Prediction of Critical Environments for Active-Passive Transition of Corrosion Resistant Alloys in Sour Environments

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The corrosion behavior, in particular passivation, of corrosion resistant alloys (CRAs) in sour environments was investigated intensively by using a duplex stainless steel and an austenitic stainless steel as representative CRAs. It was found that hydrogen sulfide significantly retarded the passivation of CRAs, whereas carbon dioxide did not. The changes in corrosion morphologies due to the changes in environmental aggressiveness were classified on the basis of the immersion test results. A new criterion for predicting the critical environments for active to passive transition was proposed. The critical environments for the transition of a given alloy can be determined by comparing the pH of environments with the depassivation pH (pH_d) of the material which is a function of environmental factors such as temperature and partial pressure of hydrogen sulfide. The locus of the points having $\text{pH}=\text{pH}_d$ gave a good estimation for the critical environments. It was confirmed that the prediction was in good agreement with the long-term immersion test results for 6 months. Since this criterion is based on the corrosion mechanism, it has many advantages; the prediction is accurate; the results for CO_2 -free environments can be extended to CO_2 -containing environments; and the prediction can be performed very quickly.

KEY WORDS: passivation; depassivation; stainless steel; sour gas; hydrogen sulfide; carbon dioxide; pH.

1. Introduction

Oil and natural gas produced recently sometimes contain a large amount of hydrogen sulfide (H_2S) and carbon dioxide (CO_2). For the exploitation of such corrosive and hostile reservoirs, low alloy steel tubulars have been used traditionally with the application of corrosion inhibitors for preventing corrosion. Chemical inhibition, however, exhibit insufficient effect for very deep wells and is very expensive for offshore wells. Thus, completion with corrosion resistant alloys (CRAs) is becoming common practice. This is very attractive especially for offshore wells because chemical inhibition can be abolished. However, it is now well recognized, mainly on the basis of laboratory experience, that even CRAs exhibit localized corrosion, stress corrosion cracking and general corrosion. Some failures of CRAs in actual oilfields have been reported.¹⁾

For the safe and economical use of CRAs, the selection of materials with necessary and sufficient corrosion resistance to a given environment is of great importance. This requires the precise determination of the application limit of each CRA. Many people have already proposed a variety of information concerning the application limits for a great number of CRAs.²⁾ However, extremely conservative materials have been chosen in many cases of actual application, presumably because the field performance estimated from laboratory data is often uncertain. The major reason for this uncertainty is that the results of conventional laboratory tests are greatly affected by

experimental parameters such as test duration, applied stress and strain rate. For example, Chaung *et al.*³⁾ reported that SCC was observed for a C-ring test after two years from the initiation of the test.

Although conventional "go/no go" type SCC tests may rank the materials performance from the viewpoint of SCC resistance in a specific condition, they do not assure integrity in the actual material application to oilfields. In order to overcome this difficulty associated with laboratory tests, thorough understanding of the corrosion mechanism in sour environments is essential as well as the material evaluation criteria that are based on the corrosion mechanism.

Since CRAs are designed to be used in a passive condition, they cannot be used with integrity in an active condition. They must be passive in any circumstances of field application. If a criterion is obtained for the prediction of passive to active transition, a necessary condition for the safe use of CRAs can be determined; the environments where a given alloy can be passivated will be predicted. By estimating the critical conditions for an alloy to be active, the environments where the alloy cannot be used will be determined. It must be noted that the fact that an alloy is in a passive condition in a given environment does not necessarily means that the alloy can be used safely. There still remains the risk for localized corrosion and SCC. The critical condition for such material degradation must also be considered. The determination as to whether or not an alloy can be passive in an environment is also important to know the integrity of the alloy in an acid stimulation

operation, where the alloy is subjected to very low pH, typically 1 to 2, aqueous solutions containing hydrogen sulfide and chloride.

In this study, the corrosion behavior of CRAs in sour environments is extensively investigated. On the basis of the results, a suitable criterion to determine the critical condition for the passivation limits of CRAs is proposed.

2. Experimental

2.1. Test Materials

Two stainless steels were subjected to investigation: one was an SUS316L (UNS S31603) austenitic stainless steel and another a duplex stainless steel of 22 % Cr type in accordance with DIN standard 1.4462 (UNS S31803). Their chemical compositions are given in Table 1. Both steels were tested without cold working after final solution heat treatment.

2.2. Test Procedure

2.2.1. Electrochemical Measurements

To determine the depassivation pH (pH_d), the changes in electrode potentials of specimens were measured. Test coupons of 3 mm thick, 15 mm wide and 20 mm long were machined from the middle of the plate thickness. They were degreased in acetone, polished with #320 grit paper and coated with silicon resin leaving 1 cm $\times$ 1 cm area for measurements. Just before immersed in test solutions, the specimens were pickled in 50 % sulfuric acid at 333 K to remove the air-formed film. This means that the initial condition of the specimens was active. They were immersed in test solutions with various pH values adjusted before immersion. The changes in electrode potentials were continuously monitored for 8.64×10^4 s. The final potential at the conclusion of immersion was adopted as a spontaneous potential in the environment and plotted as a function of solution pH. The pH_d value was defined as the pH value at which the potential shifts in the positive direction on a potential-pH diagram.

DC polarization curves were measured following the same procedure of specimen preparation in the above to estimate the pH_d . Potentiodynamic experiments were conducted at a scan rate of 50 mV/min either in the anodic or cathodic direction from the immersion potential at 300 s after being placed in the test solution.

Atmospheric pressure tests were made in glass cells, whereas high pressure and/or high temperature tests above 373 K were performed in high pressure autoclaves.

2.2.2. Immersion Tests

The relationship between environmental conditions

and corrosion morphologies was examined by immersion tests. The dimensions of the test coupons were 2 mm thick, 15 mm wide and 20 mm long. They were degreased in acetone and polished with #320 grit paper just before the tests. Atmospheric pressure tests were made in glass cells, whereas high pressure and/or high temperature tests above 373 K were performed in high pressure autoclaves. Test duration was primarily 1.21×10^6 s (336 h). Tests for 1.56×10^7 s (4 320 h) were also conducted where the corrosion morphologies had been marginal after tests for 1.21×10^6 s. After immersion, the corrosion morphology was determined for each specimen by visual and optical microscopic observations of the specimen surface. They were classified into four types shown in Fig. 1.

2.3. Test Environments

Deaerated aqueous solutions that contained 20 mass% NaCl (4.28 mol/kg- H_2O) and were in equilibrium with H_2S , CO_2 or argon at a scheduled partial pressure were selected as the test solutions. Ion exchanged and distilled pure water and analytical grade chemicals were used for preparing the test solutions. All the tests were conducted at elevated temperature ranging from 298 to 523 K. H_2S partial pressure was varied between 0.05 to 4 MPa.

3. Results and Discussion

3.1. Passivation in H_2S -containing Solution

The corrosion potential of steel 316L after 8.64×10^4 s immersion with and without H_2S was plotted against solution pH and shown in Fig. 2 for the experiments at 298 K. The pH_d values are indicated by upward arrows for both cases. Since an initial specimen surface in the pH_d measurements was in an active condition, this figure indicates that the steel can be passive in sour environments. The pH_d of 3.2 in a 0.1 MPa H_2S saturated solution was higher than that of 2.0 in an argon saturated solution. This implies that the passivation capability of the alloy decreased in H_2S environments compared with that without H_2S . The similar increase in pH_d by presence of H_2S was reported by Miyuki *et al.*⁴⁾ for a

Fig. 1. Classification of corrosion morphologies.

Table 1. Chemical compositions of test steels. (mass%)

Code	C	Si	Mn	P	S	Cr	Ni	Mo	N
316L	0.021	0.50	0.93	0.032	<0.001	17.4	12.1	2.04	—
DIN	0.019	0.43	1.78	0.027	<0.001	21.4	5.3	2.78	0.146

Fig. 2. Effect of solution pH on corrosion potential of steel 316L with and without H_2S .

duplex stainless steel of 25 % Cr type. The corrosion potential in an active state is slightly less noble than the equilibrium potential of hydrogen ion reduction reaction for both with and without H_2S . The cathodic reaction occurring in this situation is thus considered to be the hydrogen ion reducing reaction.

The test results for steel DIN are shown in Fig. 3. The same tendency was observed for steel 316L except that the corrosion potential for steel DIN in a passive state in an H_2S -saturated solution was more negative than that for steel 316L. As shown in Fig. 3, the corrosion potential *vs.* pH relationship in a CO_2 saturated solution agreed with that in an argon saturated solution. It is obvious from this result that CO_2 does not affect the passivation behavior and the pH_d of CRAs.

The effects of temperature and H_2S partial pressure on the pH_d of steel DIN are given in Fig. 4. The pH_d value increased with a temperature rise and an increase in H_2S partial pressure. These results indicate that the passivation capability of the alloy decreases, in other words, the passive film becomes unstable, as temperature becomes high and/or H_2S partial pressure increases. In Fig. 4, equi- pH_d lines of $pH_d=3.0, 3.5, 4.0$ and 4.5 are drawn on the basis of the test results. Almost the same tendency was obtained also for steel 316L.

The effect of H_2S on the anodic and cathodic polarization behavior of steel 316L is shown in Fig. 5. The corrosion current density increased approximately one order of magnitude in an H_2S -saturated solution compared to that in an H_2S -free solution. Both a critical passivation current density and passive current density in a passive region were enhanced by presence of H_2S . The same tendency was also observed for steel DIN. The increase in passive current density in presence of H_2S was also reported by Kudo *et al.*⁵⁾

3.2. Passivation Mechanism in Sour Environments

The passivation mechanism of stainless steels in

Fig. 3. Effect of solution pH on corrosion potential of steel DIN with and without H_2S .

Fig. 4. Influence of temperature and H_2S partial pressure on pH_d of steel DIN in 20 % NaCl aqueous solution. Equi- pH_d lines are drawn on the basis of the measured results.

Fig. 5. Change in anodic and cathodic polarization curves of steel 316L with and without hydrogen sulfide.

presence and absence of oxygen was already discussed in detail by both Uhlig⁶⁾ and Ogawa *et al.*⁷⁾ In absence of oxygen or other oxidant, the hydrogen ion is a passivator for the passivation of stainless steels. It should be noted that oxygen does not exist in sour

environments. Here the mechanism of pH_d determination in sour environments is discussed by comparing the pH_d estimated from polarization curves with the measured pH_d values. The estimation of pH_d was performed by following approaches of Uhlig⁶⁾ and Leckie.⁸⁾

The pH_d is controlled by the balance of anodic and cathodic polarization as schematically illustrated in Fig. 6. Case (a) in Fig. 6 shows when the pH of a solution is higher than the pH_d of an alloy; both curves cross each other in a passive region on the anodic polarization curve. In a solution having lower pH than an alloy's pH_d (case (c)), two curves have an intersection in an active region. At $\text{pH} = \text{pH}_d$, the two curves are situated at the case (b) at the transition between passivity and activity.

The following equation was assumed between critical passivation current density i_{crit} and hydrogen ion concentration $[\text{H}^+]$ according to Uhlig⁶⁾ and Leckie.⁸⁾

$$i_{\text{crit}} = K[\text{H}^+]^{\lambda} \quad \text{.....(1)}$$

where, K, λ : constants.

It has already been confirmed that this inverse linear relationship between the logarithm of the critical passivation current density and pH holds true for stainless steels in acid chloride environments.⁸⁾

In the case of active dissolution of CRAs in sour environments, the cathodic reaction is the reduction of hydrogen ion as mentioned before. The cathodic current then follows Tafel's equation in the following.

$$E + \frac{2.3RT}{F} \text{pH} = b_H \ln \frac{i_H}{i_H^0} \quad \text{.....(2)}$$

where, i_H^0 : an exchange current density of hydrogen evolution reaction.

When the pH of a solution is equal to the pH_d of an alloy, then $i_H = i_{\text{crit}}$. By making use of these equations and substituting E_F , Flade potential, for the potential corresponding to i_{crit} , the following equation is obtained for estimation of pH_d on the basis of polarization curves.

Fig. 6. Schematic illustration of anodic and cathodic polarization curves when the pH values are higher than, equal to and lower than pH_d .

$$\text{pH}_d = \frac{1}{2.3(b_H \lambda + RT/F)} \left(2.3b_H \log \frac{K}{i_H^0} - E_F \right) \quad \text{.....(3)}$$

If the pH_d estimated by the above procedure agrees with that determined by the potential measurements stated in Sec. 3.1, the mechanism of pH_d determination in sour environments mentioned previously will be confirmed.

The i_{crit} and E_F values were obtained from the polarization curves measured in an active region. They are plotted against pH in Fig. 7. An inverse linear relationship is observed between $\log i_{\text{crit}}$ and pH, which was expected from Eq. (1). This means that the hydrogen ion reducing reaction is the cathodic reaction in an active state in H_2S -containing environments.

The values of λ and K in Eq. (3) were obtained from the slope and the intercept on the abscissa in Fig. 7. The b_H was the Tafel slope of the cathodic polarization curves in an active region. The value of i_H^0 of 10^{-6} A/cm^2 was cited from the literature.⁹⁾ Though this reported value had been obtained at 298 K, it was also used in pH_d estimation at higher temperatures, because no data were available from the literature for i_H^0 at elevated temperature.

The estimated values of pH_d for steel 316L are tabulated in Table 2 together with the measured ones. The pH_d values estimated by the above calculation technique are in fairly good agreement with those measured. The similar good agreement was also obtained for steel DIN. Therefore it is confirmed that the pH_d in sour environments is controlled by the same mechanism as that in neutral chloride-containing aqueous solutions in absence of oxygen. The hydrogen evolution reaction controls the passivation of CRAs in sour environments.

3.3. Corrosion Morphologies as a Function of Environmental Factors

The relationship between the corrosion morpholo-

Fig. 7. Change in critical passivation current density (i_{crit}) as a function of pH.

Table 2. Comparison of the pH_d values of steel 316L estimated from polarization curves with those measured.

Temperature (K)		H ₂ S partial pressure (MPa)			
		0*	10 ⁻³	10 ⁻²	10 ⁻¹
298	Measured	2.0	2.5	3.3	3.2
	Estimated	2.4	2.9	3.3	3.4
323	Measured	2.0	3.3	3.3	3.3
	Estimated	2.4	3.2	3.4	3.0
353	Measured	2.0	3.3	3.3	3.3
	Estimated	2.2	3.3	3.8	2.7

* Deaerated with argon gas bubbling.

gies and the environmental conditions obtained as a result of immersion tests is illustrated in Fig. 8 for steel DIN. Almost the same results were obtained also for steel 316L. At 333 K with H₂S partial pressure of 0.05 MPa (at the point D in Fig. 8), the alloy exhibited no attack (*N*). The corrosion morphology changed to *L* (localized corrosion) with a temperature rise and an increase in H₂S partial pressure. The steel finally exhibited general corrosion (*G*) at high temperatures and high H₂S partial pressures.

Among the test results in Fig. 8, those for H₂S partial pressure of 0.05 and 0.5 MPa and temperature of 333 and 423 K (points A to D) were obtained after immersion for 1.56×10^7 s. At H₂O partial pressure of 0.5 MPa and at 423 K (point A), the corrosion morphology was at first determined as *L* after immersion for 1.21×10^6 s, where on the other hand that after 1.56×10^7 s was general corrosion. The quasi-pitting observed after 1.21×10^6 s was attributed to the incomplete dissolution of the air-formed film within a limited time of 1.21×10^6 s. At the point B in Fig. 8, the corrosion morphology was marginal between *N* and *L* after 1.21×10^6 s, but it changed to complete *L* (pitting) after 1.56×10^7 s. It is obvious from these results that the results of conventional immersion tests are significantly affected by the test duration. No changes in corrosion morphology due to prolongation of test duration were observed at the points C and D.

3.4. Prediction of "Passive to Active" Transition

The pH_d is defined as a critical pH value for an alloy to exhibit passive to active and active to passive transition. Therefore, if the pH value of a given environment is known, it is possible to determine whether or not the alloy can be passivated in the environment. If the alloy cannot be passive, the passive film does not form on the alloy surface so that the corrosion morphology must be general corrosion (active dissolution). The corrosion morphology in a situation where the alloy is passive should be no attack or pitting. Since the passive film is quite unstable in the vicinity of passive to active transition, the critical environments for this transition should coincide with the boundary between pitting and general corrosion. Therefore the critical environments for general corrosion of an alloy can be predicted by comparing the

 Fig. 8. Corrosion morphology of steel DIN as influenced by temperature and H₂S partial pressure.

 Fig. 9. Predicted critical environments for active-passive transition of steel DIN as a locus of the points representing $\text{pH} = \text{pH}_d$.

pH of environments with the pH_d of the alloy as follows.

$\text{pH} < \text{pH}_d$; active
 $\text{pH} > \text{pH}_d$; passive

Then the locus of the points representing $\text{pH} = \text{pH}_d$ gives the critical environment for passive to active transition. The pH_d can be determined by electrochemical measurements as mentioned above. A thermodynamic estimation technique was proposed¹⁰⁾ for the pH of a given environment. The validity of the estimation was confirmed by the pH measurements using a semiconductor-type pH sensor.¹⁰⁾

The critical environments for passive to active transition was determined by comparing equi- pH_d lines reported in Sec. 3.1 with equi-pH lines already reported in the literature¹⁰⁾ and given in Fig. 9. Since this alloy is active in the upper-right region of the transition, the alloy exhibits general corrosion in this region.

Fig. 10. Comparison between predicted critical environments for active-passive transition with observed corrosion morphology for steel DIN.

3.5. Comparison of Electrochemical Prediction with Immersion Test Results

Fig. 10 compares the electrochemically predicted critical environments for passive to active transition with the immersion test results of long term. Here the line in Fig. 10 is the predicted boundary for passive to active transition. As mentioned before this line should coincide with the boundary between pitting and general corrosion. The letters in the circles indicate the corrosion morphologies determined in the immersion tests. It is obvious from the figure that the electrochemically predicted transition is in good agreement with experimental results. The similarly good agreement between predicted and experimental results was also obtained for steel 316L. These clearly prove that the critical environments for passive to active transition can be predicted by the criterion proposed in Sec. 3.4.

3.6. Application of pH_a Prediction

In actual oilfield environments, H_2S and CO_2 co-exist very frequently. CO_2 does not affect the pH_a of CRAs as mentioned in Sec. 3.1. The effect of CO_2 therefore is only to lower the pH of the aqueous solutions. The pH of sour environments shifts to a smaller value with an increase in CO_2 partial pressure at a constant H_2S partial pressure.¹⁰⁾ Since CO_2 does not affect the pH_a of CRAs, the pH_a values obtained in CO_2 -free environments also stand for those in CO_2 -containing environments. Therefore, by comparing the pH_a values with the pH of the environments, which is a function of H_2S and CO_2 partial pressures and temperature, the critical environments for active-passive transition can be determined as a function of CO_2 partial pressure.

Fig. 11 shows the change in active and passive regions of alloy DIN due to an increase in CO_2 partial pressure. In obtaining Fig. 11, the pH_a values measured in a CO_2 -free condition was used. The pH and

Fig. 11. Shift of predicted critical environments for active-passive transition with increasing CO_2 partial pressure.

thus equi-pH lines as a function of CO_2 partial pressure were calculated by the thermodynamic estimation.¹⁰⁾ The passive region tends to be confined to a lower H_2S pressure and lower temperature region with increasing CO_2 partial pressure. This is the result of pH lowering of the environments caused by CO_2 .

4. Conclusions

The passivation behavior of corrosion resistant alloys in H_2S -containing aqueous solutions was investigated and a criterion for predicting the critical environments for passive to active transition was examined. The following conclusions were obtained.

(1) Hydrogen sulfide was found to retard the passivation of alloys. The pH_a value changed to a larger value with a temperature rise and/or an increase in H_2S partial pressure.

(2) The pH_a values estimated from the anodic and cathodic polarization curves in active conditions agreed well with the measured ones.

(3) A new criterion to determine whether or not an alloy can be passive in a given environment was proposed; this can be determined by comparing the pH_a of the alloy with the pH of the environment. The validity of the prediction was confirmed by the fact that the predicted critical environments for passive to active transition were in good agreement with the immersion test results for long term.

(4) The proposed criterion has an advantage in that the results with CO_2 -free conditions can be used for the critical environments in CO_2 -containing environments, because CO_2 does not affect the passivation behavior of corrosion resistant alloys.

The criterion determines the environments where CRAs cannot be used because they are active in the environments. This does not necessarily give information for the integrity of materials in a passive region. For such purpose the critical environments for localized corrosion and SCC must be determined. This will be discussed in another paper.

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