Numerical analysis model of galvanic corrosion in consideration of ion movement and reactions

N. Okada, K. Nishihara, M. Matsumoto, T. Kudo

We have developed a new numerical analysis model for galvanic corrosion that can calculate ions movement, reactions and electroneutrality. In this model, major species and reactions were considered, and ion density distribution is corrected by solving Poisson's equation to satisfy electroneutrality. Reactions are calculated based on chemical equilibrium. Galvanic corrosion of a Fe/Zn couple in a NaCl, $MgCl_2$ solutions and artificial sea water was calculated by this model. The distributions of pH, ion density and corrosion products were discussed in these solutions. The distributions of corrosion product obtained by the numerical analysis model agreed well with those measured by FT-IR method qualitatively. In 500ppm NaCl solution, $Zn(OH)_2$, $ZnCl_2/6Zn(OH)_2$ and $ZnCO_3$ were precipitated on the Zn and near the Fe/Zn interface, while there were little precipitations on the Fe far from the Fe/Zn interface. On the other hand, $Mg(OH)_2$ was precipitated on the Fe in 500ppm $MgCl_2$ solution and 1/100 artificial sea water. $Mg(OH)_2$ may contribute to corrosion protection of the Fe in the solution including Mg^{2+}. It is noted that $Mg(OH)_2$ can be precipitated only in the cathodically protected area because the solubility product constant of $Mg(OH)_2$ is larger than that of $Fe(OH)_2$.

Keywords:
numerical analysis, galvanic corrosion, electroneutrality, ion movement, corrosion product

INTRODUCTION

Mathematical models for corrosion phenomena have not been developed enough to be available for manufacturing, since corrosion phenomena are too complex to be modelled. However, galvanic corrosion is a suitable corrosion phenomenon for mathematical model because anodic and cathodic sites are clearly distinguished. Analytical methods for the galvanic corrosion were attempted in 1950s [1]-[3], and numerical models have been developed recently [4]-[10].

These ordinary galvanic corrosion models solve Laplace's equation to obtain distributions of potential and current density in an electrolyte solution under the boundary condition defined by the polarization curves of metals. The distribution of current indicates the corrosion rate of metals, and therefore it is helpful to design apparatus for corrosion protection.

In order to evolve corrosion protection performance of galvanized steel sheet, it is important to know the distribution of pH, ions density and corrosion products in the electrolyte solution as time passing. However, the ordinary model could not calculate pH, ion density or corrosion products.

In our previous paper [11], a numerical analysis model was developed, simulating the change of the geometry of zinc coating and substrate steel by anodic dissolving. In this model, a dissolving volume fraction of a metal element is calculated by a local anodic current density, and the metal element should be redefined as an electrolyte element if the whole of the metal element is dissolved. Although this model does not take into account influences of corrosion products and pH distribution, the corrosion rate of zinc coating at shear cut edge of galvanized steel obtained by this model agreed with experimental results by salt spray test. That is, ions and corrosion products do not affect the corrosion rate significantly in the salt spray test because they are washed out by a fresh electrolyte solution. However, results by salt spray test often do not agree with actual corrosion behaviours. Cyclic corrosion test, including wet and dry, has been recognized as a more reliable corrosion acceleration test. It is important to consider drying process and corrosion products for the mathematical model. So then ions movements and chemical reactions should be modelled in advance. However, it is impossible to compute all ions and reactions in the Galvanic corrosion because there are various kinds of ions, molecules, hydrates and reactions. Furthermore, electroneutrality is quite difficult to compute. Therefore, numerical analysis models for corrosion need to be simplified by addressing major ions and reactions.

The purpose of this study is to develop a numerical analysis model for the galvanic corrosion with ions movement, reactions and electroneutrality. In order to compute the electroneutrality, ions are redistributed not to generate local electric field by solving Poisson's equation. The corrosion progress on galvanic couple of Fe and Zn was investigated by this model, and influence of electrolyte species was discussed. In addition, corrosion product distributions obtained by this model were compared with the FT-IR result.

Nobuhiro Okada, Katsuhiro Nishihara,
Masamitsu Matsumoto, Takeo Kudo
Corporate Research & Development Labs.,
Sumitomo Metal Industries, Ltd.
1-8 Fuso-cho Amagasaki 660-0891, Japan

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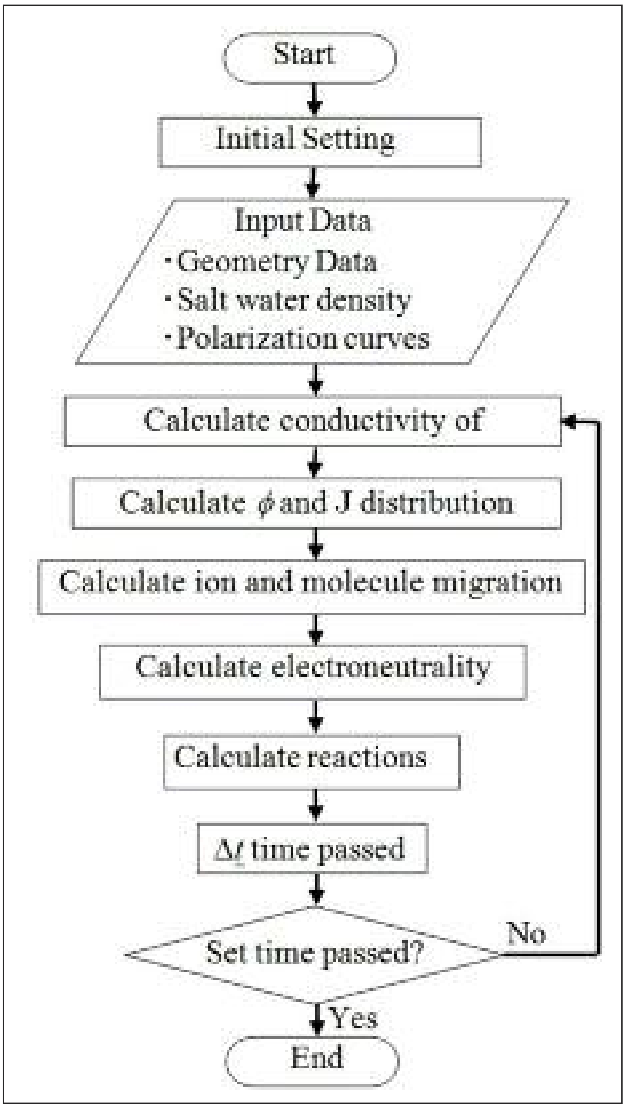


FIG. 1 *Flowchart of calculation.*

Diagramma di flusso dei calcoli.

MATHEMATICAL MODEL

Our mathematical model has been developed based on the ordinarily galvanic corrosion model and fluid dynamics analysis model. Calculation geometry is divided into small elements. Ions and molecules movement and reactions in an element are calculated for a short time step Δt.

Fig.1 shows a flowchart of the mathematical model. Geometry data and initial concentration of electrolyte solution are needed to input at first, and electric conductivity of the electrolyte is calculated. Then, the potential ϕ and the current density vector J are calculated by solving Laplace's equation. After the calculation of the electric field, accumulation of ions and molecules are calculated in considering electroneutrality. Finally, chemical reactions and precipitations are calculated. These calculations are in one time step, and the corrosion progress is able to be computed with time marching method. Details of the mathematical model has been published [12], and the outline of the model will be described in the following.

Potential and current density

The electric conductivity in each element is calculated from equation (1) [13] where z_i, u_i and c_i are valence number, mobility and concentration of ion species i, respectively. F is the Faraday constant and N is the total number of ion species.

$$\sigma = F^2 \sum_{i=1}^{N} z_i^2 u_i c_i \tag{1}$$

The current density vector J is obtained as equation (2) by Ohm's law from the potential gradient where ϕ is the potential.

$$\mathbf{J} = -\sigma \nabla \phi \tag{2}$$

Laplace's equation is given by equation (3), taking the divergence of equation (2).

$$0 = \nabla \cdot \mathbf{J} = \nabla \cdot (-\sigma \nabla \phi) \tag{3}$$

The potential and the current density distributions are computed by solving equation (3) subject to the following boundary conditions:

$J = J_a - J_c$ on the metal/electrolyte interface,

$J = 0$ on the solution surface and the symmetry boundary,

where J_a is the anodic current density and J_c is the cathodic current density. It is assumed that the anodic current density is given by Tafel equation (4) and the cathodic current density is decided by oxygen flux as equation (5).

$$J_{a0} \exp\left\{(\phi - \phi_0)\frac{\alpha n F}{RT}\right\} \tag{4}$$

$$\mathbf{J}_c = 4F\mathbf{N}_{O2} \tag{5}$$

Ions movement and electroneutrality

Assuming that convection in the thin film is small, mass balance equation of species i is described as equation (6) neglecting convection term , where N_i is the flux density, c_i is the concentration, t_i is the transference number, R_i is production or consumption rate and D_i is the diffusion coefficient.

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i + R_i = -\nabla \cdot \left(\frac{t_i}{F z_i}\mathbf{J}\right) + \nabla \cdot (D_i \nabla c_i) + R_i \tag{6}$$

Accumulation of species i for Δt can be calculated from equation (6). In order to compute equation (6), first-order upwind was used for the first term on the right-hand side and second-order central scheme for the second term [14]. However, there is no guarantee whether the distribution of ions computed from equation (6) satisfies the electroneutrality. That is, local charge density ρ expressed by equation (7) does not necessarily become zero.

$$\sum_{i=1}^{N} z_i c_i = \rho \tag{7}$$

In actual phenomena, ions do not move to generate local charge density because Coulomb force is quite strong. In other words, ions move to cancel the local electric field for an extremely brief moment. Equation (6) does not take account this phenomenon.

It is quite difficult to solve simultaneous equations of ion movement and electroneutrality. We have developed a new numerical analysis method to satisfy the electroneutrality based on Pressure-Correction method [14] which has been used for the fluid dynamics analysis. In our model, the tentative ion concentrations are calculated by equation (6), and the electric potential Φ generated by the local charge density is calculated from equation (8), where ε is the dielectric constant.

$$\Phi = -\frac{F}{\varepsilon}\sum_{i=1}^{N} z_i c_i \tag{8}$$

To satisfy the electroneutrality, the distribution of ions is required to redistribute along the electric gradient $-\Delta\Phi$. However, to solve this redistribution is quite difficult because the coefficient in the right-hand side of the equation (7) is enormous ($F/\varepsilon = 1.39\times10^{14}$ Vm/mol in a water) and the velocity of ions accelerated by the electric gradient is too fast to compute. In order to avoid this problem, we define the virtual potential P which corresponds to the electric potential yielded by distribution of charged species.

The correction flux η_i which transports with the gradient of P is defined by equation (9).

$$\eta_i = -\frac{t_i}{z_i}\nabla P \qquad (9)$$

Corrected ion concentration c_i' is obtained as equation (10).

$$c_i' = c_i - \nabla\cdot\eta_i \qquad (10)$$

Equation (11) holds to satisfy the electroneutrality for the corrected ion concentration.

$$\sum_{i=1}^{N}(z_i c_i - z_i\nabla\cdot\eta_i) = 0 \qquad (11)$$

Substitution of equation (9) in equation (11) leads to equation (12).

$$\sum_{i=1}^{N}(z_i c_i - z_i\nabla(-\frac{t_i}{z_i}\nabla P)) = \sum_{i=1}^{N} z_i c_i + \sum_{i=1}^{N}(\nabla(t_i\nabla P)) = 0 \qquad (12)$$

The equation (12) is written by following equation (13), because summation of t_i is unity.

$$\nabla^2 P = -\sum_{i=1}^{N} z_i c_i \qquad (13)$$

Term in the right-hand of equation (13) is known, and P can be obtained by a general solving method of Poisson's equation. Then, the corrected ion concentration is derived by equation (10). However, this calculation needs to be repeated several times because the electroneutrality is not satisfied by a first calculation.

Chemical reactions

We adopted Mixed Control Model to compute chemical reactions by Newton method. In this model, it is assumed that reaction rates are infinite and mass transportation controls chemical reactions in a fluid. That is, the reaction reaches equilibrium immediately after the transportation. We have taken account of major reactions in the galvanic corrosion of the Fe and Zn couple as shown in Table 1.

No.	Reactions	Log K
1	$H_2O \leftrightarrow H^+ + OH^-$	-14.0
2	$H_2CO_3 \leftrightarrow 2H^+ + CO_3^{2-}$	-16.6 [15]
3	$Zn^{2+} + CO_3^{2-} \leftrightarrow ZnCO_3\downarrow$	-10.15 [15]
4	$Zn^{2+} + 6/5OH^- + 2/5CO_3^{2-} \leftrightarrow 1/5\{3Zn(OH)_2/2ZnCO_3\}\downarrow$	-14.2 [15]
5	$Zn^{2+} + 2/5Cl^- + 8/5OH^- \leftrightarrow 1/5\{ZnCl_2/4Zn(OH)_2\}\downarrow$	-14.95 [16]
6	$Zn^{2+} + 2/7Cl^- + 12/7OH^- \leftrightarrow 1/7\{ZnCl_2/6Zn(OH)_2\}\downarrow$	-15.75 [16]
7	$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2\downarrow$	-16.72 [16]
8	$Fe^{2+} + 2OH^- \leftrightarrow Fe(OH)_2\downarrow$	-15.0 [17]
9	$Mg^{2+} + 2OH^- \leftrightarrow Mg(OH)_2\downarrow$	-10.92 [18]
10	$Mg^{2+} + CO_3^{2-} \leftrightarrow MgCO_3\downarrow$	-7.46 [19]
11	$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3\downarrow$	-8.40 [19]
12	$Al^{3+} + 3OH^- \leftrightarrow Al(OH)_3\downarrow$	-33.0 [17]
13	$Ca^{2+} + 2OH^- \leftrightarrow Ca(OH)_2\downarrow$	-5.30 [17]

TAB. 1 ***List of reactions.***

Elenco delle reazioni.

NUMERICAL ANALYSIS RESULTS AND DISCUSSION

Comparison with experiment by FTIR method

FTIR (Fourier Transform Infrared spectrometer) method [20] is suitable to measure the thin surface structure of corrosion products on metal. In order to verify the numerical result, the elemental analysis using FE-SEM/EDS was achieved for corrosion products on a Fe/Zn galvanic couple after 1600s exposure to 1mm thick layer of 500ppm NaCl and 500ppm $MgCl_2$ solution. In Fig.2 and Fig.3 (a) shows the photograph of the dried specimen, (b) shows results of FE-SEM/EDS analysis and (c) shows the distribution of the peak intensity of OH or $Mg(OH)_2$ analyzed in IR spectra of the corrosion products.

The major corrosion product in 500ppm NaCl solution is $Zn(OH)_2$. Fig.2(a) shows a large amount of corrosion products precipitated on the Fe within 2mm from the Fe/Zn interface, and the OH intensity was relatively high in the same area in Fig.2(c). On the other hand, it is found that corrosion products were not remarkably observed in FE-SEM/EDS analysis as shown in Fig.2(b), and that the amount of corrosion products was not so large. Fig.2(c) shows the distribution of $Zn(OH)_2$ by numerical analysis is similar to the FTIR results. Fig.3(a) shows that the amount of corrosion products on the Fe far from the Fe/Zn interface is more than that of corrosion products near the Fe/Zn interface. Fig.3(b) shows that the peak intensity of Mg, which is obtained from the FE-SEM/EDS

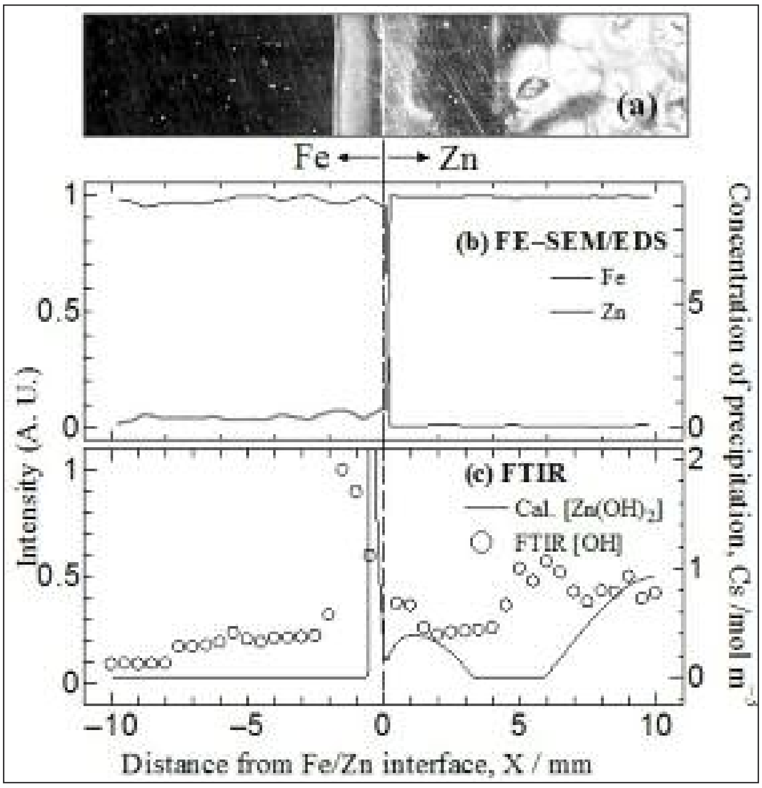
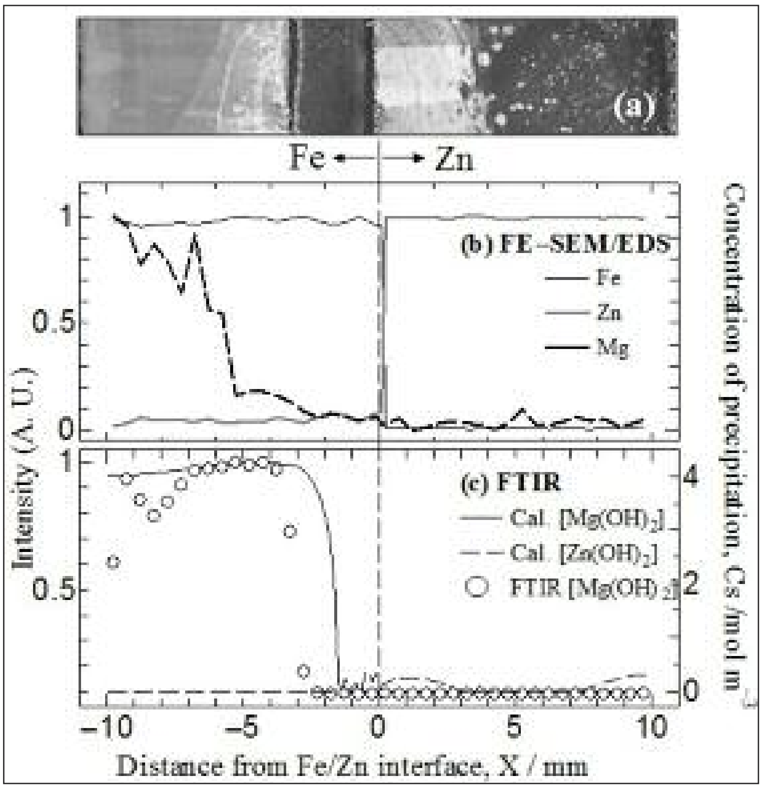


FIG. 2
(a) photograph of a specimen,
(b) distribution of FE-SEM/EDS intensity and
(c) corrosion products in 500 ppm NaCl solution for 1600 s.

(a) Immagine di un provino, (b) distribuzione dell'intensità al FE-SEM/EDS e (c) prodotti della corrosione ottenuti nella soluzione con 500 ppm di NaCl per 1600 s.

FIG. 3
(a) photograph of a specimen, (b) distribution of FE-SEM/EDS intensity and (c) corrosion products obtained in $MgCl_2$ solution for 1600 s.

(a) Immagine di un provino, (b) distribuzione dell'intensità al FE-SEM/EDS e (c) prodotti della corrosione ottenuti nella soluzione di $MgCl_2$ per 1600 s.



analysis, increase with distance from the Fe/Zn interface. $Mg(OH)_2$ is considered to be precipitated on the Fe in $MgCl_2$ solution. Fig.3(c) shows that the distribution of $Mg(OH)_2$ obtained by numerical analysis agreed with the FTIR analysis.

Corrosion near shear cut edge

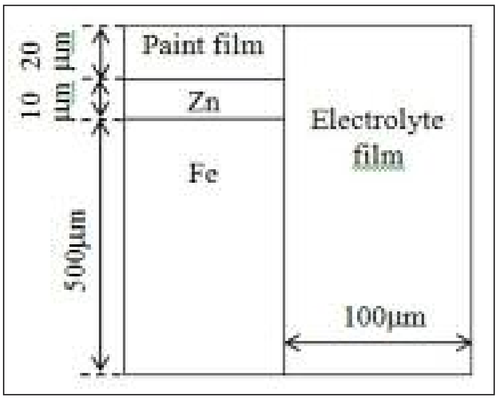
Numerical analysis for shear cut edge corrosion was achieved, when immersed for 200s in 500ppm NaCl solution, 500ppm $MgCl_2$ solution and 1/100 artificial sea water as shown in Fig.4. Fig.5 shows numerical analysis results as the distribution of pH, Cl^-, Zn^{2+}, $ZnCl_2/6Zn(OH)_2$, $Zn(OH)_2$ and $Mg(OH)_2$. In any electrolyte films, the density of Zn^{2+} increased near the Zn and pH increased on the Fe. It is noted that pH in the $MgCl_2$ solution did not increase as high as in the NaCl because OH^- is consumed to generate $Mg(OH)_2$. The corrosion products were precipitated on all over the Fe in the $MgCl_2$ and the artificial sea water, while they were precipitated only near in 100 μm from the Zn in the NaCl due to high pH on the Fe.

Corrosion under paint film

Numerical analysis for corrosion under paint film was conducted in the condition of that Zn is backed 500 μm from the edge. Fig.6(a)-(g) show

FIG. 4
Schematic diagram of shear cut edge corrosion.

Diagramma schematico della corrosione "shear cut edge".



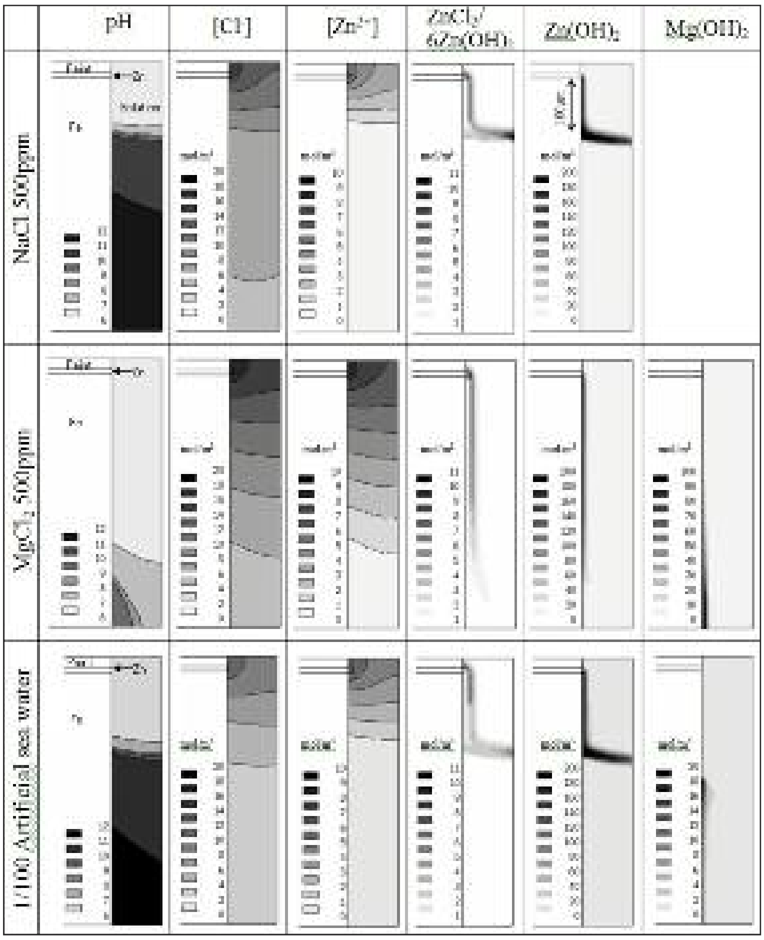


FIG. 5
Results of numerical analysis at shear cut edge of galvanized steel sheet immersed for 200s in 500ppm NaCl solution, 500ppm $MgCl_2$ solution and 1/100 artificial sea water.

Resultati dell'analisi numerica relativa al "shear cut edge" di lamiere di acciaio galvanizzato immerse per 200s nelle soluzioni di: 500ppm NaCl, in soluzione 500ppm $MgCl_2$, acqua marina artificiale 1/100.

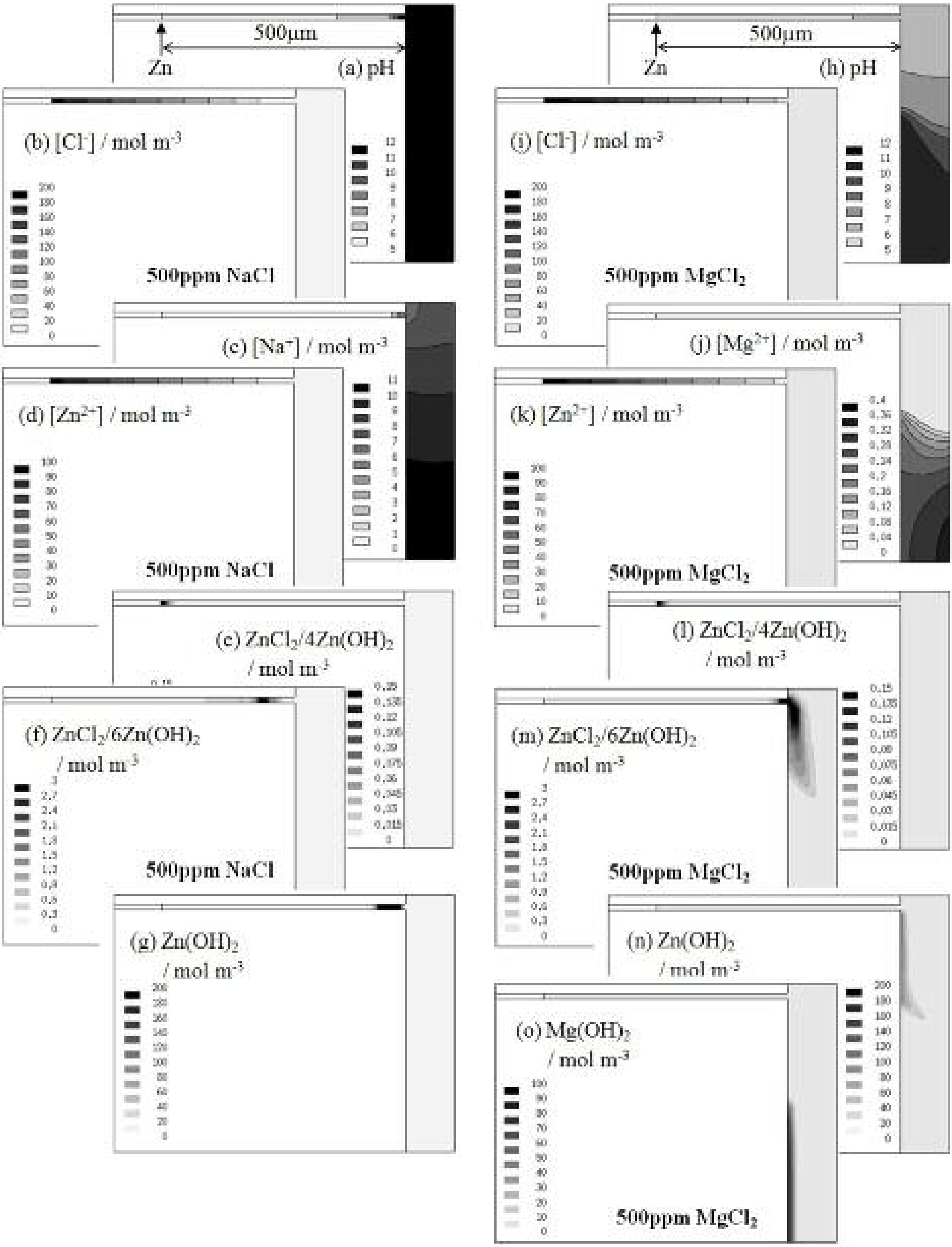


FIG. 6 ***Results of numerical analysis under paint film near cut edge of galvanized steel sheet immersed for 200s in 500ppm NaCl solution and 500ppm $MgCl_2$ solution.***
Risultati dell'analisi numerica sotto strato di vernice vicino al "cut edge" della lamiera di acciaio galvanizzato immersa per 200s in soluzione di 500ppm NaCl e in soluzione di 500ppm MgCl2.

numerical analysis results immersed for 200s in 500ppm NaCl solution and Fig.6(h)-(o) are that of 500ppm $MgCl_2$ solution. Fig.6(a)-(c) and (h)-(k) show that pH under the paint film became low, Cl^- and Zn^{2+} increased. On the other hand, Na^+ and Mg^{2+} decreased under the paint film. In the NaCl, the corrosion products including Zn were precipitated in the paint film as shown Fig.6(e)-(f). In Fig.6(l)-(o), some corrosion products were precipitated on the Fe in the MgCl. Therefore, there is $Mg(OH)_2$ on the Fe under the solution which including Mg^{2+} and it may contribute to corrosion protection. It is noted that $Mg(OH)_2$ can be precipitated only in the area of cathodic protection because the solubility product constant of $Mg(OH)_2$ is larger than that of $Fe(OH)_2$.

CONCLUSION

A mathematical model for galvanic corrosion which can simulate the ions movement and reactions in consideration of satisfying electroneutrality has been developed. The distribution of pH and corrosion products, which are difficult to measure, can be evaluated by this mathematical model. The distribution of corrosion products obtained by this numerical analysis model agreed with that measured by FTIR method.

Numerical analyses for the corrosion near shear cut edge and under paint film were conducted. The following results are obtained.

(1) Corrosion products under the paint film are different from these in the bulk solution because Zn^{2+} and Cl^- has been increased by more than factor of 10 compared to the bulk solution

(2) $Mg(OH)_2$ has been precipitated on the Fe in the electrolyte solution including Mg^{2+}, which may contribute to corrosion protection. $Mg(OH)_2$ can be precipitated only in the cathodically protected area because the solubility product constant of $Mg(OH)_2$ is larger than that of $Fe(OH)_2$.

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Abstract

Modello di analisi numerica della corrosione galvanica in considerazione di movimento di ioni e reazioni

Parole chiave: modellazione, corrosione, rivestimenti

E' stato sviluppato un nuovo modello di analisi numerica per la corrosione galvanica in grado di calcolare movimento, reazioni ed elettroneutralità degli ioni. In questo modello sono state considerate le specie e le reazioni più importanti ed è stata corretta la distribuzione della densità degli ioni risolvendo l'equazione di Poisson per soddisfare l'elettroneutralità. Le reazioni sono state calcolate sulla base dell'equilibrio chimico. Mediante questo modello è stata calcolata la corrosione galvanica di una coppia Fe / Zn in soluzione di NaCl, di $MgCl_2$ e di acqua di mare artificiale. Sono stati discussi la distribuzione dei pH, la densità degli ioni e i prodotti della corrosione in queste soluzioni. Le distribuzioni dei prodotti della corrosione ottenute mediante il modello di analisi numerica concordava anche con quelle misurate qualitativamente mediante il metodo FT-IR. Nella soluzione con 500 ppm di NaCl erano precipitati $Zn(OH)_2$, $ZnCl_2$ $6Zn(OH)_2$ e $ZnCO_3$ sullo Zn e presso l'interfaccia Fe / Zn, mentre c'erano limitate precipitazioni sul Fe lontano dall' interfaccia Fe / Zn. D'altra parte, il $Mg(OH)_2$ era precipitato sulla Fe nelle soluzioni con 500ppm di $MgCl_2$ e con 1 / 100 di acqua di mare artificiale. $Mg(OH)_2$ può contribuire alla protezione contro la corrosione di Fe nella soluzione che include Mg^{2+}. Va osservato che il $Mg(OH)_2$ può essere precipitato solo nell'area con protezione catodica perché la costante del prodotto di solubilità di $Mg(OH)_2$ è superiore a quella di $Fe(OH)_2$.