

Evaluation of Corrosion Resistance Properties by Applying Galvanostatic Nanoscale Current Density on Passive Metals

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In this study, new evaluation method for the stability and corrosion resistance properties of passive films has been suggested by means of observation of self-activation process in open-circuit state and galvanostatic nanoscale reduction test. The experiments were performed for air-formed oxide film in case of plain carbon steel, and for anodically passivated films formed in aqueous sulfuric acid solutions in case of titanium and 304 stainless steel. From these experimental results, we derived two parameters, i_0 and q_0 , which characterize the self-activation process and the properties of passive film on a stainless steel surface. The parameter i_0 was defined as the rate of self-activation, and q_0 , the reduced amount of charge during the self-activation process. In conclusion, it is considered that the stability and corrosion resistance of passive metals and alloys can be evaluated quantitatively by three parameters of τ_0 , q_0 , and i_0 , which easily obtain by means of observing the self-activation process and galvanostatic nanoscale reduction test.

Keywords : *passive film, self-activation, passive-active transition, titanium, austenitic stainless steel*

1. Introduction

Corrosion resistances of passive metals and alloys such as titanium, aluminum, nickel, and stainless steels are attributed to the formation of protective passive films on their surfaces. And, corrosion resistance is dependent on the structure and morphology of passive film.¹⁻³⁾ For the direct observation of passive films, the passivated specimens are taken out from the solution, thus, the change of morphology of passive films in air is not avoidable during this process.

Until now, there have been numerous studies on characteristics and electrochemical properties of passive films, but studies of self-activation phenomena of passivated alloy and dissolution behavior of passive film are extremely limited in number.⁴⁻⁶⁾ Kelly⁶⁾ reported the self-activation process of titanium in sulfuric acid solutions. And, Asano and Maeda^{4,5)} had made an interesting observation that the stability of oxide film on a mild steel could be determined by the self-activation time in a neutral aqueous solution. And they adopted the self-activation time as a parameter for the evaluation of the stability of an oxide film.

In this study, new evaluation method for the stability and corrosion resistance properties of passive films has been suggested by means of observation of self-activation process in open-circuit state and galvanostatic nanoscale reduction test.

We selected titanium, carbon steel, and 304 austenitic stainless steel for experimental specimens. The experiments were performed for air-formed oxide film in case of plain carbon steel, and for anodically passivated films formed in aqueous sulfuric acid solutions in case of titanium and 304 stainless steel.

From these experimental results, we derived two parameters, i_0 and q_0 , which characterize the self-activation process and the properties of passive film on a stainless steel surface. The parameter i_0 was defined as the rate of self-activation, and q_0 , the reduced amount of charge during the self-activation process. These two parameters and self-activation time were discussed in regards to the stability and properties of passive film.

2. Theoretical Background⁷⁻⁹⁾

Consider the applying nanoscale cathodic current on passivated alloy during the self-activation process in an aqueous solution.

The reduction rate of passive film can be estimated by

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considering the additive effect of the external applied current on the dissolution of film. If q_0 is the amount of passive film eliminated from the surface of alloy during the self-activation process, and i_0 is the average reduction rate of passive film, q_0 is expressed by

(1)

When the external current density, i_e , is applied to the passive-active transition process, and if i_e gives fully additive effect to the dissolution of film, the amount of passive film dissolved during the activation, q , is represented, similarly, by

(2)

where τ is the activation time.

If the value of i_e is small enough to ignore the polarization from open-circuit state, we can assume as

(3)

Hence, i_e is obtained from Eqs. (1), (2), and (3) by

(4)

This equation reveals the linear relationship between the externally applied current density and the reciprocal of the activation time.

3. Experimental

3.1 Specimens of carbon steel

The disk-type flat specimens cut from a steel rod of 15 mm diameter including a lead for electrical connection, were embedded in epoxy resin, and mechanically polished with 800 grit silicon carbide papers. Specimens were ultrasonically cleaned in acetone and rinsed thoroughly in redistilled water.

And then, specimens were exposed in air for an hour before immersing the test solutions to obtain reproducible uniform air-formed oxide films on the surface of steel specimens.

3.2 Specimens of titanium and 304 stainless steel

The specimens were prepared the same way from a rod of 25 mm diameter. The electrolytes of 1 M H_2SO_4 concentration were used in this experiment.

In order to remove the oxide film formed in air and to form a uniform anodic passive film on the surface of

electrode, electrochemical pretreatment were carried out through the potentiostatic reduction and following anodic oxidation. The specimen was first cathodically reduced at a constant potential of -0.5 V(vs SCE) for 300s in 1 M H_2SO_4 solution. The reduced specimen was oxidized potentiostatically at 0.3 V for 3600s in case of 304 stainless steel and at 0.38 V for 600s in case of titanium.

3.3 Immersion test and galvanostatic reduction test

The electrolytes were deaerated using high purity nitrogen gas for an hour before each experiment. A saturated calomel electrode was used as the reference electrode, and connected through a salt bridge.

After the pretreatment, self-activation behaviors of specimens were investigated immediately, by measuring the potential variations with time in open-circuit state. The potential was monitored until corrosion potential of active state was reached.

And, galvanostatic cathodic reduction tests were carried out by applying cathodic current density of 50-200 $nAcm^{-2}$ during the activation process.

4. Results and discussion

The results of immersion test in open-circuit state were shown in Fig. 1(carbon steel in 3.5 wt.% NaCl) and Fig. 2(titanium and 304 stainless steel in 1M H_2SO_4).⁷⁾⁻⁹⁾

Typical self-activation curves, obtained in all specimens by open-circuit immersion tests in sodium chloride solution and sulfuric acid solutions. The open-circuit potential initially indicated the passive state potential, and tended to decrease gradually with time. Then potential, which reached some potential, decreased rapidly and indicated a steady state active corrosion potential. The period of time from immersing to rapid decrease in open-circuit potential,

Fig. 1. Potential-time curves during self-activation process of carbon steel with air-formed oxide film in 3.5 wt.% NaCl borate buffer solutions at 25°C.⁷⁾

namely from passive state to active state, was measured as a self-activation time, τ_0 .

Fig. 2 shows that the self-activation time of titanium is more than twice of 304 stainless steel. It means that the depassivation of passive film on titanium is more difficult than 304 stainless steel.

In order to analyze the self-activation behavior of air-formed oxide film and passive film quantitatively, external cathodic current was applied to the specimen and potential variation with time was measured. To minimize the polarization by applied galvanostatic current, nanoscale cathodic current was applied.

The results are shown in Fig. 3(carbon steel), Fig. 4(304 stainless steel), and Fig. 5(titanium).⁷⁻⁹⁾ With increase in external applied cathodic current density, the activation time was shortened in all cases. On the other hand, application of anodic current prolonged the activation time.

Plots of i_e versus $1/\tau$ for galvanostatic reduction of passive film on carbon steel, titanium and 304 stainless steel are given in Fig. 6.⁷⁻⁹⁾ Data were taken from Fig. 3, Fig. 4, and Fig. 5. As shown in Fig. 6, plots represents the straight line, and agrees well with the Eq. (4).

The value of q_0 can be obtained from the slope of straight line, and i_0 , from the intercept on the ordinate. The negative values of q_0 and i_0 mean that the self-activation is the cathodic reduction process.

Galvanostatic reduction tests were performed for various passivation time in a 1 M H₂SO₄ solution at 30 °C(304 stainless steel) and at 40 °C(titanium). Fig. 7 shows the plots of i_e versus $1/\tau$ for galvanostatic reduction test on passivated 304 stainless steel for different passivation time at a constant potential of 0.3 V.⁸⁾ The straight lines were obtained in all conditions, and they also confirmed the validity of Eq. (4) and Fig. 6. The lines are almost parallel and slopes are nearly same values. And exactly same tendency was obtained in case of titanium.

Fig. 2. Potential-time curves during self-activation process of anodically passivated metals in 1 M H₂SO₄ solution.^{8),9)} (a) 304 stainless steel(30°C), (b) titanium(40°C).

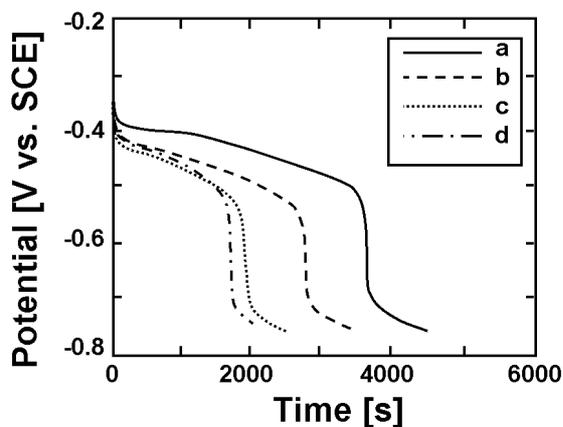


Fig. 3. Potential-time curves for galvanostatic nanoscale cathodic reduction of air-formed oxide film in 1% NaCl solution at 25 °C (carbon steel). (a) 0 nA · cm⁻², (b) 60 nA · cm⁻², (c) 115 nA · cm⁻² and (d) 170 nA · cm⁻²

Fig. 4. Potential-time curves for galvanostatic nanoscale cathodic reduction of passivated 304 stainless steel in 1M H₂SO₄ at 30°C.

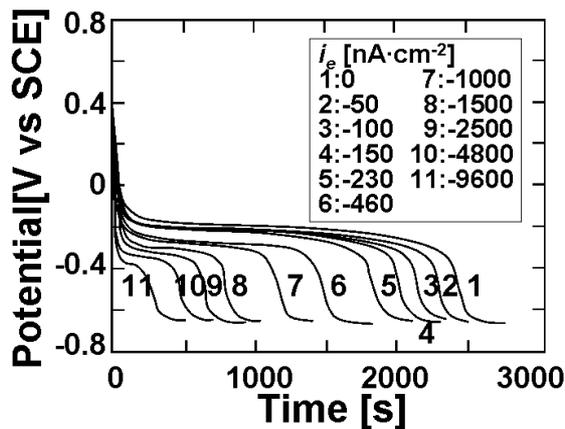


Fig. 5. Potential-time curves for galvanostatic nanoscale cathodic reduction of passivated titanium in 1M H₂SO₄ at 40°C.

Fig. 6. Plots of applied current density, i_e vs. a reciprocal of activation time, $1/\tau$.⁷⁻⁹⁾ (a) carbon steel, (b) 304 stainless steel, (c) titanium.

Fig. 7. Plots of applied current density, i_e vs. a reciprocal of activation time, $1/\tau$ by various passivation time(304 stainless steel).⁸⁾

Fig. 8. Variation of $-i_o$ and $|q_o|$ with passivation time τ_p in 1M H_2SO_4 (304 stainless steel).⁸⁾

The values of q_o and i_o obtained for passive films on 304 stainless steel and titanium formed on different passivation time at a constant potential are shown in Fig. 8 and Fig. 9, as a function of passivation time, τ_p .^{8,9)} Dissolution rate i_o decreases with increasing passivation

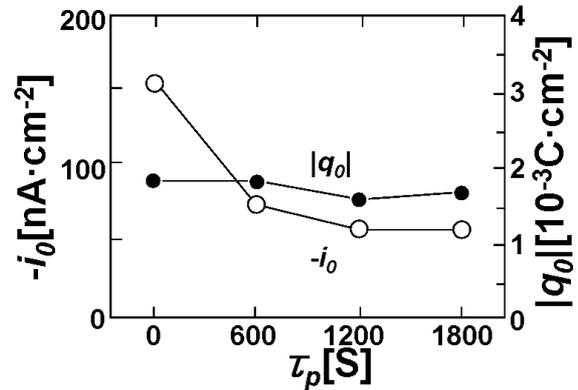


Fig. 9. Variation of $-i_o$ and $|q_o|$ with passivation time τ_p in 1M H_2SO_4 (titanium).⁹⁾

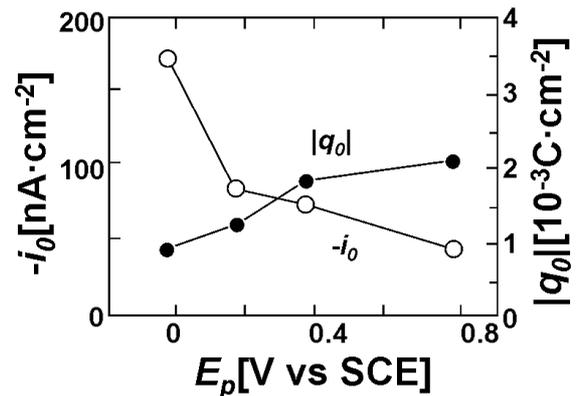


Fig. 10. Variation of $-i_o$ and $|q_o|$ with passivation potential, E_p in 1M H_2SO_4 (titanium).⁹⁾

time.

Fig. 10 shows the results obtained for passive films formed at various passivation potential(E_p) for 600s in case of titanium.⁹⁾ It is observed that q_o is increased linearly with E_p . And, this linear relationship between thickness and formation potential is also one of the characteristics of barrier-type oxide film.^{10,11)} Dissolution rate of self-activation process is decreased with increasing the film thickness, as i_o is decreased with increasing passivation potential.

Fig. 11 shows the variations of q_o and i_o with pH change in 1 M sulfate solutions in case of titanium.⁹⁾ It can be observed that the absolute value of i_o decreases with increasing of pH. It is obtained almost constant value of q_o , and q_o is not dependent upon the pH of solution.

As mentioned above, q_o and i_o could be obtained by measuring the activation time for galvanostatic cathodic reduction of specimens. It is appeared that almost all the amount of applied cathodic current up to 200 nAcm⁻² is consumed for reduction of passive film. The results reveal that the self-activation time, τ_o is prolonged in accordance

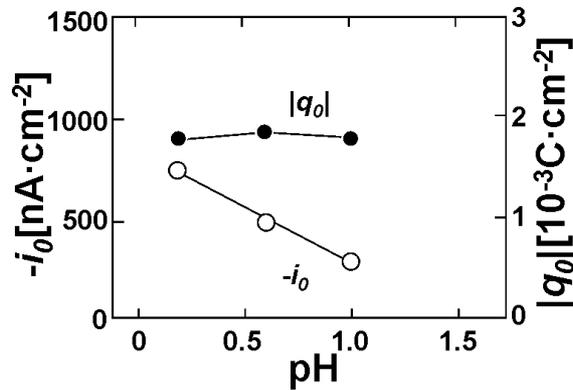


Fig. 11. Variation of $-i_0$ and $|q_0|$ with pH of the solution(titanium).⁹⁾

with increasing the value of q_0 and decreasing the value of i_0 . Therefore, it is concluded that the corrosion resistance of passivated alloy is increased with increasing q_0 and decreasing i_0 .

The amount of charge reduced during self-activation, q_0 is independent upon the pH of solution. q_0 is dependent on the passivation potential. The linear variation of q_0 with passivation potential is attributed to the formation a barrier-type passive film of titanium. Namely, this parameter represents the amount or thickness of the passive film on passive alloy.

The other parameter, i_0 is decreased with increasing the passivation potential, passivation time, and pH of solution, respectively. i_0 represents the average rate of self-activation, that is the cathodic reduction rate of passive film during the self-activation. It is considered that i_0 is balanced with the anodic dissolution rate of substrate metal through the defect of passive film. Therefore, it seemed that i_0 reflects the amount of defect area of the passive film on passive metal.

It seems that this experimental method is useful to evaluate the stability and corrosion resistance of passive metals and alloys quantitatively by three parameters of τ_0 , q_0 , and i_0 , which easily obtain by means of observing the self-activation process in open-circuit state and galvanostatic nanoscale reduction test.

5. Conclusion

The self-activation behaviors for anodically passivated titanium and 304 stainless steel, and for carbon steel with

air-formed oxide film were investigated in aqueous solutions. Two kinetic parameters, q_0 and i_0 are obtained, which are helpful to evaluate the stability of passive film, by analyzing the variation of activation time with the applied cathodic current during the activation process. q_0 is the parameter of representing the amount of the charge accumulated in the film. And it seems that the value of this parameter reveals the thickness and magnitude of passive film formed on the surface. The rate of self-activation, i_0 is considered to be the average dissolution rate of substrate metal through the defect of passive film, and reflects the amount of defect area on the passive film.

In conclusion, it is considered that the stability and corrosion resistance of passive metals and alloys can be evaluated quantitatively by three parameters of τ_0 , q_0 , and i_0 , which easily obtain by means of observing the self-activation process and galvanostatic nanoscale reduction test.

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