Two-layer Structure and Ion Selectivity of Iron Passive Film Affecting Pit Generation

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The layer structure and composition of passive films formed on iron in borate and phosphate solutions at pH 8.42 and 11.50 have been investigated by means of cathodic reduction combined with ellipsometry and chemical analysis. Breakdown of the passive films has also been examined in 0.5 kmol/m³ NaCl solution at a constant potential higher than a critical pitting potential in the same solution. It is found that the composition and breakdown of the passive films change with the potential of film formation, anion species and solution pH, while the film is always of two-layer structure consisting of a barrier layer in contact with the metal and a hydrated deposit layer next to the solution. The dependence of anion species and pH on the composition and breakdown of the films may be systematically explained in terms of an ion selective property of the passive films. Therefore it is suggested that the ion transport in the layers plays an important role in determining the passive film composition and the breakdown.

KEY WORDS: passive film; composition; layer structure; ellipsometry; ion selectivity; cathodic reduction; breakdown; ion transport.

1. Introduction

In a series of papers,¹⁻⁴⁾ it has been shown that the passive films formed on iron in borate and phosphate solutions of pH 8.42 to 11.50 are a two-layered film consisting of a barrier layer of oxide next to the metal phase and a deposit layer of hydroxide in contact with the solution phase. Furthermore the film composition has been found to depend largely upon solution pH and anion species in the solutions. These results imply that such the layer structure and film composition are not identical with those predicted by thermodynamic consideration.⁵⁻⁷⁾ On the other hand, it has been also found that the breakdown of the passive films formed in the same solutions is much influenced by solution pH and anion species,⁸⁾ which may be explained in terms of the property of ion selectivity. This suggests that the change in film composition is also affected by the ion selectivity.

In this work, therefore, the film composition and the breakdown of the passive films are systematically discussed in the light of the property of ion selectivity.

2. Experimental Method

The materials, instruments and methods employed for the present experiments are the same as those described in previous papers.^{1-4,8)} The solutions used for passivating the specimen were borate solutions of pH 8.42 and 11.50 adjusted by addition of 0.3 kmol/m³ H₃BO₃ or a small amount of NaOH to 75 mol/m³ Na₂B₄O₇ and the phosphate solutions of pH

8.42 and 11.50 prepared by mixing 0.15 kmol/m³ NaH₂PO₄ or 0.15 kmol/m³ Na₃PO₄ with 0.15 kmol/m³ NaHPO₄. The solution used in pitting experiments was 0.5 kmol/m³ NaCl solution. In addition the solution for reducing the passive films galvanostatically was 0.15 kmol/m³ borate solution of pH 6.48, in which the passive film on iron was proved to cathodically dissolve layer by layer without any appreciable change in its original composition profile.¹⁾ All solutions were made of guaranteed grade reagents and double distilled water, and then deoxygenated by injection of purified nitrogen.

The specimen surface free from oxide films was prepared by cathodic reduction at pH 8.42 and, immediately after renewing the solution, was anodically oxidized at a constant potential for 1 h to form the passive film on iron. After exchanging the solution to pH 6.48 borate solution, the passive film was cathodically reduced at a constant current of 6.0 μ A/cm² and the solution was analyzed for iron by adsorption spectroscopy as a function of time to cathodic reduction. Furthermore, optical measurements of light-intensity-following ellipsometry¹⁾ were carried out in the course of galvanostatic cathodic reduction of the passive film at an angle of incident of 74.485 with a wavelength of light 546.1 nm by use of an ellipsometer (Rudolph 43702-200E).

For the pitting experiments, the passivated specimen was further polarized at a constant potential of -0.195 V/SHE more noble than a critical pitting potential of iron in 0.5 kmol/m³ NaCl solution to follow the pitting dissolution. The critical pitting

potential was determined to be -0.295 V/SHE by means of a potential step method (0.05 V step for 600 s interval).

All experiments were conducted at 293 ± 0.5 K. The electrode potential was measured against a saturated calomel electrode (SCE) and converted to the standard hydrogen electrode scale (SHE).

3. Results

3.1. Layer Structure, Thickness and Composition of Passive Films

For depth analysis of the passive film, a galvanostatic-cathodic reduction technique combined with ellipsometry and chemical analysis¹⁻⁴⁾ was employed by using a deaerated borate solution at pH 6.48. It has been shown that in the boric-borate solution of pH 6.48 the reaction for ferric oxide films proceeds with equivalent coulomb (current efficiency=1) at a constant cathodic current of $6.0 \mu\text{A}/\text{cm}^2$. The cathodic reduction of the film produces iron(II) ions in the solution,

where, z : the oxidized state of iron in the film.

The change in two ellipsometric parameters, polarizer (P) and analyzer (A) during the cathodic reduction of the film formed on iron can be measured by using the light-intensity-following ellipsometer. Fig. 1 shows a representative example of $\delta P (=P-P_0)$ vs. $\delta A (=A-A_0)$ loci for the passive films formed at 0.845 V for 1 h in the borate and the phosphate solutions of pH 8.42, respectively, where P and A are the readings of polarizer and analyzer for the bare surface. The loci consist of two straight lines with a different slope, indicating that the passive film is composed of two layers, which are in this paper a deposit layer next to the solution and a barrier layer in contact with the metal. A discontinuous break at the deposit/barrier boundary is also found to occur in the

film dissolution curve as described later. The locus is in theory related to the optical constant and thickness of the film, and therefore can be used to determine the optical constant and thickness of the film. Computer calculations⁹⁾ were carried out, in which coulometric estimates of the film thickness were taken into account and the optical constant, $n-ik$, was limited to a range of $n=1.7-3.2$ and $k=0.0-1.0$, within which all the optical constants of known iron oxides or hydroxides are found.

With respect to the optical constants thus estimated of the passive films formed in the borate and the phosphate solutions of pH 8.42 and 11.50, the optical constant of the deposit layer changes little with passivation potential and solution pH, but anion species. The optical constant of the barrier layer, on the other hand, changes depending upon passivation potential and anion species. Specifically, the imaginary part of the optical constant of the barrier layer changes with solution pH in the range of $0.30i$ to $0.45i$,²⁻⁴⁾ which corresponds to the change in the film composition. Furthermore, these optical constants suggest that the deposit layer is of hydroxide and that the barrier layer is of anhydrous oxide.

The film thickness of the passive films may be estimated from the ellipsometric results by using the optical constants obtained above. Fig. 2 shows the film thickness as a function of potential at which the passive film was formed by anodic one-hour oxidation in the borate solution of pH 8.42, where the dashed line indicates a steady anodic current-potential curve. It is found that the barrier layer is potential-dependent except for the potential region of transpassivation where the layer thickness remains nearly constant, while the deposit layer thickness appears to remain almost unchanged except for the potentials below the Flade potential, E_f . Under the conditions of constant overpotential of film formation, the total film thickness and/or the barrier layer thickness are found to keep almost constant independent of anion species and solution pH.

The amount of iron(II) ions dissolved, W_{Fe} , as a function of cathodic charge passed, Q_c , is examined for the passive films. Fig. 3 shows the $W_{\text{Fe}}-Q_c$ curves for the passive films formed at 0.845 V for 1 h in the borate and the phosphate solutions of pH 8.42. Reference lines in the figure corresponds to stoichiometric iron oxides, $z_{\text{Fe}}=2.67$ (Fe_3O_4) and $z_{\text{Fe}}=3.00$ ($\gamma\text{-Fe}_2\text{O}_3$) and their slopes can be used as a reference for the oxidized state of the film. There are two regions where W_{Fe} increases linearly with Q_c in the curves, corresponding to the deposit layer (DL) and the barrier layer (BL). In the borate solution, the slopes for both layers are identical to that of $\gamma\text{-Fe}_2\text{O}_3$. On the other hand, in the phosphate solution, the slope for the deposit layer is very close to that of $\gamma\text{-Fe}_2\text{O}_3$ and the slope for the barrier layer is much steeper than the slope of Fe_3O_4 , which means that the barrier layer has an iron ion valency between $Z_{\text{Fe}}=2.67$ (Fe_3O_4) and $Z_{\text{Fe}}=2.00$ (FeO). In addition it is clearly found that the film dissolution curve in the borate solution is inflected with a distinct shift at the

Fig. 1. Change in ellipsometric parameters P and A during cathodic dissolution at pH 6.48 of the passive films formed at 0.845 V in borate and phosphate solutions of pH 8.42.

The dashed line: An anodic current-potential curve

Fig. 2.

Thickness-potential curve for the passive film formed in borate solution of pH 8.42.

Fig. 3. Cathodic dissolution curves of the passive films formed in borate and phosphate solutions of pH 8.42.

boundary between the deposit layer and the barrier layer. This shift, which varied depending upon the potential of film formation, indicates that either excess iron ions or iron ion vacancies are concentrated at the deposit/barrier boundary. No such shift as above is found to occur at the deposit/barrier boundary in the phosphate solution.

With an increase in solution pH, furthermore, the barrier layer in the borate solution includes iron(II) ions, which means that the iron ion valency tends to be close to that of Fe_3O_4 , but the barrier layer in the phosphate solution has no significant change in the composition. The change in the film composition corresponds to that in the optical constant depending upon anion species and solution pH.

3.2. Breakdown of Passive Film

The passive films formed at one-hour oxidation in the borate and the phosphate solutions were polarized at -0.195 V in 0.5 kmol/m³ NaCl solution, which is more noble than a critical pitting potential of iron in the same solution to obtain the pitting current (i_p) flowing during the polarization. The $\log i_p$ - $\log t$

(time) curve consists of two straight lines with different slopes. It is, however, difficult to determine the time at which the inflection occurs between the two straight lines. To obtain that time with accuracy, the $\log Q_p$ - $\log t$ curve is used instead of the $\log i_p$ - $\log t$ curve, where Q_p is the amount of electric charge passed during the polarization and is calculated by graphic integration of the i_p - t curve recorded.

Fig. 4 shows a representative example of $\log Q_p$ - $\log t$ curves for the passive films formed at 0.645 V in the borate and the phosphate solutions of pH 8.42. It is evident that the time denoted as τ in the figure can be clearly determined from the curves. The value of τ thus obtained is plotted against passivation potential for the passive films formed in the borate and phosphate solutions pH 8.42 and 11.50, respectively, as shown in Figs. 5 and 6. It is found in these figures that the value of τ increases linearly with increasing passivation potential. The value of τ at pH 8.42 is larger in the phosphate solution than in the borate solution over the whole passivation potential, while it is identically the same in the phosphate and borate solutions of pH 11.50. By comparing these two figures at a constant overpotential of film formation, it is found that the value increases in the borate solution, but decreases in the phosphate solution with increasing solution pH.

3.3. Distribution of Anion Species in Passive Film

The distribution of borate ions and phosphate ions in the passive film has been measured by using Auger electron spectroscopy (AES). Fig. 7 shows the schematic depth profiles of borate and phosphate ions in the passive films, which were potentiostatically passivated at 0.845 V for 1 h in the borate and the phosphate solutions of pH 8.42, respectively. Fig. 7 also shows a schematic depth profile for iron-oxygen ratio estimated from the film dissolution curve. Borate ions are included only in the deposit layer, but not in the barrier layer. On the other hand, phosphate ions are included in both the deposit and the barrier layers. It is also found that the amount of these ions in the passive films tends to decrease with increasing

Fig. 4. Time variation of the amount of electric charge passed, which was obtained by graphic integration of measured pitting current-time curves for the passive films formed in borate and phosphate solutions of pH 8.42.

Fig. 6. Relation between τ and passivation potential. τ was obtained for the passive films formed in borate and phosphate solutions of pH 11.50.

solution pH. For example, the barrier layer formed in the phosphate solution of pH 11.50 has no phosphate ions.

4. Discussion

4.1. Ion Selectivity of Passive Film

The experimental results show that the composition of the passive films and the behavior of their breakdown depend largely upon anion species and solution pH. These results may be explained by

Fig. 5. Relation between τ and passivation potential. τ was obtained for the passive films formed in borate and phosphate solutions of pH 8.42.

Fig. 7. Schematic depth profiles for boron or phosphorus obtained by using AES (a) and iron-oxygen ratio (b) in the passive films formed in borate and phosphate solutions of pH 8.42 at 0.845 V (SHE) for 1 h.

taking into account the property of ion selectivity of a precipitated film of ferric hydroxide formed on iron during passivation. The ion-selective property of the precipitated ferric hydroxide can be determined from membrane potential measurements as a function of the activity ratio of sodium chloride in the two neutral solutions separated by the ferric hydroxide membrane.¹⁰⁾ Fig. 8 shows the relation between the membrane potential and the activity ratio of sodium chloride for the precipitated ferric hydroxide membranes with and without adsorption of anion species such as borate ions and phosphate ions; anion adsorption was made by immersing the ferric hydroxide in borate and phosphate solutions of pH 8.42 for about one day. If the slope of the membrane potential

vs. activity ratio curve is negative, the membrane is anion-selective, whereas if it is positive, the membrane is cation-selective. It is found that the ion-selective property of the precipitated film, which itself is originally anion-selective in neutral solution, changes from an anionic selectivity to a cationic one by the adsorption of phosphates ions, but not by that of borate ions. Since the deposit layer is similar to the precipitated membrane as described later, it may be concluded that the passive film formed in the phosphate solution of pH 8.42 is cation-selective and that the passive film in the borate solution of pH 8.42 is an anion-selective.

According to Sakashita and Sato,¹⁰⁾ the ion selectivity of the precipitated film changes from anionic selectivity to cationic one at the point of iso-selectivity pH at pH 10.3. It is therefore suggested that the passive film formed in the borate solution of pH 11.50

is cation-selective. With respect to the phosphate solution, on the other hand, phosphate ions at pH 8.42 are primarily in the form of HPO_4^{2-} and at pH 11.50 are in the nearly equimolar mixture of HPO_4^{2-} and PO_4^{3-} . PO_4^{3-} is not easily incorporated into the film compared to HPO_4^{2-} at an initial stage of film formation, because the affinity of PO_4^{3-} to water is larger than that of HPO_4^{2-} .¹¹⁾ As a result, the amount of phosphorus incorporated into the passive film of pH 11.50 decreases to less than that incorporated into the passive film of pH 8.42. This may be supported by the result of AES measurements described in the previous section. Therefore the conclusion may be led that the passive film formed at pH 11.50 is less cation selective than that at pH 8.42.

From the above discussion, the property of ionic selectivity for the passive films may be illustrated as a function of solution pH in phosphate and borate solutions in Fig. 9, where the ionic selectivity of nickel passive films is also shown for comparison.

4.2. Effect of Ion Selectivity on Film Composition

At an initial stage of potentiostatic passivation, a large active dissolution current flows, which is then rapidly decreased by the formation of a passive film. When ferrous ions produced by the active dissolution exceeds the critical concentration of solubility limit on the iron surface, a deposit film will be formed, corresponding to the formation of the deposit layer. During the process of the deposition borate ions or phosphate ions are incorporated into the deposit layer.

A subsequent process is film growth. In this stage the property of ion selectivity of the passive film would make an important role in determining the film composition. In the case of the passive film with the property of anion selectivity, OH^- ion would predominantly migrate (or diffuse) into the deposit layer, since borate ions or phosphate ions in the solution are difficult to migrate because of their large ion size in comparison to that of OH^- ion. On the other hand, the passive film with the property of cation selectivity has ferrous ions as a main transport ion through the barrier layer. Fig. 10 shows the schematic representation of the ion transport through the passive films formed in the borate and the phosphate solutions of pH 8.42. It may appear that OH^- ion becomes O^{2-}

Fig. 8. Membrane potentials arising across a Fe(III) hydroxide membrane separating two NaCl solutions at concentrations $C_{II}=10 \text{ mol/m}^3$ and $C_{II}=0.1-100 \text{ mol/m}^3$.

Fig. 9. Schematic representation of the ion selectivity for passive films on iron and nickel as functions of solution pH and anion species.

pH_{pis} : the point of iso-selectivity.

Fig. 10. Schematic representation of the ion transport in the passive films formed in borate and phosphate solutions of pH 8.42.

ion at the deposit/barrier boundary to form an oxide as the barrier layer. If a sufficient supply of OH⁻ ion can be attained, no ferrous ions would be detected in the barrier layer and an excess amount of O²⁻ ion should be accumulated at the boundary, which corresponds to the case of the passive film formed in the borate solution of pH 8.42. In the case of a deficient supply of OH⁻ ion, on the other hand, ferrous ions would be accumulated in the barrier layer and no accumulation of O²⁻ ion at the boundary would be observed. This may be the case of the passive film formed in the phosphate solution of pH 8.42.

The above consideration can be applied to the passive films formed in the borate and the phosphate solutions of pH 11.50. The change in their property of ion selectivity should lead to the change in the behavior of ion transport through the passive film. Thus the film composition is subjected to the ion transport such as OH⁻ ion and Fe²⁺ ion followed by the property of ion selectivity.

4.3. Effect of Ion Selectivity on Film Breakdown

Fig. 11 shows the characteristic time for film breakdown, τ , as a function of the thickness of the barrier layer (L_b), which was obtained for the passive films formed in the borate and phosphate solutions of pH 8.42. The dashed line shows τ as a function of the total thickness of the passive films formed in the same solution. It is found that τ is proportional to L_b and becomes zero as L_b approaches zero. Furthermore, it appears that the value of τ in the phosphate solution is larger than that in the borate solution at constant thickness of the barrier layer. Fig. 12 shows the relation between τ and L_b obtained for the passive films formed in the borate and the phosphate solutions of pH 11.50, where the thin lines indicate the results for the passive films formed in the two solutions of pH 8.42. As shown in Fig. 12, τ values in the two solutions are proportional to L_b . At a con-

Fig. 11. Effect of the thickness of the barrier layer and the total layer on τ for the passive films formed in borate and phosphate solutions of pH 8.42.

Fig. 12. Effect of the thickness of the barrier layer on τ for the passive films formed in borate and phosphate solutions of pH 11.50.

stant thickness of the barrier layer, the value of τ in the borate solution is the same as that in the phosphate solution. It is concluded from these results that τ is the time required to perforate completely the barrier layer and therefore is defined as an induction time for pit growth. In other words, the first straight line of the pitting current may be considered to correspond to the period of pit nucleation and the second straight line to that of pit growth.

The dependences of anion species and solution pH on the time, τ , may be explained in terms of the ion selectivity shown in Fig. 9. The ion selective property of the passive film will greatly affect τ , because

the cation selective passive film would inhibit the penetration of Cl^- ions and the anion selective film would promote it. In the borate and the phosphate solutions of pH 8.42, therefore, the τ value for the passive film with the property of cation selectivity in the phosphate solution becomes larger than that for the passive film with anion selectivity in the borate solution. In addition, the dependence of solution pH on the τ value can also be explained by the ion selectivity of the passive film shown in Fig. 9.

5. Conclusion

The results obtained are summarized as follows:

(1) The layer structure of the passive films consists of a deposit layer and a barrier layer in a wide range of film formation potential, anion species and solution pH.

(2) The film composition, especially of the barrier layer, depends upon the potential of film formation, anion species and solution pH.

(3) The film breakdown is also found to depend upon the film formation potential, anion species and solution pH.

(4) The dependences of these three parameters on the film composition and on the film breakdown are explained in terms of the ion selective property of the

passive film such as anion selectivity or cation selectivity.

(5) It is suggested that the ion transport in the layers plays a crucial role in determining the film composition and the film breakdown.

REFERENCES

- 1) R. Nishimura, K. Kudo and N. Sato: *Denki Kagaku*, **44** (1976), 198, 518.
- 2) R. Nishimura, K. Kudo and N. Sato: *Corros. Eng. (Jpn.)*, **25** (1976), 83; **26** (1977), 305.
- 3) R. Nishimura, K. Kudo and N. Sato: *J. Jpn. Inst. Met.*, **40** (1976), 118; **45** (1981), 581.
- 4) N. Sato, K. Kudo and R. Nishimura: *J. Electrochem. Soc.*, **123** (1976), 1419.
- 5) H. Gohr and E. Lange: *Z. Electrochem. Ber. Bunsenges. Physik Chem.*, **61** (1957), 1292.
- 6) K. J. Vetter: *Z. Electrochem. Ber. Bunsenges. Physik Chem.*, **62** (1958), 642.
- 7) M. Nagayama and M. Cohen: *J. Electrochem. Soc.*, **109** (1962), 781.
- 8) R. Nishimura, M. Araki and K. Kudo: *Corrosion*, **40** (1984), 465.
- 9) K. Kudo and N. Sato: *Bull. Facul. Eng., Hokkaido Univ.*, (1971), No. 61, 45.
- 10) M. Sakashita and N. Sato: *Corros. Eng. (Jpn.)*, **28** (1979), 450.
- 11) T. Saji: *J. Metal Finish. Soc., Jpn.*, **28** (1977), 2.