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Anomalous dimension in pitting corrosion of SUS304 in a NaCl solution

M. Saitou, W. Oshikawa, and T. Ishikawa

Department of mechanical systems engineering University of the Ryukyus
1 Senbaru Nishihara-cho Okinawa 903-0213 Japan

The current-potential relations of SUS 304 for a NaCl solution in water ranging from 0.01 to 2 mol/dm³ over a 298-333K temperature range were investigated in order to exhibit the presence of anomalous dimensions that characterize the phase transition such as pitting corrosion. Using the anomalous dimension, all the experimental current points can be represented by a single curve in a reduced variable.

Keywords: anomalous dimension, pitting corrosion, self-similarity,

Introduction

Many investigations into pitting corrosion [1] have been made in order to make clear passivity of stainless steels, which are of technological and practical importance. Especially the problem of instability in the passive layers formed on stainless steels is an attractive area of research. The measurements of the current-potential of stainless steels have been used to find the breakdown of passive layers in a solution of Cl^- ions. As widely known, Cl^- ions retard the oxide formation reaction. Electrochemical research has played a main role in so many models of passivity. Unfortunately there have been very few studies that focus on self-similarity and anomalous dimension in corrosion.

We have had interests in the scaling behavior of corrosion [2-3]. Scaling and self-similarity are important concepts in modern statistical physics [4-5], especially in phase transitions. Scaling is often described by simple power laws consisting of the exponents that determine universality classes characterizing the scaling behavior, irrespective of experimental details.

In order to introduce the concepts of scaling and self-similarity, we briefly see phase diagrams for a liquid and for a magnetization. The phase diagram for the liquid at a fixed pressure indicates regimes where the liquid, gas and the mixture of the gas and liquid exit. The difference of density between the liquid and gas phase, $\Delta\rho$ obeys $\Delta\rho \propto |T - T_c|^\gamma$ where T_c is the critical temperature and γ is the critical exponent independent of particular fluid systems. Then we see a magnet such as iron that shows a magnetization below the critical temperature T_c . The magnetization M also obeys $M \propto |T - T_c|^\gamma$. The two quantities, $\Delta\rho$ and M follow power laws. The power law or the exponent is often deduced from anomalous dimensional analysis [4,6]. This accounts for the fact that anomalous dimensional analysis is a useful tool for phase transitions described by power laws. The value of γ is the same within the accuracy of the experiments. The two systems are apparently different physical systems but share the same sets of exponents. Hence these systems behave in a remarkably similar fashion, which is called universality.

The next step is how we can compute the exponents. The equation of state in phase transitions may be written by a solution of the form $u(x,t) \propto t^\alpha f(xt^\beta)$ where u is some solution such as the magnetization M , α and β are the exponents characterizing the self-similarity of $u(x,t)$, and x and t are variables. The formula for $u(x,t)$ indicates the fact that $u(x,t)$ must be rescaled in two ways: a horizontal scale xt^β and a vertical scale

t^α . In this sense, $u(x,t)$ is called a self-similar solution that can be obtained by the transformations. These exponents, α and β are derived not from simple dimensional analysis but from the calculation of the anomalous dimensions.

Corrosion, considered to be a kind of phase transitions, should exhibit scaling and self-similar properties. For example, anomalous dimensions [4] will give the form of the asymptotic function unknown generally in phase transitions such as pitting corrosion. We start examining the existence of the anomalous dimension in pitting corrosion, which implies the presence of microscopic length scale. Many examples of anomalous dimensions were provided by Barenblatt [6]. In this study, the current-potential relations of SUS304 stainless steels for several NaCl solutions and temperatures were measured and the anomalous dimension in pitting corrosion was derived by the method of Barenblatt, which is the first attempt to find a value of the anomalous dimension in pitting corrosion.

The purpose of this study is to exhibit the presence of the anomalous dimension in pitting corrosion and show that for the anomalous dimension of SUS304, all data from the polarization curves lie on a single curve.

Experiments

SUS 304 stainless steel specimens of size $10^{-2}\text{m} \times 10^{-2}\text{m}$ for working electrodes were prepared, which were mechanically polished, cleaned by a wet process and not sensitized. The reference electrode Ag/AgCl was placed to one side near the 304 stainless steel specimen. The apparatus for measurement of potential-current relations were a conventional electrolytic cell comprising a still bath, a counter platinum electrode, a Ag/AgCl reference electrode and potentiostat. The potential curves were recorded from the bath containing NaCl in a range of 0.01 to 2 mol/dm³ over a temperatures range from 298 to 333K with a swept potential rate of 20mV/min.

Results and discussion

Fig.1 shows the current-potential curves for SUS304 stainless steels in NaCl solutions from 0.01 to 2 mol/dm³ at temperatures from 298 to 333K. The sudden increases in the current density in Fig.1 correspond to the breakdown of the passive layers.

First we derive a formula for the anomalous dimension α . We do not know the functional form that describes the pitting corrosion behavior. However the dissolution of passive layers on stainless steels will obey governing equations related to the transport of ions in water and to chemical reactions at the interface between the

electrolyte and anode electrode. This implies that pitting corrosion obeys some similar dissolution mechanism and shows the scaling behavior [2-3]. The curves in Fig.1 for the different conditions are different. However using a kind of scaling properties, an appropriate value of the anomalous dimension, it will be seen later that all the experimental points locate on a single line.

First, we start explaining dimensional analysis. Physical laws do not depend on arbitrarily chosen basic units of measurements. The dimension of a physical quantity is described by chosen systems of units. For example, the density ρ in the LMT unit where L, M and T are the units of length, mass, and time is $[\rho]=ML^{-3}$. It is customary to denote the dimension of a quantity ϕ by $[\phi]$. This example shows that the dimension of a physical quantity is a power-law monomial. In order to analyze pitting corrosion by dimensional analysis, we must choose a system of units, a physical quantity a and governing parameter a_i that describe a physical relationship as $a=f(a_1, a_2, \dots, a_n)$. In this study, the [C, V, sec, m] unit where C is the coulomb and V is the voltage is chosen. In addition, we choose the governing parameters such as the current density j , the diffusion coefficient D , the applied potential V , the thermal energy $k_B T$ where k_B is the Boltzmann constant and T temperature, the ion charge density q and some reaction constant . The validity of the choices of these parameters depends on whether all the experimental data, irrespective of the experimental details, collapse on a single line. This is because metal atoms should dissolve into a NaCl solution in a similar fashion, that is, according to the same dissolution mechanism, which supports the presence of anomalous dimensions. These parameters have the following dimension in the [C, V, sec, m] unit:

$$[j] = \left[\frac{C}{\text{sec} \cdot m^2} \right], [D] = \left[\frac{m^2}{\text{sec}} \right], [\gamma] = \left[\frac{m^3}{\text{sec}} \right], \quad (1)$$

$$[V] = [V], [k_B T] = [CV], [q] = \left[\frac{C}{m^3} \right],$$

where [] indicates the dimensions of the parameter. We can assume that the current density j has the form

$$j = f(D, \gamma, V, kT, q), \quad (2)$$

where f is a certain function. Here we simply shows the procedure of dimensional

analysis following the Barenblatt's method [6]. A physical quantity a has a form

$$a = f(a_1, \dots, a_k, b_1, \dots, b_m), \quad (3)$$

where a_i and b_i are governing parameters. The parameter a_i has independent dimensions that cannot be represented in the terms of a product of powers of the dimensions of the remaining quantities b_i . Hence the dimension of b_i can be expressed as products of powers of the independent dimensions a_i ,

$$b_i = [a_1]^{p_i} \cdots [a_k]^{r_i}, (i = 1, \dots, m), \quad (4)$$

where p_i , and r_i are the exponents. The dimension of the physical quantity a can be expressed by

$$[a] = [a_1]^p \cdots [a_k]^r, \quad (5)$$

where p and r are the exponents. We introduce the dimensionless parameters

$$\Pi_i = \frac{b_i}{a_1^{p_i} \cdots a_k^{r_i}}, \quad \Pi = \frac{a}{a_1^p \cdots a_k^r}, \quad (6)$$

which yield

$$\Pi = \frac{f(a_1, \dots, a_k, \Pi_1 a_1^{p_1} \cdots a_k^{r_1}, \dots, \Pi_m a_m^{p_m} \cdots a_k^{r_m})}{a_1^p \cdots a_k^r} = F(a_1, \dots, a_k, \Pi_1, \dots, \Pi_m). \quad (7)$$

When the parameter a_i can be changed by an arbitrary factor, Π remains unchanged [6]. This means that the function F is independent of a_i . Hence we have

$$\Pi = \Phi(\Pi_1, \dots, \Pi_m). \quad (8)$$

Finally, Eq.(3) has the following form

$$a = a_1^p \cdots a_k^r \Phi(\Pi_1, \dots, \Pi_m). \quad (9)$$

Applying the above procedure to Eq.(2), we have

$$j = D \left(\frac{Vq^4}{kT} \right)^{1/3} \psi \left[\frac{\gamma}{D} \left(\frac{qV}{kT} \right)^{1/3} \right], \quad (10)$$

where ψ is a dimensionless function. Taking into consideration $q \propto c$ where c is the concentration of Cl^- ions, we can rewrite Eq.(10) as follows:

$$j = A \left(\frac{c^4 V}{T} \right)^{1/3} \psi \left[\left(\frac{cV}{T} \right)^{1/3} \right], \quad (11)$$

where A is a constant.

Next, we consider the dependence of Φ on Π_m in Eq.(9). Suppose that as $\Pi_m \rightarrow 0$ or ∞ , the function Φ tends to zero or infinity. In this case, Π_m remains essential and we cannot delete Π_m from the function Φ . However we can assume that the function Φ has the power-type asymptotic form

$$\Phi = \Pi_m^{-\alpha} \Phi_1(\Pi_1, \dots, \Pi_{m-1}) + O(\Pi_m^{-\alpha}), \quad (12)$$

where α is a constant. Eq.(12) indicates a form of a self-similar solution. Thus, scaling is recovered with the exponent α that does not follow from simple dimensional analysis. The deviation α is called an anomalous dimension. Using the power-type asymptotic form Eq.(12) including the anomalous dimension α [6], finally we can reduce from Eq.(11)

$$j = B \left(T^{-1+\alpha} V^{1-\alpha} c^{4-\alpha} \right)^{1/3}, \quad (13)$$

where B is a constant. The values of anomalous dimensions can be determined by the renormalization group techniques [5]. However, because the governing equations for pitting corrosion are unknown, instead of the renormalization group techniques we find $\alpha=4.428$ so that all the experimental points in Fig.1 can collapse on a single line. Not only the parameters chosen in this study but also other parameters such as specimen finish, sweep rate, sensitization, inclusion contents and so on will affect the behaviors of pitting corrosion. However as mentioned above, we consider the choices of the

parameters to be valid. Fig.2 illustrates the current density vs the reduced variable $(T^{-1+\alpha}V^{1-\alpha}c^{4-\alpha})^{1/3}$ for $\alpha=4.428$. The points on the abscissa in Fig.2 correspond to those on the abscissa in Fig.1.

Generally pitting corrosion is considered as the stochastic process. The pit profiles in pitting corrosion have scaling properties described by the fractal dimension and the scaling exponents [7-9]. The anomalous dimension α is also a kind of the scaling exponents found from the stochastic studies such as Monte Carlo simulations and may be related to the fractal dimension and other scaling exponents.

The value of α is considered to characterize the dissolution mechanism in corrosion. Hence further detailed experimental studies on anomalous dimensions will need to ascertain whether different mechanisms in dissolution have their own anomalous dimensions.

Conclusion

The analysis of the polarization curves finds the presence of anomalous dimension α that characterizes the phase transition. For $\alpha=4.428$, all the data from the polarization curves certainly lie on a single line.

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Figure captions

Fig.1 Current-potential curves for the stainless steels (SUS 304) for the bath containing NaCl in a range of 0.01 to 2 mol/dm³ over a temperature range:

(a) 298 K, (b)313K, (c) 333K

Fig.2 Plot of current density vs a new variable $(T^{1+\alpha}V^{1-\alpha}c^{4-\alpha})^{1/3}$ derived in this study where T is the bath temperature, V is the potential, and c is the NaCl concentration in the bath. For $\alpha=4.428$, all experimental data from Fig.1 collapse on one line.

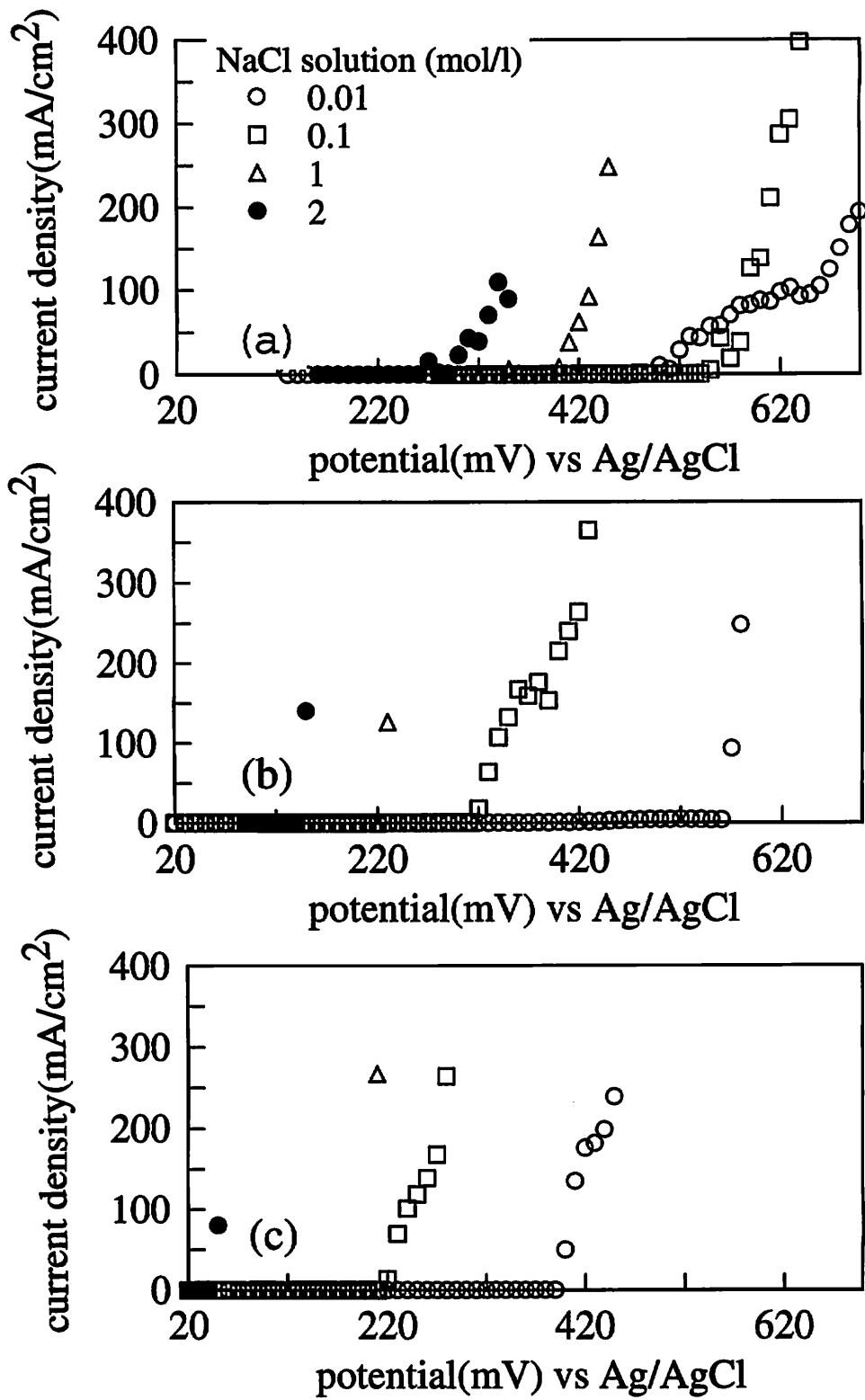


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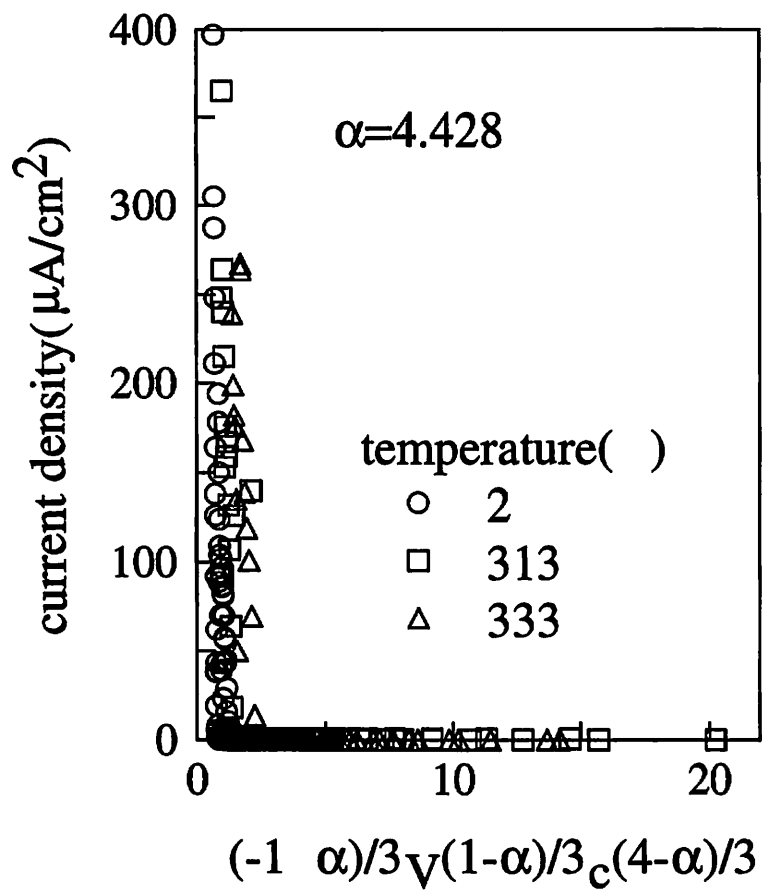


Fig.2 Plot of current density vs a new variable $(T-1+\sqrt[3]{V(1-\alpha)/3} c^{(4-\alpha)/3})^{1/3}$ derived in this study where T is the bath temperature, V is the potential, and c is the NaCl concentration in the bath. For $\alpha=4.428$, all experimental data from Fig.1 collapse on one line.