Testing Method for Localized Corrosion of Stainless Steel Considering the Corrosion Potential in its Environment

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An electrochemical testing method has been proposed to predict the localized corrosion of stainless steels in chloride media. The method is characterized by the comparison of the critical potential for growth or propagation, which is determined by using an artificial specimen, with the spontaneous corrosion potential measured under the practical condition. The critical potential is the potential at which the rate of formation of corrosive products within the occluded anode is equal to that of consumption and/or dissipation of the products. If the critical potential is more noble than the spontaneous corrosion potential, the EMF between the local anode and the cathode becomes negative, so that the localized corrosion can not occur. This testing method was proved to be effective for the selection of construction materials for chemical plants, and for the analysis of localized corrosion formed in chemical equipments.

1. Introduction

The prediction for localized corrosion of stainless steel used in chemical equipments, especially pitting corrosion, crevice corrosion, and stress corrosion cracking (SCC) in chloride media, has been made empirically by considering the alloy composition, chloride ion concentration, and temperature of the solution. However, this method is difficult to use in quantitatively evaluating the redox nature of the environment, which is an important factor for localized corrosion. In this paper an electrochemical testing method which considers all factors has been proposed to predict the localized corrosion in chemical equipments.

2. Critical Potential for Growth of Localized Corrosion

The critical potential exists for the initiation of pitting and SCC of stainless steels in chloride media. Pitting and SCC can, however, grow or propagate at a potential more active than the critical potential for the initiation, and crevice corrosion may initiate in this potential range. These facts show that the critical potential for initiation can not be used as the criterion whether or not the localized corrosion occurs.

The method proposed in this paper is characterized by the comparison of the critical potential for growth or propagation (E_g), not for initiation,

with the spontaneous corrosion potential measured in chemical equipments under their practical operating condition. If E_g is more noble than the corrosion potential, the localized corrosion can not occur.

Some authors point out the existence of the protection potential¹⁻³⁾ or the termination potential⁴⁾ in a potential range more active than the initiation potential for pitting. The initiated pit can not grow below the protection potential, which is determined by the potentiodynamic hysteresis technique. As pointed out by Wilde⁵⁾ and Hisamatsu⁶⁾, this potential varies depending on the current density value of the reversing point on the potentiodynamic cyclic polarization curve and on the potential sweep rate in the reversing polarization measurement. The facts suggest that the characteristic potential determined by the above methods is insufficient as a criterion for predicting practical pitting.

The authors previously measured the critical potential for growth (E_g) of various types of localized corrosion^{7,8)} and discussed its physical meaning in relation to the chemical and electrochemical characteristics of the solution within the local anode.⁹⁾ The authors believe that E_g should be the potential at which the rate of formation of corrosive products represented by hydrogen ions in the solution within the occluded anode is equal to that of consumption and/or dissipation of the products. The rate of formation is determined by the anodic dissolution which supplies the metal ions and causes the migration of Cl^- to the ano-

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lyte, and the metal ions hydrolyze to produce hydrogen ions. The rate of consumption is determined by the cathodic reduction rate of H^+ , and the rate of dissipation is determined by the diffusion rate of corrosive products out of the local anode.

In pitting where the geometry is favorable for relatively easy mass transport, a large rate of dissolution is necessary to continue the active dissolution within the anode, therefore E_g becomes more noble. E_g for crevice corrosion becomes more active because it is difficult for the mass transport of both metal and hydrogen ions to occur and a small rate of dissolution is enough to maintain active corrosivity in the local anode. Thus, the critical potential E_g varies depending on the degree of occlusion. The relationship between E_g and anodic and cathodic polarization curves is shown schematically in Figure 1. Under the same geometrical condition, E_g also depends on the degree of anodic polarization of steels in an acidic concentrated chloride solution, and the less the polarization, the more active the critical potential, E_g . In most cases E_g of austenitic stainless steels exists in the potential range of -0.4 to -0.2 volt vs. SCE, and it corresponds to the potential range of peak current of passivation in acid solution. At a potential more active than E_g , corrosiveness of the solution within the local anode decreases to result in repassivation of the anode, while at a potential more noble than E_g , the anolyte becomes aggressive and the anode continues to dissolve with a limiting current determined by the dissipation of corrosion products.

The critical potential E_g is a potential of the local anode at which the anode can repassivate, and may not be so active as to shift the anode to

immunity. The bulk potential necessary to prevent the localized corrosion may be more or less noble than E_g because there exists iR -drop between the bottom of the anode and the bulk surface. For the sake of safety, the authors have not considered this drop in practical applications of this method. Hisamatsu *et al.*¹⁰⁾ reported that potential difference of about 150 mV was observed between inner and outer surfaces of active pits.

3. Measuring Method for E_g

To know the critical potential for the formation of localized corrosion, it is desirable to determine the minimum potential below which no dissolution current is observed under natural conditions, but this method is not practical because it requires a long experimental period. Therefore, the authors have determined the critical potential E_g as a minimum potential below which the previously activated local anode can be repassivated. The accurate E_g value will be determined by the following procedure:

1. An artificial specimen having a local anode insulated electrically from a cathode must be used. Conventional specimens are not suitable because the polarization effect of the local cell current may lead to an error for measured E_g value.
2. In order to eliminate the iR -drop, the potential of the anode should be measured directly with a Luggin capillary inserted into the bottom of the anode.
3. The local anode is activated galvanostatically by an externally applied anodic current until it reaches a steady state potential, then the potentiostatic dissolution current is recorded for a long time at a predetermined potential more active than the steady state potential. The critical potential, E_g , is the minimum potential above which the dissolution current of the local anode does not decay.

Experimental results clarify⁸⁾ that for pitting, E_g corresponds to the open circuit potential immediately after activation, and for crevice type corrosion, E_g corresponds to the most active open circuit potential reaching the steady state condition, respectively.

4. In the case of an artificial specimen for SCC in which a capillary can not be inserted, E_g should be determined as the potential at which the coupled cell current flowing between the local anode and cathode becomes zero when polarized cathodically. To obtain the accurate E_g value, the sweep rate of this cathodic polarization should be rapid for

Fig. 1. Anodic and cathodic polarization curves for occluded anode surfaces and critical potential for growth of pitting ($E_{g(p)}$) and that of crevice corrosion ($E_{g(c)}$) (Schematic).

Table 1. Critical potential value of stainless steel in reagent chemical of chloride.

Type of corrosion	Steel	Solution	Temperature °C	Critical potential V vs. SCE
Pitting	Type 304L	0.5 N NaCl	70	−0.32
	Type 316L			−0.25
	18 Cr–16 Ni–5 Mo			−0.25
	Type 316L	0.88 N NaCl	70	−0.25
			30	−0.23
			10	−0.18
	Type 316L	1 N NaCl	70	−0.26
		0.1 N NaCl		−0.22
		0.01 N NaCl		−0.18
Crevice corrosion	Type 316L	0.5 N NaCl	70	−0.36
SCC	Type 316L	35% MgCl ₂ (pH 3)	126	−0.375
	30 Ni–20 Cr–2.5 Mo			−0.32

pitting and slow for crevice type localized corrosion containing SCC.

Artificial specimens for some types of localized corrosion were previously shown elsewhere.⁸⁾ The critical potential values of some stainless steels in reagent chemicals are summarized in Table 1. The critical potential varies depending on the geometry, even though the steel has the same alloy composition. For example, under the same environmental conditions, the critical potential for pitting is always more noble than that for crevice corrosion. If geometry is the same, nobility of the critical potential depends on the anodic polarization in an acidic concentrated chloride solution; the greater the polarization, the more noble the critical potential.

The critical potential for SCC is almost equal to that for crevice corrosion.

4. Measurement of Corrosion Potential

The corrosion potential should be measured either for the chemical equipment itself under practical operating conditions or for the stress relieved, crevice free test coupon inserted into the equipment. A saturated calomel electrode (SCE) is generally used as a reference electrode in these measurements. A metallic zinc electrode, often used in cathodic protection in sea water, is also used in more severe environments where a SCE can not be applied because of its mechanical fragility. The potential of the zinc electrode must be predetermined in the same process liquor under the same physical conditions.

The reference electrodes used in these measurements are shown in Figure 2.

5. Practical Applications

This testing method was applied to the selection of construction materials for chemical plants or to the analysis of localized corrosion formed in some chemical equipments.

A typical time variation of corrosion potential for an aerobic fermenter, made of Type 304L, together with the critical potential for pitting ($E_{g(p)}$) and crevice corrosion ($E_{g(c)}$) is shown in Figure 3. This fermenter suffered from marked pitting after several years of operation. In this case, the critical potential for either pitting or crevice corrosion was more active than the corrosion potential, and both localized corruptions could occur.

In contrast with the above case the corrosion potential for an unaerobic fermenter, made of Type 316L, is shown in Figure 4. Since little dissolved oxygen exists in the process liquor, the

Fig. 2. Reference electrodes used for measurement of corrosion potential for chemical equipment.

Table 2. Corrosion potential and critical potential for chemical equipment made of stainless steel.

Equipment	Steel	Environment	Corrosion potential (V, SCE)	Type of corrosion	Critical potential (V, SCE)	Decision
Evaporator (LTV type)	316L	pH 8.0 Cl ⁻ 0.75 % 45°C	-0.42— -0.35	Pitting	-0.23	Not occur
Evaporator (Plate type)	316L	pH 4.0 Cl ⁻ 0.5 % 60°C	-0.16— 0	Crevice	-0.32	Occur
Crystallizer	316L	pH 7.0 Cl ⁻ 1.2 % 70°C	-0.20— -0.10	Pitting	-0.25	Occur
Reactor	316L	pH 3.2 Cl ⁻ 0.5 % 95°C	-0.32— -0.25	SCC	-0.36	Occur

Fig. 3. Time variation of corrosion potential for an aerobic fermenter made of type 304L.

Fig. 4. Time variation of corrosion potential for an unaerobic fermenter made of type 316L.

corrosion potential becomes more active. Therefore, in spite of its high concentration of chloride, neither pitting nor crevice corrosion has been observed for about one year of operation.

Some other examples of the test results are summarized in Table 2. This method has been effective in predicting or analyzing localized corrosion in stainless steel chemical equipment.

6. Conclusions

Results of these investigations have shown that:

1. There exists the critical potential for growth of localized corrosion, below which the already initiated localized corrosion can repassivate. This potential can be measured only in an artificial specimen having a local anode insulated from a cathode.

2. The localized corrosion of stainless steels used in chemical equipment can be predicted by comparing the critical potential with the corrosion potential under its operating condition. If the critical potential is noble than the corrosion potential, the localized corrosion can not occur.

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