arrangement with the exposed area of 10 mm² each, as shown in Fig. 1, was used as a corrosion-monitoring probe. In this electrode system, one alloy plate was served as the working electrode and other as the counter electrode. The specimen was cut into small plate of dimension 13 × 110 mm² and cleaned by sonicating in acetone for 120 s. One side of the plate was connected to the lead wire using silver paste. The connection of the plate and wire was covered by quick drying epoxy to make sure that the connection was secured. Two plates, separated apart by 0.1 mm with the help of a polyester sheet, were then mounted in an ambient temperature solidifying epoxy resin in such a way that exposed surface area was 10 × 10 mm². Before embedding the plates into the epoxy resin, they were subjected to...
Electro-deposition coating at 170 V employing an organic resin for 180 s, which was followed by curing at 443 K for 1.2 ks. The aim was to minimize the possibility of occurrence of crevice corrosion at the sides of the specimen. The results of GL alloy were compared with that of zinc sample (99.5%), which was exposed together with GL alloy.

Two holes (1.7 mm diameter), as shown in Fig. 1, were drilled at the middle of the epoxy resin to contain the salt bridge, which acted as the effective Luggin probe tip during the dry cycles for the Ag/AgCl, KCl reference electrode. This helped to achieve the continuous monitoring of corrosion potential. Prior to exposure, the electrode surface was mechanically polished with wet SiC papers up to grade 1000 and then ultrasonically cleaned in distilled water. Afterwards, a peripheral ban of 0.5 mm thick polyester sheet was glued on it surface. This served to control the amount of solution, which remained on the electrode surface at the on set of each dry cycle. A three-electrode cell configuration was employed for polarization measurement with an Ag/AgCl, KCl (sat) reference electrode (SSE) and Pt sheet as a counter electrode.

The corrosion-monitoring probe (sample) was set inside a temperature and humidity controlled chamber with its metal surface facing upwards and a water leveler was used to ensure that the cell was placed horizontally. To ensure that the cell was placed horizontally, the wet–dry condition for 1 h in a 0.05 kmol/m3 NaCl solution and drying for 7 h at 298 K were conducted by exposing the probes to an alternate impact and the corrosion attack was homogeneous, as compared to thick and porous corrosion products and heterogeneous corrosion attack on zinc or galvanized steel. The high corrosion rate of zinc led to the formation of voluminous corrosion products, which enhanced heterogeneous deposition of salt and hence the heterogeneous corrosion in contrast to GL alloy. From Fig. 2(a) and Fig. 3(a), it can be seen that the corrosion rate, $R_p^{-1}$, of GL alloy was almost constant with the progress of wet–dry cycles. Initially the surface was almost dried up during the drying periods, however, after the 9th cycles (72 h) the surface could not dry due to accumulation of corrosion products, which retain moisture. The corrosion products were thin and compact and the corrosion attack was homogeneous, as compared to thick and porous corrosion products and heterogeneous corrosion attack on zinc or galvanized steel.

To better understand the corrosion process in a single wet–dry cycle, plots of $R_p^{-1}$ and $E_{corr}$ of GL alloy and Zn within the 15th wet–dry cycle against time is made in Figs. 4(a) and 4(b), respectively. Each cycle can be divided into three different periods, immersion, drying and dried-up, as shown in Fig. 4, where the dried-up state was defined in this study as time period when the solution conductance obtained from high frequency impedance was lower than $1 \times 10^{-3} \Omega^{-1}$. The variation of $R_p^{-1}$ of both samples reveals that the corrosion rates increased sharply just after the

A frequency response analyzer (FRA, Schlumberger SI 1280) with a multiplexer controlled by a personal computer was used to continuously monitor the impedance. High frequency limit of FRA and low frequency limit was set at 10 kHz ($Z_H$) and 10 mHz ($Z_L$), respectively. The impedances were simultaneously measured at these frequencies, and the polarization resistance, $R_p$, was determined by subtracting $Z_H$ from the $Z_L$, i.e.,

$$R_p = Z_L - Z_H$$

This is based on the assumption that the high frequency impedance gives the solution resistance and the low frequency impedance gives a sum of solution resistance and polarization resistance. Each single value of $R_p$ was obtained at the time interval of 900 s.

It is well known that the corrosion current density $i_{corr}$ is proportional to the value of $1/R_p$.

$$i_{corr} = k/R_p$$

The proportional constant $k$ is theoretically calculated from the Tafel slopes of anodic and cathodic polarization curves.

3. Results and Discussion

3.1. Corrosion Monitoring under Wet–Dry Cycles

The results of the corrosion monitoring and the corrosion potential variation of GL alloy under immersion for 1 h in a 0.05 kmol/m3 NaCl solution and drying for 7 h at 298 K and 60% RH are shown in Figs. 2(a) and 2(b), respectively. For the comparison, monitoring results of zinc under similar condition are shown in Fig. 3. The $R_p^{-1}$ is taken as the index of corrosion rate. The corrosion rate, $R_p^{-1}$, of GL alloy became almost constant with the progress of wet–dry cycles. Initially the surface was almost dried up during the drying periods, however, after the 9th cycles (72 h) the surface could not dry due to accumulation of corrosion products, which retain moisture. The corrosion products were thin and compact and the corrosion attack was homogeneous, as compared to thick and porous corrosion products and heterogeneous corrosion attack on zinc or galvanized steel.

The high corrosion rate of zinc led to the formation of voluminous corrosion products, which enhanced heterogeneous deposition of salt and hence the heterogeneous corrosion in contrast to GL alloy. From Fig. 2(a) and Fig. 3(a), it can be seen that the corrosion rate, $R_p^{-1}$, of GL alloy was much lower than zinc.

The frequency limit of FRA was set at 10 kHz ($Z_H$) and low frequency limit was set at 10 mHz ($Z_L$). The impedances were
probe was submerged in the test solution. In the drying period, GL alloy (Fig. 4(a)) showed only small increase of \( \frac{1}{R_p} \) as compared to a large increase for zinc (Fig. 4(b)). This suggested that the corrosion process of GL alloy was different from that of zinc under a thin layer of electrolyte. The reason for this difference in the corrosion behavior of GL alloy and zinc under thin electrolyte layer will be discussed later.

The corrosion reaction of Zn consists of anodic dissolution of zinc (\( \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \)), though Al may dissolve simultaneously in case of GL alloy, and cathodic reduction of mainly oxygen (\( \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \)) in a neutral chloride solution. According to a mixed potential theory, a balance of these reactions of anodic and cathodic determines the corrosion rate (current) and corrosion potential. As can be seen in Fig. 4(a), the corrosion potential of GL alloy became most negative in the last stage of the drying period, the corrosion rate \( \frac{1}{R_p} \) being decreased (Fig. 4(a)). According to a mixed potential theory, this indicated that the oxygen reduction was greatly inhibited in the progress of drying; nevertheless the electrolyte layer became thinner. This may be attributed to accumulation of a protective corrosion product layer during the drying. On the other hand, in the case of zinc, the corrosion potential during the drying process did not shift to negative value and maintained either a constant value or slightly shifted to positive value and the corrosion rate \( \frac{1}{R_p} \) was gradually increased in the drying period (Fig. 4(b)). This implies that enhancement of oxygen reduction by thinning of the electrolyte layer. Thus, the corrosion products accumulated on the zinc surface during the drying did not inhibit the oxygen reduction process.

To have a better understanding on the corrosion process, an optical photograph of GL alloy, observed normal to the sheet surface, was taken and is shown in Fig. 5. A cored
dendrite aluminum-rich matrix can be seen with zinc-rich interdendritic alloy filling in the interstices. The results of corrosion monitoring and corrosion potential variation suggested that the zinc-rich inter-dendritic phase of the alloy corroded preferentially. According to Zoccola et al., the zinc corrosion product gradually fills up the interdendritic interstices and the alloy is transformed into a composite of an aluminum-rich matrix and zinc corrosion products mechanically keyed into the interdendritic labyrinth. The low corrosion rate of GL alloy as compared to zinc or galvanized coating was because of the relatively small area of exposed zinc and that aluminum rich dendrite was covered with aluminum oxide. With the progress of corrosion no breakdown of aluminum oxide film occurred as can be judged from the low corrosion rate. However, as is evident from Fig. 4(a) pitting of the aluminum oxide film seemed to have occurred during the drying process.

The corrosion products were identified using an X-ray diffractometer at the end of wet–dry cyclic test and the X-ray pattern is shown in Fig. 6 together with zinc sample under identical condition. Since the amount of corrosion products of GL alloy was very limited, it was not possible to use powder sample. The corrosion products identified from X-ray peaks were ZnO and ZnCl\(_2\) \(4\)Zn(OH)\(_2\) both in GL alloy and zinc though there were large number of peaks in zinc sample. There were no peaks for Al\(_2\)O\(_3\). However, the low corrosion rate suggested the presence of Al\(_2\)O\(_3\) in the aluminum-rich dendrite.

3.2. Polarization Behavior

The polarization behavior of the as-polished as well as corroded GL alloy and zinc was investigated in 0.05 kmol/m\(^3\) NaCl at a scan rate of 0.5 mV/s. The current-potential response is shown in Figs. 7(a) and 7(b), respectively. The cathodic current density due to oxygen reduction on GL alloy was approximately 5 mAc m\(^2\) at \(-1.1\) V, which was more or less 5 times lower than those on zinc (Fig. 7(b)) and galvanized coating. Accordingly, the improvement of corrosion resistance of zinc coating by the addition of aluminum could be attributed to the inhibition of the oxygen reduction. The cathodic side of the polarization curve, Fig. 7(a), showed a peak or a shoulder at around \(-1.20\) to \(-1.25\) V (vs. SSE). This range of potential is very close to that obtained by deferential capacitance measurements for the formation/removal of a zinc oxide/hydroxide film. In the later stage of cathodic polarization (\(-1.5\) V vs. SSE), reduction of H\(_2\)O started with the progressive increase in the current density.

Contrary to the inhibition of cathodic reaction, the anodic current was found to increase abruptly after the potential was made slightly positive. To know the reason, a laser microphotograph of the specimen surface was observed before and after the anodic polarization and is shown in Fig. 8. It is evident that a selective dissolution of zinc from interdendritic phase has occurred, which account for the sharp increase of anodic current. The anodic Tafel slope had a typical value observed among galvanized coatings.

3.3. Impedance Characteristics

Typical impedance spectra measured at different expo-
sure time for GL alloy and zinc are shown in Figs. 9(a) and 9(b), respectively. The points in the plots indicate the experimental value and the lines are the results of curve fitting using the equivalent circuit shown in Fig. 10. The main features of these Nyquist diagrams of GL alloy involved a capacitive semicircle in the high frequency region followed in the low frequency part by an approximately linear behavior with a slope close to unity corresponding to a phase angle of 45° to the real axis. At short exposure time (1 cycle), the high frequency locus was dominated by an apparent resistive-capacitive system that contained information on the charge transfer kinetics. The capacitive contribution merged as a slight distorted loop as a consequence of surface inhomogeneities. The impedance spectra recorded at increasing exposure time (30 cycles) exhibited the same general characteristic features, but the magnitude of the overall impedance gradually decreased. The kinetics of interfacial reaction became faster (decreasing $R_{ct}$) with the progress of corrosion. The shape of the impedance diagrams at low frequencies was clearly related to the relaxation of a mass transport process that can be attributed to the oxygen reduction reaction.

In the case of zinc, the Nyquist plots were characterized by two depressed capacitive loops expanding towards lower frequencies. The capacitive loops were fairly well resolved to obtain the individual time constants. However, with the progress of corrosion (after 9th cycle exposure), the two time constants were no longer separable and a single time constant obtained.

From the results of impedance measurements, the interface of GL alloy and zinc can be best described in terms of an equivalent circuit shown in Fig. 10, where CPE and $R_{ct}$ represent the capacitance and charge transfer resistance, respectively; $Z_w$ represents the infinite length Warburg impedance in the case of GL alloy and finite length Warburg impedance in the case of zinc; and $R_{W}$ is a combination of solution and film resistances. The constant phase element (CPE), which was used instead of capacitance ($C_{dl}$) due to depressed semicircle, can be given by the expression:

$$Z(CPE) = \frac{1}{[T_{c}(j\omega)^{\alpha_c}]^{-1}}$$

where $j$ is the imaginary number ($j^2 = -1$), $T_c$ is a constant representing capacitance, $\omega$ is the angular frequency, and $P_c = \alpha_c\pi/(\Pi/2)$, and $\alpha_c$ is the phase angle of the CPE. The factor $P_c$ is an adjustable parameter that usually lies between...
0.5 and 1. The value of $P_\text{c}$ has been found to be almost constant at the value of 0.72.

The Warburg impedance, $Z_\text{w}$ is given by

$$Z_\text{w} = R^* \tanh((j \omega T_D)^{1/2}) (j \omega T_D)^{-P_\text{c}}$$

The effective diffusion resistance $R^*$ is obtained at $\omega \to 0$ limit and the parameter $T_D$ is a time constant, which denotes $T_D = (L^2/D)$, $L$ and $D$ being the effective diffusion thickness and effective diffusion coefficient, respectively. $P_D = \alpha_D (\Pi/2)$, and $\alpha_D$ is the phase angle of the $Z_\text{W}$. From the polarization curves of both samples in Fig. 7, the $Z_\text{w}$ seems to be a diffusion impedance due to oxygen reduction in the cathodic process. The $T_D$ value for GL alloy was much larger than that for zinc, if compared in the same cycle. This indicates that a corrosion product layer formed on GL alloy acts more effectively as a diffusion barrier against oxygen transport.

4. Conclusions

From the present study, the following conclusions were made on the corrosion behavior of GL alloy in wet–dry cyclic marine environment:

1. The results of corrosion monitoring and corrosion potential variation in wet–dry cyclic marine environment have shown that the corrosion process of GL alloy was different from that of pure zinc during drying process. The corrosion potential of GL alloy shifted to less noble value during the drying periods in contrast to shift in the noble direction in the case of zinc.

2. The corrosion rate of GL alloy was approximately much lower than that of zinc. The low corrosion rate of GL alloy as compared to zinc was due to the inhibition of the cathodic process.

3. The corrosion attack on GL alloy was more or less homogeneous with the formation of thin and compact layer of corrosion products in contrast to heterogeneous corrosion on zinc. With the progress of corrosion, the kinetics of interfacial reaction became faster and the overall impedance also decreased.

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