Straining Electrode Behavior of Pure Iron in High Temperature and High Pressure Borate Buffer Solution

By Toshio Shibata* and Shinji Fujimoto**

The repassivation process of pure iron was investigated by a rapid straining electrode technique in a high temperature and high pressure borate buffer solution up to 553 K. The repassivation rate was more rapid than that expected from the parabolic rate law, which was generally observed for corrosion of iron and carbon steels in the high temperature and high pressure water environments. The reaction process is determined by diffusion of Fe$^{2+}$ ion in the aqueous phase contained in pore or other defects in the oxide layer. The rapid repassivation rate is supposed to be attained owing to the decrease in the number and the size of these diffusion paths before the magnetite layer reaches a steady state.

The repassivation behavior is divided into two groups according to the applied potential, the critical potential for the division being around $-0.5 \ V_{\text{SHE}}$ at 523 K. The slower repassivation rate is observed at the nobler potentials. The transformation of reaction product from Fe$_3$O$_4$ to Fe$_2$O$_3$ seems to occur at this critical potential. Based on the results, a favorable condition for SCC of iron base alloys in the high temperature and high pressure water is discussed.

(Received September 19, 1986)

Keywords: straining electrode, high temperature and high pressure water, borate buffer solution, pure iron, parabolic rate law, passivity, magnetite, stress corrosion cracking

I. Introduction

In a previous paper(1), we have reported on the initial stage of anodic behavior of pure iron in a high temperature and high pressure sodium sulphate solution by means of a rapid straining electrode technique. A passive film grew following the parabolic growth law, but the reaction constant showed a negative temperature dependence at passive potentials in the range from 503 to 573 K. Therefore, it has been concluded that a more compact and more protective film is formed at the higher temperatures. Furthermore, no passivation was observed in the temperature range between 373 and 463 K.

Sodium sulphate solution has been used widely as an electrolyte for the electrochemical measurement in the high temperature and high pressure water. However, we have found that SO$_4^{2-}$ ion causes the breakdown of passivity of nickel in the temperature range between about 400 and 450 K(2). It was also found that a similar breakdown or no passivation occurred for pure iron owing to the presence of SO$_4^{2-}$ ion(3)(4). Therefore, the sulphate solution seems to be unsuitable for the electrochemical measurements simulating the corrosion behavior in the high temperature and high purity water.

Iron is, however, known to form a stable passive film(4) in a borate buffer solution at room temperature. Therefore, the borate buffer solution was used in the present work for the analysis of the initial process of dissolution and repassivation of pure iron by using the rapid straining electrode technique.

II. Experimental

A thin iron wire 0.35 mm in diameter was used as the working electrode, whose chemical composition is as follows: O 0.029, N 0.0004, C 0.001, Si 0.003, Mn $< 0.001$, Ni $< 0.001$, P 0.002, S 0.001, Al $< 0.001$ (mass%) and Fe balance. The wire specimens were made of electrolytic iron which was remelted in a vacuum.

* Department of Metallurgical Engineering, Faculty of Engineering, Osaka University, 2-1 Yamada-oka, Suita Osaka 565, Japan.
** Graduate Student of Osaka University, 2-1 Yamada-oka, Suita Osaka 565, Japan.
The specimen was degreased in acetone and was subjected to solution annealing in a vacuum at 1073 K for 900 s, followed by water quenching. The specimen surface was neither polished nor given any further treatment. The electrolyte used in the present work was the borate buffer solution of 0.15 kmol·m⁻³ H₂BO₃ + 0.0375 kmol·m⁻³ Na₂B₄O₇ prepared with reagent grade chemicals and distilled water, and was deaerated with high purity N₂ gas at room temperature before heating.

The straining electrode technique has been described in previous publications\(^{(1)-(3)}\). The wire electrode was elongated rapidly to yield a newly created surface at a constant applied potential in an autoclave. The anodic current increases rapidly to a maximum and decays with time due to formation of passive film. The changes in strain and anodic current with time were recorded. The experimental procedures were almost the same as those described in the previous paper on the straining electrode behavior of pure nickel in the same environment\(^{(5)}\). In the present work, the strain given by an elongation was about 0.8%, and the strain rate was between about 0.3 and 0.4 s⁻¹.

III. Results

1. Polarization behavior

Polarization curves of pure iron in the borate buffer solution at 423 and 523 K are shown in Fig. 1. Iron shows a wide and steady passive region at both temperatures, in contrast to the fact that iron showed a passive state at 523 K but no passivation at all at 423 K in 0.1 kmol·m⁻³ Na₂SO₄\(^{(3)}\).

It is noticeable that the current density passes a minimum at about -0.5 V\text{SHE}, then increases with increasing potential and comes to the secondary passive state in the potential region from 0 to 0.7 V\text{SHE} at 423 K and around 0.5 V\text{SHE} at 523 K.

2. Repassivation behavior

Typical changes in the anodic current with time are shown in Fig. 2. The current density on the newly created surface decayed following a power law:

\[
i = at^{-n}.
\]

The value of \( n \) was about 0.75 and almost independent of potential. The value of \( n \) was in the range from 0.7 to 0.8 at temperatures between 473 and 553 K, and changed from about 0.5 to 0.7 with increasing temperature from 313 to 423 K.

Figure 3 shows the potential dependence of
current density. The suffix to each $i$ indicates the time in second after the elongation was stopped. The transient currents are divided into two groups with respect to their potential dependences. Every current density from $i_0$ to $i_{10}$ shows no potential dependence in the potential region nobler than $-0.2 \text{ V}_{\text{SHE}}$. It is called a plateau region. $i_0$, $i_1$ and $i_{10}$ increase with increasing potential in a less noble potential region. However, $i_{0.01}$ and $i_{0.1}$ show a small negative potential dependence. These facts suggest that the repassivation rate at an early stage in the less noble potential region is different from that in the noble potential region. A similar potential dependence was observed at temperatures between 313 to 553 K.

The mean values of the current density in the plateau region are shown for various temperatures in Fig. 4. $i_0$ increases with increasing temperature, shows a maximum at 503 K and then decreases slightly. The distance between neighboring curves in this figure is proportional to the repassivation rate. The wider distance means the faster repassivation. The repassivation rate shows almost no temperature dependence in the temperature range from 423 to 553 K, but decreases with decreasing temperature below 423 K.

The repassivation rate was able to be discussed quantitatively by analyzing the relation between current density and electric charge passed on the newly created surface, because the anodic current is suppressed by the formation and thickening of passive film which is proportional to the accumulated charge.

The charge density that has passed until a time $t$ after the stop of straining, $Q(t)$, is defined by

$$Q(t) = Q_0 + \int_0^t i(t)dt,$$

(2)

where $Q_0$ is the charge density passed during elongation. The integration in eq. (2) was performed by summation of $i$ vs $t$ curves measured in the experiment.

Relations between log $i$ and $Q$ at 523 K are shown in Fig. 5. log $i$ vs $Q$ curves at various
potentials are divided into two groups. The decay behavior of \( \log i \) with the increase in \( Q \) shows no apparent potential dependence at noble potentials of 0.4, 0.2, 0 and \(-0.2 \) V\( _{\text{SHE}} \). The other group of the decays at \(-0.5, -0.7 \) and \(-0.9 \) V\( _{\text{SHE}} \) also has no potential dependence, although relations between \( i \) and \( t \) have the potential dependence, as shown in Fig. 3. But, an obvious difference in the \( \log i \) vs \( Q \) relation between these two groups is found. Two groups were also admitted at 473 and 423 K.

IV. Discussion

1. Initial current on the newly created surface

The initial process of anodic reaction on the newly created surface of iron is supposed to be controlled by dissolution of Fe\(^{2+} \) ion at the metal/solution interface, because \( i_0 \) showed a positive potential dependence in a potential range near the open circuit potential. Thus, the rate determining step of the initial dissolution process seems to be an activation controlled one. On the other hand, \( i_0 \) showed the plateau region in the nobler potential region, as shown in Fig. 3. \( i_0 \) at the plateau region showed a monotonous temperature dependence in a temperature range from 313 to 503 K, as shown in Fig. 4. The Arrhenius plot of \( i_0 \) at the plateau region is shown in Fig. 6. A linear relation between \( \log i_0 \) and the reciprocal of absolute temperature, \( 1/T \), is recognized, the apparent activation energy being 36 kJ/mol. The value suggests that the initial dissolution of Fe\(^{2+} \) in the plateau region is determined by diffusion in the aqueous solution, because the activation energy for diffusion in the aqueous solution is known to be in the range of few tens kJ/mol\(^6\). On the contrary, \( i_0 \) showed a negative temperature dependence above 503 K, as was seen clearly in Figs. 4 and 6. It is unreasonable that the diffusion process shows a negative temperature dependence. It should be noted that \( i_0 \) is actually not the true initial current density on the bare surface. The film formation had been already started before straining was stopped, because a little time was always needed to give a constant amount of elongation. Therefore, \( i_0 \) includes influences of both active dissolution and the early stage of repassivation on the newly created surface. Thus, it is supposed that the decrease in \( i_0 \) above 503 K is due to the rapid film formation before elongation is stopped.

2. Repassivation behavior

Corrosion mechanisms of carbon and low alloy steels in the high temperature water environment are recently reviewed and discussed in detail by Tomlinson\(^7\). A porous double magnetite layer has been demonstrated to form on iron and carbon steels in high temperature and high pressure aqueous solutions. The corrosion process involves the transportation of reaction species by diffusion in the liquid phase contained in pores or other defects in the magnetite layer\(^8\)(9).

Potter and Mann\(^{10}(11)\) reported that the corrosion rate of mild steel in a high temperature caustic solution decreased with time following the parabolic law. They concluded that the rate of the process is controlled by the diffusion in the liquid phase.

The mechanism of magnetite formation is generally accepted as follows. Fe\(^{2+} \) ion which is dissolved at the metal/film interface diffuses outward through the diffusion paths which consist of pores, grain boundaries or other defects in the magnetite layer. Then Fe\(^{2+} \) deposits on the outer surface of the magnetite layer, and
also a considerable number of Fe$^{2+}$ ions are dissolved away into bulk solution at the same time. Therefore, the rate of this process is determined by diffusion of Fe$^{2+}$ ion in the liquid phase which is contained in the diffusion paths. Thus, the parabolic rate law is observed.

An analysis of the relation between the current density and the charge density provides some information about the film formation mechanisms. In the case of parabolic rate law, a linear relation between $1/i$ and $Q$ is to be expected. This relation, however, was not observed in the present experiment except in the cases at 313 and 353 K.

Most of kinetic studies in the past have been performed for a rather longer duration than that in this study. On the other hand, the straining electrode test examines the very initial process after emergence of bare surface for few tens of seconds. Therefore, the film growth process has not reached a steady state even at the end of the straining electrode test. The rate of initial dissolution proved to be determined by diffusion in the aqueous solution, as stated before. Furthermore, relations between log $i$ and $Q$ showed no potential dependence, as shown in Fig. 5, although the relations were divided into two groups according to the potential. These facts suggest that the film growth is not controlled by the applied potential either. Therefore, the initial process of film formation, observed in the present experiment, is controlled by the diffusion of ions in the aqueous solution. The first process at the emergence of bare surface is considered to be the dissolution of Fe$^{2+}$ ions, a part of which are dissolved away into solution and/or precipitate at the outer surface of the magnetite layer. It is also considered that the precipitation/dissolution ratio changes with time. Consequently, the parabolic rate law has to be modified by assuming the above factors.

In general, the relationship between $J$, the flux of reaction species through the reaction products, and $d$, their thickness, is expressed by the following equation.

$$J = kD/d,$$  \hspace{1cm} (3)

where $k$ is a constant and $D$ is a diffusion constant, on the assumption that the diffusion paths are present uniformly in the reaction products. In the case of anodic film growth, eq. (3) is equivalent to the next equation, which is known as the parabolic law for anodic film growth:

$$i = k'/Q,$$  \hspace{1cm} (4)

on the assumption that the charge density, $Q$, is proportional to the film thickness.

The flux of Fe$^{2+}$ ion is proportional to the number of diffusion paths per unit area, $N(Q)$, and their size, $A(Q)$, both of them being functions of $Q$. In addition, since the film thickness is proportional to the precipitation charge which is a part of the total charge density, the ratio of $Q_{\text{precipitation}}/Q_{\text{total}}$ is also a function of $Q$, $\alpha(Q)$. Thus, eq. (3) is modified to the following equation:

$$i = N(Q) \cdot A(Q) \cdot k'/\alpha(Q) \cdot Q.$$  \hspace{1cm} (5)

Figure 7 shows the relationship between $i$ and $Q$ in log-log plots in the plateau potential region for various temperatures. Their slopes ranged from $-2.5$ to $-3.5$ above 423 K and were about $-1$ at 313 and 353 K. If the relation between $i$ and $Q$ followed eq. (4), namely the parabolic law, the slope should be $-1$. This figure shows that the parabolic law can be
applied only to 313 and 353 K. The slopes at the higher temperatures were rather larger than those expected by eq. (4). This fact suggests that the three factors of $N(Q)$, $A(Q)$ and $\alpha(Q)$ in eq. (4) depended on $Q$. These three factors are possible to be expressed by power functions of $Q$ as a first approximation, because almost linear relations were observed in $\log i$ vs $\log Q$ plots. The large change in $\alpha(Q)$, however, can not be expected, because the precipitation ratio, $\alpha(Q)$, is in the range from 0 to 1 and does not show any large change at the initial stage of repassivation\(^{(12)}\). Thus, this factor, $\alpha(Q)$, can be equated to a constant value, $\alpha$. Therefore, eq. (5) is modified to

$$i = k^* Q^{m+l}/\alpha \cdot Q \quad (6)$$

$$= k^* Q^{m+l+1}/\alpha \cdot Q \quad (7)$$

$$= k^* Q^{m+l+1}/\alpha \quad (8)$$

The slope of $\log i$ vs $\log Q$ is $-2.5--3.5$. Thus, $m+l=-1.5--2.5$ is obtained. This result indicates that a large change in the structure of the magnetite layer took place with the accumulation of charge density.

In the previous paper, we have reported that pure iron showed a very slow repassivation rate in 0.1 kmol.m\(^{-3}\) Na\(_2\)SO\(_4\) above 503 K, until the charge density reached $10^7-10^8$ C.m\(^{-2}\). After this initial dissolution period, the repassivation followed the parabolic law. A considerable amount of charge was consumed by the dissolution of ions into solution or the formation of non-protective hydroxide in the initial period in the sulphate solution. A porous magnetite layer which was less protective than that formed in the borate buffer solution was formed during the initial dissolution period. Then, this initially formed porous magnetite layer grew continuously with the constant number and the constant size of pores. Therefore, the parabolic law was observed.

On the other hand, it is well known that the magnetite layer formed on iron in high temperature and high pressure water consists of crystalline particles larger than a few $\mu$m\(^{(7)}\). Thus, it is supposed that such large size particles can not fully cover the bare surface during the short time of the straining electrode test. Therefore, the nucleation and rapid growth of the particles occurred with a rapid change in the size and the number of diffusion paths, defined as $A(Q)$ and $N(Q)$, during the initial period. Thus, a large change in the structural factors expressed as $Q^{m+l}$ was expected with the power of $m+l$ being $-1.5--2.5$. Consequently, the more rapid repassivation was observed compared with that of the parabolic law.

### 3. Effect of potential

The change in current density was divided into two groups according to the applied potential, namely, the noble and less noble potential groups. The critical potential for the dividing was about $-0.5$ V at 523 K. The current density of the polarization curves increased slightly from $-0.6$ V at 523 K and from $-0.4$ V at 423 K, as shown in Fig. 1. This increase seems to be related to the oxidation of Fe\(^{2+}\) ion to Fe\(^{3+}\) ion. Fujii et al.\(^{(13)}\) observed that the corrosion products formed on mild steel were Fe\(_3\)O\(_4\) at around the corrosion potential, and that a small amount of $\gamma$-Fe\(_2\)O\(_3\) was also detected together with Fe\(_3\)O\(_4\) at the higher potentials by transmission electron diffraction. Thus, they concluded that a peak potential observed in the polarization curve at around $-0.25$ V at 553 K corresponded to the oxidation of Fe\(_3\)O\(_4\) to Fe\(_2\)O\(_3\), this potential being measured by the external SCE reference electrode. Thus, the potential seems to be equivalent to about $-0.5$ V\(_{\text{SHE}}\) at 553 K. It is supposed that the change in repassivation behavior at the critical potential around $-0.5$ V is due to the change in the reaction species from Fe\(^{2+}\) to Fe\(^{3+}\) and/or in the structure of reaction products. Thus, the film composition is prone to change from magnetite to hematite in this noble potential region. The larger anodic current than that at the less noble potentials flows, because the formation of Fe\(^{3+}\) needs more charge than that of Fe\(^{2+}\).

Umemura and Kawamoto investigated the SCC susceptibility of carbon steel in the high temperature and high pressure water by SSRT\(^{(14)}\). They reported that carbon steel is susceptible to SCC in aerated pure water at 523 K, namely at a noble corrosion potential, but is not in deaerated pure water, in which the
corrosion potential is less noble. They also reported that SCC occurs only in a potential region nobler than \(-0.4\ V_{\text{SHE}}\) in 0.1 kmol \cdot m\(^{-3}\) Na\(_2\)SO\(_4\) under controlled potential condition. Thus, it is more likely that the change in repassivation behavior observed for iron at the critical potential has a close relation to the susceptibility of SCC of iron base alloys.

4. Effect of temperature

There are some reports that corrosion rates of iron, carbon steels and stainless steels show a maximum around 523 K\(^{(15)- (17)}\) in various environments. The relation between \log i\ and \log Q\ in Fig. 7 showed the maximum current density at 503 K, and also \(i_0\) showed a maximum at 503 K. In a previous paper on the straining electrode behavior of pure iron in 0.1 kmol \cdot m\(^{-3}\) Na\(_2\)SO\(_4\), we have reported that the passive film on a newly created surface of pure iron grows following the parabolic growth law, \(i = k/Q\), above 503 K up to 573 K. The rate constant, \(k\), however, showed a negative temperature dependence. Namely, the repassivation rate showed a minimum at 503 K in the temperature range. Moreover, the initial dissolution charge, \(Q_{di}\), which had passed before the parabolic film growth started, showed a maximum at 503 K\(^{(10)}\). It should be noted that the maximum repassivation rate was observed at around 500 to 520 K not only for the long time but also for the very early period examined by the straining electrode test.

The repassivation rate was independent of temperature above 423 K, and the maximum initial current density was found at 503 K, as discussed in Fig. 4. Consequently, a favorable condition for SCC was attained at 503 K, at which the highest dissolution on the bare surface took place with a rapid repassivation.

5. Conclusions

The initial stage of repassivation process of pure iron was investigated in the high temperature and high pressure borate buffer solution by a rapid straining electrode technique.

1. The current density on the newly created surface decayed following a power law: \(i = at^{-n}\) with \(n\) ranging from 0.7 to 0.8 above 473 K.

2. The repassivation process seems to be controlled by the diffusion in aqueous solution, but was more rapid than that expected for the parabolic rate law.

3. The repassivation process was controlled by diffusion of Fe\(^{2+}\) ions in diffusion paths, which consisted of pores or other defects in the magnetite layer. The rapid repassivation rate was supposed to be caused by the decrease in the number and the size of these diffusion paths with time during the initial stage of film formation.

4. The repassivation behavior was divided into two groups according to applied potential, the critical potential being around \(-0.5\ V_{\text{SHE}}\) at 523 K. The more rapid repassivation rate was observed at the nobler potentials. A change in reaction products from Fe\(_3\)O\(_4\) to Fe\(_2\)O\(_3\) seemed to occur above the critical potential.

5. A favorable condition for SCC was attained at 503 K, at which the highest dissolution on the bare surface took place with a rapid repassivation.

REFERENCES

1. T. Shibata and S. Fujimoto: Trans. Japan Inst. Metals, 25 (1984), 553.
2. T. Shibata and S. Fujimoto: Corrosion, 41 (1985), 177.
3. T. Shibata and S. Fujimoto: Boshoku Gijutsu, 34 (1985), 72.
4. M. Nagayama and M. Cohen: J. Electrochem. Soc., 109 (1962), 781.
5. T. Shibata and S. Fujimoto: Trans. Japan Inst. Metals, 28 (1987), 224.
6. R. Parsons: Handbook of Electrochemical Constants, Butterworth Sci. Publ., London, (1959).
7. L. Tomlinson: Corrosion, 37 (1981), 591.
8. J. E. Castle and H. G. Masterson: Corros. Sci., 6 (1966), 93.
(9) G. J. Bignold, R. Garnsey and G. M. W. Mann: Corros. Sci., 12 (1972), 325.
(10) E. C. Potter and G. M. W. Mann: Proc. 1st Int. Cong. on Metallic Corros., London, (1961), p. 417.
(11) G. M. W. Mann: *High Temperature High Pressure Electrochemistry in Aqueous Solution*, NACE (1976), p. 34.
(12) J. B. Lumsden and R. W. Staehle: *High Temperature High Pressure Electrochemistry in Aqueous Solution*, NACE (1976), p. 400.
(13) T. Fujii, T. Kobayashi and G. Ito: *High Temperature High Pressure Electrochemistry in Aqueous Solution*, NACE (1976), p. 416.
(14) F. Umemura and T. Kawamoto: Boshoku Gijutsu, 30 (1981), 276.
(15) T. Maekawa, M. Kagawa and N. Nakajima: J. Japan Inst. Metals, 31 (1967), 1213.
(16) M. Warzee, J. Hennaut, M. Maurice, C. Sonnen, J. Waty and Ph. Berge: J. Electrochem. Soc., 112 (1965), 670.
(17) G. Ito, Y. Shimizu and S. Sato: Boshoku Gijutsu, 18 (1969), 345.
(18) H. Choi, F. H. Beck, Z. Szklarska-Smialowska and D. D. MacDonald: Corrosion, 38 (1982), 136.
(19) N. Ohnaka, S. Shoji, E. Kikuchi, A. Minato and H. Ito: Boshoku Gijutsu, 32 (1983), 214.