Assessment of Galvanic Corrosion in Galvanic Couples of Sensitized and Nonsensitized AISI Type 304 Stainless Steel in Nitric Acid

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Waste vault tanks made of 304 stainless steel (SS) meant for the storage of high level liquid waste of 6M HNO₃ showed precipitation of M₂₃C₆ in heat affect zone (HAZ) in the weldments and high corrosion rates in boiling nitric acid test (ASTM A262 Practice C test). In this connection a study of possible galvanic corrosion effect at the junction of sensitized HAZ and the adjacent base metal in 304 SS in sulphuric as well as nitric acid, was undertaken. The galvanic couples were prepared using sensitized 304SS as the anodes, and the base metal as the cathodes, electrically connected in different anode to cathode ratios. Potentiodynamic anodic polarization studies were conducted in deaerated 0.5M sulphuric acid whereas electrochemical noise (ECN) experiments were performed in 3M deaerated nitric acid at room temperature as well as 60°C. The data analysis of current and potential signals was conducted using statistical methods; the data was analysed in the frequency domain using Maximum Entropy Method (MEM). The corrosion rates observed in nitric acid medium at room temperature did not show enhanced corrosion rate due to galvanic coupling. However, the corrosion rates were higher at 60°C in the same medium. Based on these results, a drastic rise in corrosion rate and the subsequent failure of the waste vault tank was not expected.

Keywords: Stainless Steels, Corrosion, Nitric Acid

1. INTRODUCTION

Nuclear fuel reprocessing activities create large amounts of radioactive waste. Much of this liquid waste is stored in stainless steel tanks that face the potential of corrosion, a destructive electrochemical process that eats away the metallic surfaces, eventually destroying the integrity of the material. Care must be exercised in selecting the material of construction of such tanks as well as the fabrication procedure.
Waste vault tanks of AISI Type 304 SS were made from 12 mm thick plates. Studies were undertaken to assess suitability of these tanks for storing waste. These tanks showed ditched structure in the HAZ at the dished end to shell joints, using in-situ metallography. Intergranular corrosion (IGC) tests using ASTM A262 practice C \[1\] showed high corrosion rates. It is proposed to store liquid waste in these tanks for a period of 10 years. Thus, a proper assessment of the corrosion behaviour of the tank vis-à-vis the galvanic corrosion due to the possible galvanic coupling of sensitised HAZ (anode) and the adjacent base metal (cathode) was required.

In this connection, galvanic corrosion studies were performed using the galvanic couples formed between the sensitized 304SS (anode) and nonsensitized 304SS (cathode) connected in different area-ratios in sulphuric as well as nitric acid environment. A corrosion monitoring technique using ECN, which tracks extremely small current and voltage fluctuations among three electrodes and provides real-time corrosion information, was employed to study the corrosion behaviour of the galvanic couples in nitric acid. ECN technique is extremely useful in studying the electrochemical corrosion characteristics of a specimen at open circuit potential (OCP), as it does not need any external perturbation. The ECN technique has been extensively used for characterization of corrosion processes for over 20 years \[2-4\]. This technique can capture information about not only the rate of corrosion but also about the mechanism of corrosion processes \[5, 6\]. Since the DC polarization studies performed in the sulphuric acid medium could give quicker results owing to the fact that SS exhibits both active/passive states in this medium, thereby corrosion rates could be easily obtained using Tafel slope fitting technique. However, in case if the experiment is performed in nitric acid medium, the system does not show anything other than the pure passive behaviour, consequently no additional information (other than the current in the passive state) can be obtained. However, studies conducted using EN technique give different statistical parameters that can give additional information about the behaviour of the metal/alloy in the medium of interest, apart from the corrosion rate. Particularly, the visual records of current and the potential noise give a lot of information of the type of corrosion mechanism. Thus, ECN technique was preferred while studying the galvanic couples in nitric acid medium.

2. EXPERIMENTAL PART

AISI Type 304 SS (C – 0.040%, Si – 0.375%, P – 0.023%, Mn – 1.660%, S – 0.003%, N – 0.087%, Cr – 18.3%, Ni – 9.250%, Fe balance) was used in these investigations. Time – Temperature – Sensitization (TTS) diagram for this alloy with different degrees of cold work was established as per ASTM A 262 practice E test \[7\]. From this diagram it can be inferred that the minimum time required for sensitization at 650°C was about 1 h. It is well-known that austenitic SS gets sensitized and becomes prone to intergranular corrosion (IGC) either during fabrication processes like welding/hot forming or during isothermal exposure to elevated temperature in sensitization temperature range. As per ASTM Standard A 262 -2a \[1\], the HAZ microstructure of the weldment can be simulated by heat treating at 675°C for 1h followed by air-cooling (AC). In the present study, 304SS is selected for which isothermal TTS diagram is well established. From this diagram, it was inferred that by exposing this material at 650°C for 24h followed by air cooling will result in high degree of sensitization (DOS)
(this temperature/time combination lies well within the sensitization regime of the diagram) so that the material will be very much anodic compared to as-received material in the mill-annealed condition. Hence 304SS sensitized at 650°C-24h-AC is taken as anodic material and as-received 304SS in the mill-annealed condition was considered as cathodic material. The 304SS specimen in the mill-annealed condition would be referred to as as-received throughout this paper.

As per the required area ratio the sensitised specimen (anode) as well as the non-sensitised specimen (cathode) were chosen; they were mounted together in the araldite resin such that they made the physical contact with each other and a threaded brass rod (about 8 – 10 mm dia. and 15 mm length) was used to connect this galvanic couple along with a specimen holder with the electrochemical system. In this manner, the galvanic couples could be produced with the suitable dimensions so as to fit into the polarization cell easily. The galvanic couples mounted in araldite resin, polished up to 1μm, cleaned using soap solution and degreased were used in all experiments. Thus, in order to study the behaviour of the galvanic couples in the corrosive environment, potentiodynamic anodic polarization as well as ECN techniques were employed.

Although the nuclear waste is stored in about 3 - 6 M Nitric acid, which is a perfectly passivating medium for SS, presence of ionic impurities might alter the solution composition, thereby the passive state of SS might become unstable. In order to simulate this borderline active-passive transition state of SS, deaerated 0.5M Sulphuric acid is commonly used. Thus, it was felt that the corrosion rates of the area-ratio specimens could be studied in both the media.

Potentiodynamic anodic polarization experiments were conducted in deaerated 0.5M H₂SO₄ solution at a scan rate of 10 mV/min. The corrosion rates of the galvanic couples were calculated using Tafel slope fitting technique. Electrochemical noise studies on the galvanic couples were performed such that two nominally identical specimens of the same area are taken, wherein one specimen is a galvanic couple and the other one is 304 SS coupon (in as-received condition) with the same surface finish. The specimens were polished up to 1μm finish, washed in soap water and degreased in acetone. Potential and current noise measurements were performed by shorting together the galvanic couple with 304 SS as two working electrodes. The current flowing between the two working electrodes, as well as the potential between the working electrode and a reference electrode are monitored. The area of the specimen exposed to the solution was about 0.8 cm².

The potentiostat, which can perform this experiment actively, holds the working electrode connection at the ‘ground’ potential by a small amplifier circuit. If one ‘working’ electrode is directly connected to ground and the other is connected to the working electrode cable, they are both held at the same potential and are, in effect, ‘shorted’ together. Any current, which flows between the two electrodes, is measured by the instruments of current measurement circuits thus creating a Zero Resistance Ammeter (ZRA). The potential is measured between the ‘working’ electrodes (since they are shorted together, both ‘working’ electrodes are at the same potential) and a reference electrode.

The correlated signals of current and potential were collected at the sampling frequency of 4 Hz for 4 h in deaerated 3M nitric acid at room temperature. The potential signal was measured against a saturated calomel electrode (SCE). The same set of experiments was conducted at 60°C by using a constant temperature water bath.
Since in ECN studies, the signal is mostly non-stationary, the drift or the trend gets introduced. Therefore, the drift or the trend removal was carried out, which is an accepted practice, before calculating the statistical parameters as well as power spectral density (PSD) values. A set of 1024 data points was analysed at a time interval of 2500s for convenience to calculate statistical parameters as well as PSD plots. The data in the time domain was transformed into the frequency domain after linear detrending, using a Welch window to obtain PSD plots using Maximum Entropy Method (MEM); the MEM order was 15 in order to obtain smooth curves.

### 3. RESULTS AND DISCUSSION

Corrosion rates were calculated using Tafel slope fitting technique using the potentiodynamic anodic polarization curves for (i) as-received, (ii) sensitized, (iii) galvanic couples of different anode to cathode area ratios viz. 1:1, 1:2, 1:3, 1:4.5 and 1:8 in deaerated sulphuric acid are shown in Table 1. It was observed that, sensitised specimen showed higher corrosion rate as compared to the as-received specimen. The galvanic couples too showed a gradual increase in the corrosion rates (except the couple with the area ratio 1:2) with increasing cathode to anode area ratio. Thus, the effect of increase in the cathode to anode area ratio in increasing the galvanic corrosion was clearly observed, though the increase was not drastic.

**Table 1.** Corrosion rates of as-received, sensitised and galvanically coupled specimens in deaerated sulphuric acid

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Corrosion rate, A/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Received</td>
<td>2.765E-5</td>
</tr>
<tr>
<td>Sensitised</td>
<td>7.381E-5</td>
</tr>
<tr>
<td>Area-Ratio 1:1</td>
<td>7.935E-5</td>
</tr>
<tr>
<td>Area-Ratio 1:2</td>
<td>6.067E-5</td>
</tr>
<tr>
<td>Area-Ratio 1:3</td>
<td>8.513E-5</td>
</tr>
<tr>
<td>Area-Ratio 1:4.5</td>
<td>9.140E-5</td>
</tr>
<tr>
<td>Area-Ratio 1:8</td>
<td>1.518E-4</td>
</tr>
</tbody>
</table>

The potential and current signals for the galvanic couples with different anode to cathode area-ratios along with as-received and sensitized specimens in deaerated nitric acid at room temperature as well as 60°C are presented in Fig. 1(a, b) and Fig.2 (a, b) respectively. It was observed that the potentials of the specimens (Fig. 1a) fell typically in the passive region of the stainless steels, although the potentials ennobled initially before decrease, except for the specimen with anode to cathode area
ratio 1:2, which showed the constant ennoblement of the potential. Other specimens showed gradual ennoblement of potential up to a certain value and a gradual decrease thereafter. The decrease of potential was substantial for sensitised specimen in a stepladder pattern. The potential signal plots in deaerated nitric acid at 60°C (Fig. 1b) presented altogether a different picture. The potential values were found to be in the passive region with a rapid initial rise, however, on account of the partial passive film damage, there was an abrupt drop in the potentials. This is noticed predominantly in as-received, sensitized and anode to cathode area-ratio 1:2 specimens; subsequent repassivation followed by film break-up was seen only in as-received specimen. The current noise plots show (Fig. 2 a, b) some distinct differences. Studies at room temperature showed (Fig. 2a) cathodic currents for all the

![Figure 1. The potential signal for area-ratio specimens in deaerated nitric acid at room temperature as well as 60°C (a, b).](image)
specimens initially for up to about 1000-2000s, followed by the rise in the current. The current potential signal plots signify an initial build-up of the passive film which broke down at around 1000-2000s, however, the break-down of the passive film being only partial, the specimens still showed passive potentials. The current rise for the sensitized specimen was much faster. However, at 60°C, (Fig. 2b) there was a rapid initial rise in the anodic current signals noted, and a subsequent stabilization of the current value for every specimen. All the specimens showed anodic currents except specimen with anode to cathode area-ratio 1:2, which showed a constant cathodic current indicative of a stable passive film. Thus, it is apparent that the partial dissolution and repassivation of the passive film took place at 60°C whereas the passive film was more stable at room temperature for the specimens.

**Figure 2.** Current noise plotted as a function of time at room temperature as well as at 60°C (a, b).

Statistical analysis of the ECN current and potential data was carried out at the interval of 2500s. The plots of standard deviation of current ($\sigma_I$) and potential ($\sigma_V$) are plotted as a function of
time (Fig. 3 a-d). Searson and Dawson [8] estimated the corrosion rates of the mild steel specimens as a function of time and made measurements of electrochemical potential fluctuations in chloride containing solutions and found that corrosion rates were directly proportional to $\sigma_V$ values. Though the overall trend in the corrosion rates, as signified by the $\sigma_V$ values, seems to be decreasing with exposure time, there is no clear distinction among the graphs making the qualitative judgment difficult. Somewhat scattered data points in these plots are explained to result from the noise signals, which are instantaneous representation of the corroding system under study. However, the variance of the potential as well as current signals when plotted (Fig. 4a-d) as a function of $\frac{1}{\sqrt{t}}$ where $t$ is the exposure time, somewhat clearer distinction is possible. The variance values decrease with increase in exposure time almost linearly for all the specimens. It was from these plots that it was noticed that the last three points of $\sigma_I^2$ were very close; thus a mean of the last three points of the $\sigma_I^2$ values was plotted (Fig. 4e). It was clear from Fig. 4(e) that galvanically coupled specimens with different area ratios showed almost similar corrosion rates as that of the sensitized as well as as-received specimens;

Figure 3. Standard deviation of current and potential signals at room temperature (a, c) and at 60°C (b, d) in deaerated nitric acid.
there was some scatter in the $\sigma^2_I$ values. Noise Resistance ($R_N$) is defined as $R_N = \frac{\sigma_V}{\sigma_I}$. Noise resistance was found to be comparable to the polarization resistance ($R_p$), $R_N \approx R_p$ [8] and the relationship was found to be valid in some laboratory studies [8-13]. Thus, the reciprocal of $R_N$ could

Figure 4. Variance of potential and current signals in deaerated nitric acid at room temperature (a, b) and at 60°C (c, d). Average of the variance of current of the last 3 points plotted as a function of time in (e).
be roughly used as a measure of corrosion rate by substituting it in place of $R_p$ in the Stern-Geary equation as follows:

$$I_{cor} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta) R_p}$$

where, $I_{cor}$ is the corrosion current, $\beta_a$ and $\beta_c$ are the anodic and cathodic Tafel slopes. Figure 5(a, b) show the plots of $1/R_N$ values at room temperature and at 60°C. It was observed that the corrosion rates at 60°C for the specimens were higher by one order of magnitude than at room temperature. The corrosion rates at room temperature were found to fall within a scatter band and a definite rise in the corrosion rates with increase in the cathodic area was not observed; the plot showed consistently very low corrosion rates. The same pattern was also observed at 60°C, where somewhat higher corrosion rates could be explained based on the partial dissolution of the passive film supported by the potential and the current signal patterns observed in Fig. 1b and Fig. 2b.

![Figure 5. Reciprocal noise resistance ($1/R_N$) at room temperature and at 60°C (a, b) in deaerated nitric acid.](image-url)

Mean current values showed (Fig. 6a, b) continuously increasing trend for the sensitized specimen at room temperature, but a decrease after a rise at 60°C. The average of the last three mean current values were plotted in Fig. 6c. No significant variation in the mean current values at room temperature was observed for the sensitized specimen compared to the other specimens, but at 60°C, mean current values were somewhat higher and showed wide scatter.

Estimation of the power or energy in a signal is done by calculating the PSD values as a function of frequencies in the given signal. The spectral estimation was done using MEM that ensures mathematically the fewest possible assumptions made about unmeasured data by choosing the spectrum, which is the most random or has the maximum entropy for the process under investigation and is consistent with all known data [14]. In the recent findings [15, 16], the average PSD (1) at a
higher frequency interval (from 10 mHz – 250 mHz) was found to have correlated well with the measured corrosion current density as:

$$\text{PSD}(I)(\sigma_2 - \sigma_1) = \frac{1}{(\sigma_2 - \sigma_1)} \sum_{\sigma_i} F(\sigma)^2 \Delta \sigma$$

where $$\sigma_2 - \sigma_1$$ is the frequency interval on a log scale, $$F(\sigma)^2$$ is the PSD value of the electrochemical current noise in decibels (dB), and $$\Delta \sigma$$ is the frequency step on a log scale. The corrosion current density to which electrochemical noise was correlated expressed the general or uniform corrosion rate.

This correlation between PSD (I) and $$I_{\text{corr}}$$ values was used to study the relative tendency of corrosion of 304SS in passive state in nitric acid at room temperature as well as 60°C. The PSD (I) values were obtained between $$10^{-2}$$ – 1Hz and presented in Fig.7. The last values of 1/R_N too have been plotted for the sake of comparison. Linear fit lines were plotted for PSD (I) as well as 1/R_N values. The PSD (I) plot as well as the plot of 1/R_N were alike and did not show any variation with increase in the cathode

**Figure 6.** Mean current at room temperature (a) and at 60°C (b) in deaerated nitric acid. Mean of the last three points for mean current is plotted in (c).
to anode area-ratio at room temperature; the best fit lines for the corrosion rates ($1/R_N$ as well as PSD (I)) at $60^\circ$C showed increase in the corrosion rates as well as PSD (I) values with increase in the cathode to anode area-ratio. However, from the above observations, it could be concluded that, although there was slight increase in the corrosion rates of 304SS specimens due to galvanic coupling at $60^\circ$C compared to the corrosion rates at room temperature, the specimens dissolved in their passive state with partial dissolution of the passive film. The dissolution process steadied at the end of the 4 h experiment to a constant lower value. The optical microscopic observations conducted after completion of the ECN tests at $60^\circ$C, did not show any corrosion attack on the anode (sensitized 304 SS) in the couples. It was concluded that, the apparent increase in the corrosion rates at $60^\circ$C caused due to the partial dissolution of the passive film, which was not very significant. Thus, it is apparent that, the dissolution of 304SS in the vicinity of the sensitised HAZ would not cause any catastrophe by way of its accelerated dissolution following any galvanic coupling effect in nitric acid medium.

![Figure 7. Comparison of the calculated PSD (I) values in deaerated nitric acid at room temperature and at $60^\circ$C.](image)

4. CONCLUSIONS

Based on the corrosion studies and observations regarding the galvanic couples between a sensitized (anode) and a nonsensitised (cathode) specimens in different area ratios, it was concluded that,

1. Results in deaerated sulphuric acid showed gradual increase in corrosion rates due to galvanic coupling; the corrosion rates were higher in the galvanic couples than the as-received specimen.

2. The potential and current signals in nitric acid showed that the passive film was stable at room temperature whereas, it was unstable at $60^\circ$C and subject to frequent breakdown and
healing. Better passivation at room temperature was noticed from the cathodic current signals.

3. Variance values of potential as well as current signals clearly showed, decreasing trend of the corrosion at both temperatures than the values of standard deviation of current.

4. The corrosion rates in terms of \( I/R_N \) as well as PSD (I) showed no change due to the increase in the cathode to anode area-ratio at room temperature. The corrosion rates showed a definite increase at 60°C with increase in the cathode to anode area-ratio. Corrosion rates at 60°C were almost higher by one order of magnitude compared to the ones at room temperature.

5. Considering all the results, it appears that there was no effect of galvanic coupling on the corrosion rates of the specimens with different area-ratios at room temperature. There was an increase in the corrosion rates at 60°C compared to room temperature on account of partial dissolution of the passive film. Under such operating conditions, the failure of sensitised HAZ due to galvanic coupling is not expected in nitric acid either at room temperature or at 60°C.

References