The effect of heat treatment on the corrosion resistance of AISI 304L stainless steel is studied in the present investigation. As-received samples of 304L stainless steel were solution annealed at 1050°C for 90 minutes followed by thermal ageing at 750°C for various time durations (upto 24 days). ASTM standard A-262 practice A test was used to detect susceptibility of inter-granular attack. Electron dispersive spectroscopy attached to scanning electron microscopy was performed for identification of carbides. It was observed that no significant amount of attack took place upto 1 day. The extent of sensitization was quantitatively evaluated using double loop electrochemical potentiodynamic reactivation test. The results obtained showed that corrosion resistance decreased with an increase in thermal ageing duration. This behavior was attributed to the precipitation of chromium carbides causing depletion of chromium in the areas adjacent to the grain boundaries (as determined by electron probe micro analyzer). The degree of sensitization of highly aged sample was found to be 24.6%. Further, the degree of sensitization in terms of polarization resistance was computed in the middle of the transpassive potential region (at 1.1 V) using electrochemical impedance spectroscopy.

KEY WORDS: 304L stainless steel; inter-granular corrosion; SEM-EDS; double loop electrochemical potentiodynamic reactivation; electrochemical impedance spectroscopy; electron probe micro analyzer.

1. Introduction

Stainless steels are having 16–25% chromium and sufficient amount of austenite stabilizing elements like nickel, manganese and nitrogen, so the steels austenitic at the room temperature are called “austenitic stainless steels (ASSs)”. The most commonly used ASS is the AISI 304 grade also called as “18-8 steel” (containing 18% chromium and 8% nickel).1 Austenitic stainless steels have high ductility, low yield stress and relatively high ultimate tensile strength. They also offer excellent corrosion resistance in many organic, acidic, industrial and marine environments. Hence they are widely used in steam generating plants as piping and superheating tube materials due to their good mechanical properties and corrosion resistance at elevated temperatures.2,3 However, when ASSs have undergone a treatment like welding in the temperature range between 450°C to 850°C, there is a breaking corrosion resistance inter-granularly as a result of segregation of carbides (M23C6, where M = Cr Fe Mo). This mechanism of precipitation of carbides consisting predominantly chromium carbide (Cr23C6) at the grain boundaries, results in the formation of chromium-depleted zones adjacent to it, called as sensitization.4

The basic type 304 stainless steel is highly susceptible to sensitization induced inter-granular corrosion (IGC) which leads to the decrease in the corrosion resistance of steel. The susceptibility to IGC is decreased in stainless steels by reducing their carbon content to less than 0.03 wt.%; the main type of this stainless steel class is AISI 304L, which have been developed for minimizing the effect of complex carbide precipitation (M23C6), preferentially precipitate carbon and prevent depletion of chromium.5 A decrease in carbon content from 0.08–0.02 wt%, the nose of the time temperature sensitization curve is shifted from 0.1 h to 100 h and chromium carbide formation can be greatly delayed by using this low carbon variant.6,7 However, it can still prove to be detrimental and lead to sensitization. The precipitation of carbides during welding is eliminated due to low concentration of carbon (0.03 wt.%).8 Consequently, this 304L stainless steel can be used in the “as welded” state even in severe corrosive conditions. In many cases it eliminates the necessity of post-annealing of weldments, which is strictly followed for the 304 type.1–3

The sensitization behavior of ASS grades which leads to IGC attack has been extensively studied by many researchers using various electrochemical tests. Usually the sensitized region is evaluated using various qualitative methods mentioned in ASTM standard A 262 Practice A-F. Except Practice A, all the other tests are destructive and require dif-
ficult preparation. The Practice A is rapid qualitative and most commonly used test in laboratory. However, from industrial point of view, it is necessary to develop non-destructive test methods (like double loop electrochemical potentiodynamic reactivation-DLEPR and electrochemical impedance spectroscopy-EIS) for the quantitative assessment of IGC in the localized region. Pedro de Lima-Neto et al. worked on the welded AISI 304 stainless steel using DLEPR and EIS test to determine the length of the sensitized zone (SZ). A. Arutunow et al. investigated the dynamic changes of impedance of AISI 304 stainless steel dissolution process in conditions of IGC using dynamic EIS. R. V. Taiwade et al. worked on the qualitative and quantitative comparison of degree of sensitization (DOS) of AISI 304 stainless steel and Cr–Mn ASS to conclude recovery from sensitization which was observed only in AISI 304 grade. R. V. Taiwade et al. worked on effect of solution annealing on susceptibility towards IGC of ASS using electrochemical tests. They concluded that the effect of cumulative sensitization and the area of sensitization zone get reduced after solution annealed (SA) heat treatment. These extensive researches have led to the remedy for the complications placed by IGC on ASS grades specifically AISI 304 SS. It comprises of eliminating or reducing the formation of chromium carbides that can be done by selecting an extra low modification of 304, that is 304L. V. Kain et al. worked on testing sensitization and predicting intergranular corrosion and intergranular stress corrosion cracking susceptibility of ASSs (304/304L) using fast, nondestructive and quantified electrochemical tests. S. Bhise et al. worked on potential measurement for predicting corrosion behavior of SS 304L in boiling nitric acid containing oxidizing ions. They concluded that IGC of type 304L SS is dictated by the trans-passive potential in nitric acid medium.

However, the collective and systematic assessments of IGC in 304L SS using both qualitative and quantitative techniques are limited. Therefore, in the present investigation various electrochemical tests like ASTM A-262 A, DLEPR and EIS were conducted along with electron dispersive spectroscopy attached to scanning electron microscopy (SEM–EDS) and electron probe micro analyzer (EPMA) for IGC characterization.

2. Experimental

The AISI 304L SS was procured from market in the form of sheet. The chemical composition (as determined by optical emission spectrometer) is given in Table 1. Samples for ASTM standard A-262 Practice A and electrochemical tests were cut from the sheet by wire-cut electrical discharge machine to avoid heating zone during cutting operation. Samples for practice A and other tests were 10 mm × 10 mm × 3 mm. All the samples were solution annealed (SA) at a temperature of 1 050°C for 1.5 h, followed by water quenching. The solution annealed samples were then subjected to isothermal ageing treatment at temperature of 750°C for various time durations ranging from 3 h to 576 h (i.e. 24 days) followed by air cooling. Silicon carbide (SiC) muffle furnace (Lenton, UK) was used for this purpose. The sample preparation for size 10 mm × 10 mm × 3 mm is described as follows.

The samples were joined with a brass stud (8 mm Φ) using silver paste for electrical connections. The stud was connected to brass wire (3 mm Φ) via M3 threads. The assembly was then mounted in cold setting resin, leaving one of the surface of sample open for testing. The open surface of samples were wet polished on emery papers (180, 240, 400 and 600 grit), and then on velvet cloth smeared with 0.75 μ alumina (Al₂O₃) slurry. The samples were ultrasonically cleaned in distilled water prior to each test.

A Potentiostat (Solartron-1285) was used for ASTM standard A-262 practice A test. In practice A, the samples were electrolytically etched in 10 wt.% oxalic acid solution with current density of 1 A/cm² for 90 seconds. It was carried out using a Potentiostat (Solartron-1285), in conventional three-electrode electrochemical cell, with platinum electrode as counter electrode, saturated calomel electrode (SCE) as the reference electrode and sample as the working electrode. Before exposing the sample, the test solution was de-aerated using dry (oxygen free) nitrogen gas for 1 h. All the DLEPR experiments were initiated after attaining nearly steady-state open circuit potential (about 45 min). The potential range chosen from −500 mV (SCE) to +500 mV (SCE) for forward scan. The scanning direction was then reversed, and the potential was reduced back to −500 mV (SCE) to obtain reverse scan. The peak activation current density (Ia) and the peak reactivation current density (Ir) were measured during forward and reverse scans, respectively. The % DOS was then computed as the ratio of (Ir/Ia) x100.20,21)

EIS test was performed using EG & G PAR Versa STAT 3 in a solution consisting of 0.5 M H₂SO₄ + 0.001 M NH₄SCN having a scan rate of 6 V/h at room temperature (27°C). It was carried out using a Potentiostat (Solartron-1285), in conventional three-electrode electrochemical cell, with platinum electrode as counter electrode, saturated calomel electrode (SCE) as the reference electrode and sample as the working electrode. Before exposing the sample, the test solution was de-aerated using dry (oxygen free) nitrogen gas for 1 h. All the DLEPR experiments were initiated after attaining nearly steady-state open circuit potential (about 45 min). The potential range chosen from −500 mV (SCE) to +500 mV (SCE) for forward scan. The scanning direction was then reversed, and the potential was reduced back to −500 mV (SCE) to obtain reverse scan. The peak activation current density (Ia) and the peak reactivation current density (Ir) were measured during forward and reverse scans, respectively. The % DOS was then computed as the ratio of (Ir/Ia) x100.20,21)

EIS test was performed using EG & G PAR Versa STAT 3 in a solution consisting of 0.5 M H₂SO₄ + 0.2% NaCl and the remaining setup was same as that of DLEPR test. The potential step was 10 mV and the testing frequency range was 0.01 Hz to 1 MHz. The test was performed at potential 1.1 V. During test the sample was potentiostatically cleaned at −500 mV (SCE) for 2 min to remove air-formed oxide film. The measured impedance was automatically recorded and saved in a personal computer to obtain the Nyquist plots. Charge transfer resistance (Rct) was evaluated from the Nyquist plots.22) Origin PRO 8.5 software was used for the analysis. In the present investigation the chromium concentration across the grain boundary was measured using electron probe micro analyzer (EPMA). Approximately 25 data points were collected across the grain boundary.

3. Results and Discussion

It is previously mentioned in the introduction section that

<table>
<thead>
<tr>
<th>Elements</th>
<th>Cr</th>
<th>Ni</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight%</td>
<td>19.610</td>
<td>8.301</td>
<td>0.018</td>
<td>1.362</td>
<td>0.381</td>
<td>0.001</td>
<td>0.011</td>
</tr>
</tbody>
</table>
SS 304L gets sensitized in longer ageing duration due to formation of carbide precipitation. This section deals with the various electrochemical tests beginning with ASTM standard A 262 practice-A followed by SEM, SEM-EDS, DLEPR, EIS and EPMA for characterization of carbides and identification of IGC susceptibility.

3.1. Qualitative Analysis

3.1.1. ASTM Standard A-262 Practice A Test

This electrochemical test deals with the measurement of potential difference after applying a current (1 A/cm²) which results in preferential attack of high energy sites that is grain boundaries. A typical curve obtained from galvanostatic mode of electrolytic etching is shown in Fig. 1 and indicates the time potential relationship for the investigated sample which is heat treated at 750°C for 24 days.

According to the microstructures obtained after ASTM standard Practice A test, the samples are classified as follows:

1. Step structure: Absence of carbides (that is steps only between grains, no carbides at grain boundaries).
2. Dual structure: Discontinuous carbide precipitation (that is some carbide at grain boundaries in addition to steps, but no single grain completely surrounded by carbides).
3. Ditch structure: One or more grain is completely surrounded by carbides.

Figures 2(a)–2(i) shows the optical micrographs of the solution annealed and heat treated samples of AISI 304L SS after etching as per ASTM standard A-262 Practice A test. In Fig. 2(a), single phase austenite structure observed and no trace of secondary phases like carbides was found. Figures 2(b)–2(i) shows the optical micrographs of thermally aged samples of the 304L SS at 750°C for various durations of time. In Figs. 2(b)–2(d) very less attack and no carbide precipitation is observed in the microstructures and hence it is called as the “Step” structure. In Figs. 2(e)–2(f), partial attack or precipitations of carbides are observed at few places and hence they were classified as “dual” structure. In Figs. 2(g)–2(i), it can be seen that the carbides are precipitated along the grain boundaries. These microstructures can be classified under the category of “ditch” structure. Figure 2(i) shows the sample that was thermally aged for the maximum duration of time and it is evident from the microstructure that the ditching characteristic was highest in this case. Hence it signifies that the ditching phenomenon increases with increase in aging time. Therefore, as per ASTM standard Practice A test, it can be concluded that the 304L SS samples when heat treated, indicate variations in their microstructure in terms of carbide precipitation and the sample which is aged for the highest duration will show a dense carbide attack along the grain boundaries (highly sensitized).

Figure 3(a) shows the well labeled SEM micrographs of thermally treated samples at 750°C for 2, 16 and 24 days, where carbides are prominently observed at the grain boundaries in all the cases. Figure 3(b) indicates the carbide point of interest in SEM micrograph. Also Fig. 3(c) shows the EDS spectra of selected point. It is found that the carbides at the grain boundaries consisted of ~75% Fe, ~19% Cr and 5% Ni (as determined by SEM-EDS). Therefore, from the micrographs of Figs. 2(d)–2(i) and 3(a)–3(c), the IGC attack is qualified in the investigated steel.

3.2. Quantitative Analysis

3.2.1. Double Loop Electrochemical Potentiodynamic Reactivation (DLEPR) Test

This quantitative nondestructive electrochemical test method is used to estimate the extent of IGC in terms of DOS. The schematic diagram with log current on abscissa and potential on the ordinate indicating the various elements of DLEPR curve consisting of active, passive region along with anodic and reverse scan as shown in Fig. 4. This test is based on the assumption that only sensitized grain boundaries are active, whereas the un-sensitized grain matrix is

![Fig. 1. Typical time-potential curve of electrolytic etching in galvanostatic mode for the sample heat treated at 750°C for 24 days.](image-url)
passive (due to formation of chromium oxide film). This passive corrosion resistant film of Cr₂O₃ may weaken locally due to the formation of heterogeneous microstructures at the grain and grain boundaries which results in potential difference. IGC is accelerated by the potential difference between the grain (exhibit passive behavior) and the grain boundaries (exhibit active/anodic behaviour). During this phenomenon, the chromium depleted alloy sets up passive-active cell. Further by decreasing the potential, the protective passive film over chromium-depleted areas is more easily dissolved than that over un-depleted (i.e. non-sensitized) surfaces.

In the current investigation, the sensitivity of aged 304L SS samples at 750°C towards IGC was evaluated using the DLEPR test, which consists of a potentiokinetic scanning in a suitable electrolyte, from an active to a passive domain (activation or anodic scan), followed by a return to the initial potential (reverse or reactivation scan). The ratio of reactivation and anodic current densities \( \frac{I_r}{I_a} \) permit the evaluation of the DOS. The development of the reactivation peak current density can be attributed to metal dissolution during reverse scan. Higher value of the reactivation current implies greater is the DOS and more is the metal dissolution. The quantitative effect of time and temperature on IGC of 304L SS is apparent from the DOS values and DLEPR curves (Fig. 5). Table 2 shows the DOS data obtained from DLEPR tests. The \( I_r \) value of SA sample is very small which is also evident from the microstructure of SA sample (Fig. 2(a)) as it has no carbide since they were totally dissolved after SA treatment. The \( I_r \) values of the samples heat treated at 6 h, 24 h (1 day) and 576 h (24 days) was 0.001107, 0.002018 and 0.018513 A/cm² and their DOS values were 1.47, 2.76 and 24.46 respectively. The value of \( I_r \) increases by one order of magnitude in case of highly sensitized condition (576 h) which is attributed to increase of chromium depleted zones. This indicates that during reactivation, the metal dissolution is increasing with the ageing time. In other words, it can be said that the protective passive film which forms over chromium depleted areas is getting easily dissolved with the increment of ageing time duration. These quantified results are in good agreement with results of microstructural studies carried out in this investigation.

![Optical micrographs of 304L SS after solution annealing + heat treatment at 750°C acquired using practice-A test.](image)

Fig. 2. Optical micrographs of 304L SS after solution annealing + heat treatment at 750°C acquired using practice-A test.
3.2.2. Electrochemical Impedance Spectroscopy (EIS)

The various electrochemical tests like anodic polarization, potentiostatic pulse techniques etc. have been extensively used by many researchers to identify anodic dissolution behavior in austenitic stainless steels. Basically, the anodic polarization test emphasized on active-passive and transpassive behavior of the materials.

In the transpassive potential region of the anodic polarization curve, three types of anodic dissolution viz. passive dissolution, grain boundary attack and pitting can be characterized. Also it is well known from literature that the DOS can be correctly evaluated in the middle of transpassive potential region where anodic dissolution is of grain boundary attack type.\(^{12,22}\)

In the present investigation a quick and rapid electro-

![Fig. 3. SEM micrographs and SEM-EDS images of thermally aged (750°C) 304L SS samples. a) SEM micrographs of aged samples (at 2, 16 and 24 days), b) Carbide point of interest for EDS scan, c) EDS spectra of selected point.](image)

![Fig. 4. Schematic diagram of the active-passive DLEPR curve.](image)
Fig. 5. Obtained DLEPR curves of 304L SS, solution annealed and thermally aged samples at 750°C.
chemical impedance spectroscopy (EIS) test was incorporated in the middle of the transpassive potential region for DOS measurement. Figure 6 shows the transpassive potential region in anodic polarization curve obtained in the solution (0.5 M H₂SO₄ + 0.2 % NaCl) for sample heat treated at 750°C for 576 h (24 days).

In this work, the electrochemical impedance spectroscopy (EIS) test was carried out to find the corrosion resistance of few thermally aged samples. This test was performed in the frequency domain of 10 kHz to 10 Hz. The remaining points from high and low frequency were eliminated to process the data in order to obtain the significant corrosion resistance values. Figure 7 shows the Nyquist plots of the heat treated samples polarized at 1.1 V and indicates the AC impedance response in this trans-passive potential. The charge transfer resistance (Rct) values of 6 h (less sensitized) sample was found to be 327 Ω and for 24 days (highly sensitized) it was 171 Ω. Increase in the ageing time leads to a shift of the curves to higher ohmic resistance values due to acceleration in the dissolution kinetics, which explains decrease in corrosion resistance with increased ageing time. Such variations may suggest differences in the thickness of corrosion resistant film that would delay the charge transfer and hence helping in improving the corrosion resistance until achieving a robust and stable passive film. The current results of EIS test are in agreement with the findings of Huang et al.²²) The Rct values of less and highly sensitized samples indicate good correlation with DOS that is, higher the sensitization, lower will be the Rct values. This correlation is evident from the microstructures (Figs. 2(c) and 2(i)) and DLEPR curves (Figs. 5(c) and 5(i)). Thus, with the help of values obtained from Nyquist plots the corrosion resistance behavior of the investigated 304L SS was verified.

### Table 2. DOS values for solution annealed and thermally aged samples.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Time (h)</th>
<th>Reactivation current, Ir (A/cm²)</th>
<th>Activation current, Ia (A/cm²)</th>
<th>%DOS (Ir/Ia)*100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution annealed</td>
<td>–</td>
<td>0.000715</td>
<td>0.076033</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.000979</td>
<td>0.072051</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.001107</td>
<td>0.075008</td>
<td>1.47</td>
</tr>
<tr>
<td>Solution + Thermal aged</td>
<td>12</td>
<td>0.001738</td>
<td>0.072231</td>
<td>2.40</td>
</tr>
<tr>
<td>at 750°C</td>
<td>24</td>
<td>0.002018</td>
<td>0.072890</td>
<td>2.76</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>0.006700</td>
<td>0.071966</td>
<td>9.35</td>
</tr>
<tr>
<td></td>
<td>192</td>
<td>0.008383</td>
<td>0.070463</td>
<td>11.89</td>
</tr>
<tr>
<td></td>
<td>384</td>
<td>0.008839</td>
<td>0.072616</td>
<td>12.17</td>
</tr>
<tr>
<td></td>
<td>576</td>
<td>0.018513</td>
<td>0.075671</td>
<td>24.46</td>
</tr>
</tbody>
</table>

3.2.3. Electron Probe Micro-analyzer (EPMA) Line Scans

EPMA was used to predict the wt.% of chromium concentration across the grain boundary. Figure 8 shows the chromium concentration profile (wt.%) along the grain boundaries for SA, and thermally aged samples (at 750°C for 6 h, 1 day and 24 days). The Cr concentration along the grain boundary in SA sample is almost constant around 19.5 wt.% for all the data points and no depleted region was identified. The Cr concentration was observed to be declin-
ing with the ageing time. For the less sensitized (6 h) sample, chromium concentration amounted to be around 17.8 wt.%, and for partially sensitized (1 day) sample it was 15.8 wt.%, while for the highly sensitized (24 days) sample it was 10.2 wt.%. Since, the minimum chromium concentration values indicate that the passive film is weakened with increase in ageing time.

4. Conclusion

(1) Collective and systematic investigation of IGC behaviour of 304L SS was carried out using various electrochemical techniques including practice A, DLEPR, EIS, and EPMA.

(2) Results of optical micrograph show that the extent of ditching was found to be highest for 24 days of ageing.

(3) SEM-EDS studies show that the carbides at the grain boundaries consisted of ~75% Fe, ~19% Cr and 5% Ni.

(4) Degree of sensitization for thermally aged samples increased with ageing time which means that the extent of carbide precipitation is increasing with increasing time duration. Thermal ageing at 750°C for 24 days (highly sensitized) had to highest degree of sensitization of 24.46%.

(5) In case of DLEPR test, the value of $I_r$ increases by one order of magnitude in case of highly sensitized condition which is attributed to increased metal dissolution.

(6) For EIS test, increase in the ageing time leads to a shift of the curves to higher ohmic resistance values due to decrease in corrosion resistance.

(7) EPMA line scan showed that chromium concentration is almost constant for solution annealed sample and minimum for the highly sensitized sample. This indicates weakening of the Cr$_2$O$_3$ passive film as we go away from the grain boundary for the highly sensitized sample.

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