Propagation and Repassivation of Pits on Stainless Steel in Aqueous Solutions Containing Chloride Ions

Yuan Haun Lee*, Zenichiro Takehara* and Shiro Yoshizawa*

**Department of Industrial Chemistry, Faculty of Engineering,
Kyoto University*

Pitting corrosion and its protection of stainless steel were studied by using an electrochemical technique. In order to prevent pitting corrosion, it is important to know the inversion potential at which the repassivation of pit begins to undergo. This potential was a function of the bulk concentration of chloride ions and the time of polarization. The alkylamines which had the alkyl groups of large carbon numbers, i. e., di-n-amylamine and di-n-hexylamine were beneficial as the inhibitors of pitting corrosion of stainless steel. Pitting corrosion played an important role in stress corrosion cracking. Inversion potential was also important as a characteristic value to determine the susceptibility to such a cracking. And such a cracking will be prevented in the region between the inversion and the protection potentials.

1. Introduction

It is well known that pits initiate on the passivated surface of steel in chloride aqueous solution, when it is polarized to a potential more positive than the pitting potential. After pit initiates, it propagates even at a potential more negative than the pitting potential¹⁾. To prevent the propagation perfectly, steels must be polarized to a potential more negative than a protection potential for the pit propagation. Generally, such critical potential is determined by the potential scanning method¹⁾. While such method is very convenient, the observed potentials are dependent on the scanning rate of the potential, and it is very difficult to determine the precise value^{2,3)}. In order to prevent such a pitting corrosion, it is important to know whether the pre-existing pits continue to propagate or undergo repassivation. Suzuki and Kitamura have proposed that the critical potential that the local anode in pit continues by active dissolution is important for the pit propagation⁴⁾. Such critical potential was determined from the fact that the dissolution current of the activated artificial pit anode kept at that potential was not changed with time. The measurement of the dissolution current of such pit is very complicated. In previous paper⁵⁾, simplified measurement of a critical potential at which the repassivation of pit began to undergo was designated as the inversion potential and proposed as a characteristic value

that determined susceptibility to pitting corrosion. And then, as an example, the inversion potential of a carbon steel in chloride aqueous solution was discussed. In this paper, the effects of the concentration of chloride ions, and the addition of dialkylamines as the corrosion inhibitors on the inversion potential of an austenitic stainless steel were examined. Then, stress corrosion cracking (SCC) of the stainless steel is discussed in conjunction with the inversion potential.

2. Experimental Procedures

An austenitic stainless steel (SUS 304) was used as the test piece. It was annealed in an argon atmosphere at 1000°C for 20 min and then its surface was abraded with 400 and 1000 grade emery papers. The corroding solution was 0.15 N boric acid containing various concentrations of chloride ions and its pH was adjusted by the addition of sodium borate to pH 7. By the bubbling with nitrogen through it, dissolved oxygen was removed. A test cell previously used⁶⁾, with a platinum counter electrode and a saturated calomel electrode (SCE) as a reference was set at 25°C. A disk specimen mounted onto a cylindrical holder of acrylic plastics (effective surface area 0.5 cm²) was used as a working electrode. For SCC test, a test specimen was covered with Teflon sheet except for an exposure, having 1 cm² at the middle part to contact the test solution in a cell (Fig. 1). The mechanical properties of specimen were measured. Yield stress (0.20% strains), ultimate

* Yoshida-Honmachi, Sakyo-ku, Kyoto 606, Japan

Fig. 1. The specimen and the cell for SCC test. a: stainless steel, b: cell, c: counter electrode (Pt), d: exposed part (1 cm^2), e: Luggin capillary, PS: potentiostat, SCE: saturated calomel electrode.

tensile strength and elongation were $25 \text{ kg} \cdot \text{mm}^{-2}$, $80 \text{ kg} \cdot \text{mm}^{-2}$ and 70% , respectively. Thus, a stress between 25 and $80 \text{ kg} \cdot \text{mm}^{-2}$ was applied in the SCC test.

Current-potential curves were observed by the potential sweep method at a scanning rate of $0.025 \text{ V} \cdot \text{min}^{-1}$ to determine the pitting and the protection potentials. The inversion potential previously designated⁵⁾ was determined as follows: After anodic and cathodic pre-treatments to reduce the surface oxide, the specimen was polarized anodically at a scanning rate of $0.025 \text{ V} \cdot \text{min}^{-1}$ until the pitting potential, and was kept for 5 min at this potential. Then the imposed potential was changed rapidly to -0.45 V (vs. SCE), which was a potential more negative than the protection potential and kept for 5 min to repassivate the pits. The potential of the specimen on which pits

had initiated by the above procedure was then rapidly changed to a potential between the protection and the pitting potentials and the current-time relation was determined. Subsequently, the potential was changed rapidly back to -0.45 V and kept for 5 min. Then the potential was set rapidly at a new potential more positive than the previous one. By repeating this procedure, current-time relationship at various potentials was determined.

3. Results and Discussion

3.1 Typical current-time relations and inversion potentials

The $\log i$ and $\log t$ relations at various potentials existing between the protection and the pitting potentials were obtained from current-time (i - t) relation at each potential (Fig. 2). The positive slope indicates propagation of pre-existing pits and the negative one shows repassivation. The critical potential at which the slope changes its sign corresponds to the inversion potential. Though $\log i$ and $\log t$ at each potential showed a linear relation in the case of carbon steel⁵⁾, a complicated relationship appeared near the inversion potential in the case of stainless steel, especially, in highly concentrated chloride solutions.

The $\partial \log i / \partial \log t$ vs. potential curves in the solution containing various concentrations of chloride ions obtained from Fig. 2 are shown in Fig. 3 (a). A potential showing zero value of $\partial \log i / \partial \log t$ could not be determined from Fig. 3 (a), and it was given as a wide region between two potential values, e. g., 0.46 V and 0.27 V (vs. SCE) in the solution containing $5 \times 10^{-2} \text{ M Cl}^-$. This

Fig. 2. Typical current-time curves at various potentials in the solution containing (a) $5 \times 10^{-3} \text{ M Cl}^-$ and (b) $5 \times 10^{-1} \text{ M Cl}^-$.

Fig. 3. (a) plots of $\partial \log i / \partial \log t$ against potentials and (b) inversion potentials as the function of time in the solution containing various concentrations of Cl^- ions. a: 5×10^{-1} M Cl^- , b: 5×10^{-2} M Cl^- , c: 5×10^{-8} M Cl^- .

indicates that the inversion potentials can be represented as a function of time of polarization (Fig. 3 (b)). The left part of the region of inversion potential in Fig. 3 (b) indicates the region in which the propagation of pit can not occur. The right part indicates that in which the pitting corrosion does not stop. This phenomenon indicates that the repassivation process of pits changes to the propagation process after induction period. The length of this period was dependent on the imposed potential and the concentration of chloride ions. It is presumably due to that the increase in the concentration of chloride ions in pits of stainless steel by continuous polarization is more remarkable than that of carbon steel⁶⁾.

The inversion potential region existed between the pitting and the protection potentials determined by the potential sweep method (Fig. 3 (a), Fig. 8). In this measurement, the specimen existed pre-initiated pits was kept at a potential more negative than the protection potential. Thus, at the start of the measurement of current-time relationship at various potentials, the solution composition on the pre-initiated pits may become the same as that of

the bulk^{*1}. The inversion potential obtained at such condition was more negative than the pitting potential. This shows the pre-initiated pits propagate even on the same solution as that of the bulk at a potential more negative than the pitting potential of the free surface. The surface having micro-pits has the high sensitivity for the pitting corrosion. The determination of such inversion potential region is important and useful to discuss the pitting corrosion in practice.

3.2 Effects of corrosion inhibitors

In the case of carbon steel, the addition of dial-

Fig. 4. Effects of di-n-butylamine on the induction period from repassivation to propagation of pits at (a) 0.3 V and (b) 0.4 V (vs. SCE) in the region of inversion potential in the solution containing 5×10^{-2} M Cl^- . a: no inhibitor, b: 2×10^{-8} M, c: 4×10^{-8} M, d: 8×10^{-8} M, e: 2×10^{-2} M di-n-butylamine.

*1 The critical potential proposed by Suzuki and Kitamura⁴⁾ shows the potential for the propagation of pits in the more enriched solution of hydrogen and chloride ions than that of the bulk. Therefore, the inversion potential may be considered to be the potential to prevent the pit-propagation obtained at more mild condition than the critical potential by Suzuki and Kitamura. The inversion potentials are represented as a function of time of polarization. This is due to the enrichment of hydrogen and chloride ions in the pits by the continuous polarization. Thus, the most negative potential in the region of inversion potential may correspond to such critical potential.

kylamines had an effect to shift the inversion potential to more anodic value⁵⁾. However, in the case of stainless steel, these inhibitors did not bring such shift of inversion potential clearly. The inversion potential behaved as a function of time of polarization as Fig. 3 (b). The induction periods from repassivation to propagation of pits in the region of inversion potential increased with the increasing addition of the dialkylamines in the solution (Figs. 4 and 5). This indicates that the addition of amines prevents the adsorption of chloride ions in the pits, which is well known to be responsible for the progress of pitting corrosion, and in consequence it is effective to prevent pit-propagation. In the solution containing 5×10^{-2} M Cl^- , the pit-propagation on stainless steel begins after about 30 sec at 0.3 V (vs. SCE), but in the solution containing 2×10^{-2} M dialkylamine, it can not occur even after a longer period than 500 sec at 0.4 V.

The effect of the additions of various dialkylamines on the induction period at various imposed potential was examined and shown in Figs. 6 and 7. These figures indicate that dialkylamines which had the alkyl groups of a large carbon number, i. e., di-

n-amyamine and di-n-hexylamine, are effective to prevent pit-propagation. The pit-propagations are not observed even at more anodic potential than 0.5 V (vs. SCE) in the solution containing 8×10^{-3} M di-n-hexylamine.

3.3 Stress corrosion cracking in respect of the pit-propagation

Time to failure of the stainless steel in the neutral aqueous solution containing chloride ions under the applied stresses between its yield strength and ultimate tensile strength was measured. Nearly the same failure time, despite pre- or non-pitting was observed. But, the smaller the stress applied, the longer the failure time was, e. g., in 0.1 M NaCl solution, the failure times of sample kept at 0.5 V (vs. SCE) existed in the region of 200~300, 500~3,000 and 10,000~30,000 min for the applied stresses of 45, 40 and 35 $\text{kg} \cdot \text{mm}^{-2}$, respectively. (Measurements were carried out for four times under each condition.) In the pitting region, failure surface showed that half of specimen's width corroded in pitting, then a mechanical fracture in 45° followed rapidly.

Fig. 5. Effects of di-n-amyamine on the induction period at (a) 0.3 V and (b) 0.4 V (vs. SCE) in the region of inversion potential in the solution containing 5×10^{-2} M Cl^- . a: no inhibitor, b: 2×10^{-3} M, c: 4×10^{-3} M, d: 8×10^{-3} M, e: 2×10^{-2} M di-n-amyamine

Fig. 6. Effects of various amines on the induction period at (a) 0.3 V and (b) 0.4 V (vs. SCE) in the region of inversion potential in the solution containing 5×10^{-2} M Cl^- . a: no inhibitor, b, b': di-n-propylamine, c, c': di-n-butylamine, d, d': di-n-amyamine, e, e': di-n-hexylamine, b, c, d, e: 2×10^{-3} M inhibitor; b', c', d', e': 8×10^{-3} M inhibitor.

Fig. 7. Effects of various amines on the induction period at 0.5 V (vs. SCE) in the solution containing 5×10^{-2} M Cl^- . 1: no inhibitor, 2: 8×10^{-3} M di-n-propylamine, 3: 8×10^{-3} M di-n-butylamine, 4: 2×10^{-3} M di-n-amylamine, 5: 4×10^{-3} M di-n-amylamine, 6: 8×10^{-3} M di-n-amylamine, 7: 2×10^{-2} M di-n-amylamine, 8: 8×10^{-3} M di-n-hexylamine

Sometimes, crevice corrosion on the interface between the steel and Teflon sheet was observed and pitting on the middle part of specimen disappeared. At such specimen, the region of its inversion potential shifted to more cathodic values and the failure time became longer than the ordinary ones, e.g., in 0.1 M NaCl that region existed between 0.3 and 0 V (vs. SCE) at such specimen, but between 0.4 and 0.2 V at the ordinary ones, and the failure times of the former were about 30,000 and 2,300 min at the applied stresses of 35 and 40 $\text{kg} \cdot \text{mm}^{-2}$, but those of the latter were about 15,000 and 500 min at 35 and 40 $\text{kg} \cdot \text{mm}^{-2}$, respectively. These phenomena may be explained by that in the case of occurrence of crevice corrosion, the enrichment of chloride ions in the crevice causes to shift the inversion potential apparently to more cathodic values and the acceleration of general corrosion in the crevice retards the pit-propagation in the middle part of specimen. Thus, times to failure of the specimen, which did not show the crevice corrosion, were measured in respect of pitting, protection and inversion potentials (Fig. 8). Fig. 8 shows that SCC of the stainless

Fig. 8. Time to failure (min) under the applied stress of 45 or 35 $\text{kg} \cdot \text{mm}^{-2}$, written in the figure of pitting, protection and inversion potentials as the function of the concentration of Cl^- ions in the solution. (pit) shows the sample having the pre-existing pits formed by keeping it on the pitting potential for 5 min.

steel will be prevented in the region between the inversion and the protection potentials, and the sensitivity for SCC will be enlarged at the more anodic region than that of inversion potential. The inversion potential at which the repassivation of pit begins to undergo is also important as a characteristic value to show the susceptibility to SCC induced by pitting corrosion.

4. Conclusion

The inversion potential, i. e., the critical potential at which repassivation of pit began to undergo was important to prevent the pitting corrosion of stainless steel. The region of inversion potential was observed in the region between the pitting and the protection potentials. With increasing chloride ions in the solution, this region shifted in the cathodic direction and the susceptibility of pitting corrosion increased. The dialkylamines which had the alkyl groups of a large numbers have an effect to increase the induction period from repassivation to propagation of pits in the region of inversion potential and beneficial as the inhibitors for pitting corrosion. Pitting corrosion plays an important role in SCC of stainless steel. SCC will be prevented in the region between the inversion and the protection potentials, but accelerated at the more anodic region than the inversion potential.

(Received February 22, 1980)

References

- 1) M. Pourbaix *et. al.*: *Corrosion Science*, **3**, 239 (1963).
- 2) B. Wilde: *Corrosion*, **28**, 283 (1972).
- 3) Y. Hisamatsu: *Corrosion Engineering, Japan (Boshoku Gijutsu)*, **21**, 503 (1972).
- 4) T. Suzuki & Y. Kitamura: *Corrosion*, **28**, 1 (1972)
- 5) Y. H. Lee, Z. Takehara & S. Yoshizawa: *Corrosion Engineering, Japan (Boshoku Gijutsu)*, **27**, 117 (1978).
- 6) Y. H. Lee, Z. Takehara & S. Yoshizawa: *Corrosion Science*, to be published.