



ISSN 2278 – 0211 (Online)

Corrosion Behaviour of Stainless Steel Grade 304 IN–1MHCL

Ajit Kumar

M.Tech, Materials Science and Engineering
National Institute of Foundry and Forge Technology, Hatia, Ranchi, Jharkhand, India

Nitesh Kumar

M.Tech, Materials Science and Engineering,
National Institute of Foundry and Forge Technology, Hatia, Ranchi, Jharkhand, India

Anjani Kumar Singh

Ph.D Scholar, Materials and metallurgical Engineering
National Institute of Foundry and Forge Technology, Hatia, Ranchi, Jharkhand, India

G. Das

Assistant Professor, Materials and metallurgical Engineering
National Institute of Foundry and Forge Technology, Hatia, Ranchi, Jharkhand, India

Abstract:

The corrosion behaviour of 304 grade stainless steel is studied in presence of HCl solution with concentration of 1M. The experiment is tested by the potentiostatic polarization techniques. Due to the presence of chloride ions(Cl⁻) 304 grade is very much susceptible to the corrosion of pitting type. The low corrosion resistance was due to surface passive film with less protective to reveal high anodic dissolution rate. The mechanism of corrosion is as also discussed. The oxidised 304 stainless steel is active on immersion, resulting in a low corrosion potential and a high weight loss. After certain duration the stainless steel either remains active or becomes passive depending on HCl content. At low HCl contents, an ongoing active-to-passive transition results in localised corrosion at pits, grain boundaries and honeycombed recesses. Because of anodic brightening, the 304 stainless steel is always active as HCl is concentrated. There is also some parameters which affects the corrosion of 304 stainless steel in HCl which have been taken under consideration during the test such as: Solution Acidity, Oxidizing Agents, Temperature, Films, Dissolved salts, Fluid velocity, Impurities.

Key words: Pitting corrosion, AISI 304 grade stainless steel, 1M Hydrochloric acids, Corrosion parameters, Corrosion Mechanism, Surface texture

1. Introduction

Stainless steel 304 contains typically 18 wt. % chromium, 8 wt. % nickel and less than 0.03 wt. % carbon, with the low nickel content contributing a fully austenitic structure at room temperature. Stainless steel type 304 is widely used in many applications such as desalination plants, construction materials, pharmaceutical industry, thermal power plant, chemical cleaning and pickling process, due to their stability, good corrosion resistance, high strength, workability and weldability [1]. Steel is the most important engineering and construction material in the world. It is used in every aspect of our lives, from automotive manufacture to construction products, from steel toecaps for protective footwear to refrigerators and washing machines and from cargo ships to the finest scalpel for hospital surgery. Corrosion is the deterioration of essential properties of a material due to reactions with its surroundings. Corrosion damage can cause leakage of fluids or gases. Even more dangerous is a loss of strength of the structure induced by corrosion and subsequent failure [2].

1.1. Corrosion Mechanism

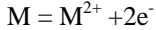
Most metal corrosion occurs via electrochemical reactions at the interface between the metal and electrolyte solution. A thin film of moisture on a metal surface forms the electrolyte atmospheric corrosion[3]. Corrosion normally occurs at a rate determined by equilibrium between opposing electrochemical reactions. The first is the anodic reaction, in which a metal is oxidised, releasing electrons into the metal. The other is the cathodic reaction, in which a solution species is reduced, removing electrons from the metal. When these two reactions are in equilibrium the flow of electrons from each reaction is balanced, and no net electron flow occurs. The

two reactions can take place on the one metal or on two dissimilar metals that are electrically connected. Since corrosion is actually a process involving electrochemical oxidation and reduction reactions. In order for the reaction to occur, the following conditions must exist [4]:

- A chemical potential difference must exist between adjacent sites on a metal surface (or between alloys of a different composition).
- An electrolyte must be present to provide solution conductivity and as a source of material to be reduced at the cathode.
- An electrical path through the metal or between metals must be available to electron flow.

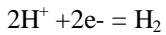
During the test an ionic conduction path is provided through the solution separating the working electrode and the counter electrodes while the electrical conduction path is provided through the potentiostat. This potentiostat is then used to control the driving force for electrochemical processes taking place at the working electrode. The magnitude of the driving force indicates which processes are taking place at the anode and at the cathode as well as their rates. Electrons flow from the anode to the cathode by the electrical path as stated above. Anode is thought to be a negative electrode and cathode the positive one [5].

At the anode oxidation takes place, which can be represented as:



Where M represent the metal or alloy, M^{2+} represent the ion of the metal and $2e^{-}$ represent the number of electrons transferred in the processes.

At the cathode reduction takes place, reaction such as reduction taking place at the cathode surface may takes place as:



In summary, the corrosion occurs when metal atoms detach themselves from the metal surface at the anode and enters the solution as ions, leaving behind the negatively charged electrons in the metals. The electrons flow through the metal to the cathode and neutralize positively charged hydrogen atoms that collect at the surface. The neutral hydrogen atoms combine to form hydrogen gas. In solution where hydrogen tends to evolve to slowly, oxygen is reduced and combines with hydrogen ions or water to form water or hydroxyl ions [6, 7].

Corrosion can be attacking the overall surface or be a local phenomenon, depending on the relative proportion of anodic and cathodic areas. When the areas are approximately equal, corrosion is usually uniform over the whole surface. However when the cathodic area is large compared to the anodic area, the localized attack at anodic sites can be intensified [8].

1.2. Corrosion Parameters

Atmospheric corrosion of steels proceeds at rates up to 0.1mm per year in environments free from chemical splash. This corrosion resulted from condensing moisture, sulphur dioxide from fuel combustion, dust bearing corrosives and the remoteness of structures and equipment from the wain effect of rain water. The seven major corrosion parameters are as: (a) solution acidity, (b) oxidizing agents, (c) temperature, (d) films, (e) dissolved salts, (f) fluid velocity, and (g) impurities. Each of these parameters is explained as follows:

- **Solution Acidity**

Solution acidity is represented by the concentration of hydrogen ions with the relation:

$$pH = -\log[H^{+}]$$

The tendency for metals to corrode by displacing hydrogen ions from solutions as in electromotive series. Metals above in the series displace hydrogen more readily than do those below hydrogen. Since the discharge of hydrogen ions takes place in most corrosion reactions, acidity of a solution is one of the most important factors in corrosion combating. As a general rule, acid ($pH < 7$) solution are more corrosive than neutral ($pH = 7$) solutions or alkaline ($pH > 7$) solution. In acidic environment (HCl addition) where $pH = 2.9$, the corrosion rate is above 0.8mm per year.

- **Oxidizing Agents**

In some corrosion processes such as the solution of zinc in HCl, hydrogen evolves as gas. The removal of hydrogen is effected by a reaction between hydrogen and some oxidizing chemical, such as oxygen, to form water. Oxidizing agents may accelerate the corrosion of one class of materials and retard the corrosion of another class. In the latter case, the behaviour of the material usually represents the surface form anion of oxides or layers of absorbed oxygen which make the material more resistant to further chemical attacks. The corrosion rate is almost linearly proportional to the concentration of dissolved oxygen.

- **Temperature**

Rate of corrosion tends to increase with rising temperature. Higher temperatures accelerate the diffusion of oxygen through cathodic layers of protective oxide film. Temperature also has a secondary effect through its influence on the solubility of air or (Oxygen).

- **Films**

There are films of metal oxide, oil and grease that may protect a material from direct contact with corrosive substances. Such oil films may be applied intentionally or may occur naturally as in the case metals submerged in sewage or equipment used for the processing of oily substances. Once corrosion starts its further progress often is controlled by the nature of films that may form or accumulate on the metallic surface. Films may tend to retain or absorb moisture and thus, by delaying the time of drying, increase the extent of corrosion resulting from exposure to the atmosphere or to corrosive vapours.

- **Dissolved salts**

Acid Salts, such as aluminium chloride, ferrous chloride, ammonium chloride, etc, hydrolyze to form acid solutions. Acid salts have a low pH, which will accelerate corrosion simply because of their acidic effect. Alkaline salts hydrolyze to increase solution pH that may sometimes act as corrosion inhibitors. The presence of acid or neutral salts may increase corrosion rate, whereas the presence of alkaline salts may decrease the corrosion rate.

- **Fluid velocity**

An increase in the relative velocity between a corrosive fluid and a metallic surface tends to accelerate the corrosion rate. This effect is due to the higher rate at which corrosive chemicals, including oxidizing substances such as air, are brought to the corroding surface. Velocity effects can be divided into four ranges according to velocity magnitude.

(1) Slight motion (less than 0.3m/sec) may stop localized attack such as pitting.

(2) At about 0.3m/sec, the flow may increase the oxygen supply to a level that raises the corrosion rate to as much as 1.0mm per year.

(3) At a velocity range from 2.4 to 3.0 m/sec, corrosion rate will be about 0.3 to 0.8 mm per year, depending on the surface roughness.

(4) At velocities over 4.5 m/sec, turbulence may greatly accelerate the corrosion rate up to 5mm per year.

- **Impurities**

Impurities in a corrodent can be good or bad. The chloride ion is a good example; the presence of small amount of chloride in a fluid can break down the passive oxide film on the steels. Inorganic oxidizers such as chromates are used as a corrosion inhibitor in cooling water systems. However, if the impurity is removed, marked increase in corrosion rates may result [9].

2. Experimental Methods

2.1. Materials

In the experiment, sample of AISI 304 stainless steel grade is used and its composition is as given below: Grade 304 stainless steel (Disc) and electrolyte used is 1M Hydrochloric acid and the solution is prepared with the distilled water.

Element	C	Mn	Si	P	Cr	Ni	Cu	Sn
Wt%	.06	1.6	.4	.01	17.5	7.4	.4	.02

Table 1: Chemical composition of 304 ss.

2.2. Sample Preparation

The steel specimens were made by cutting short lengths from the cylindrical rod having 20mm dia. and 6mm of thickness of which 1 cm² was the area exposed to the electrolyte.

The surface finishing procedure recommended by ASTM with the polishing procedure used as standard practice in metallography laboratories. Specimen preparation or polishing is very necessary to study the microstructure because the microscope makes use of the principle of reflection of light to obtain the final image of the metal structure. Following steps have been taken during the preparation of sample. The finishing was checked under the optical microscope at 100x.

Then a reasonably flat surface of the specimen is achieved by using a fairly coarse file or by grinding. After intermediate and fine grinding carried out by using emery papers progressively finer grade. Here 80 grit, 120 grit, 180 grit, 220 grit, 320 grit, 400 grit, 600 grit, 800 grit emery papers were used. The specimen is first ground on 80 grit paper, so that scratches are produced roughly at right angle to those initially existing on the specimen and produced through grinding or coarse filing operation. Which removes the primary grinding marks, the specimen is washed free of no. 80 grit. Grinding is then continued on the 120 grit paper again, turning the specimen through 90° and polishing until the previous scratch marks are removed. The processes are repeated with the no. 180, 220, 320, 400, 600, 800 grit papers.

The final step is the fine polishing of the surface which is obtained by using alumina (Al₂O₃) powder placed on a cloth covered rotating wheel. Distilled water is used as a lubricant. Fine polishing removes fine scratches and very thin distorted layer remaining from the rough polishing stage.

The measurements are usually made employing a potentiostat. This instrument automatically maintains the desired potential between the working and reference electrodes by passing an appropriate current between the working and counter electrodes. A potentiostat is a controller circuit that maintains the potential between the working and the reference electrodes equal to the value E. If there is a small difference E volts, this is sensed, amplified and a current I flows. This process continues till the difference AE becomes zero. The direction of the current flow depends upon the sign of AE. Since the input impedance is very high, very low current flows through, and the reference electrode is not polarised. Using the potentiostat, polarization may be accomplished either potentiostatically (in steps) or potentiodynamically (continuously).

Electrochemical studies were carried out in a conventional three-electrode single-compartment (Model NOVA 1.18, serial no. 12800817 Pyrex cup, 300 ml volume, with the cover model AUTOLAB one channels/openings, software NOVA 1.8.17). Sample was used as the working electrodes by putting only one side of the specimen in contact with the electrolyte (1 cm²).

The remaining sides were covered with varnish. The electrical contact with the test electrode was made using a clip attached on a small strip of the sample. Potentiostatic experiments were performed using each of the cylindrical specimens in turns, in which 1 cm²

surface area of the specimen was exposed to the test solution at room temperature. The experiments were performed using a polarization cell of three – electrode system consisting of a reference electrode (saturated $-AgAgCl/KCl$ 0.197V), a working electrode (WE); and a counter electrode (CE) made of platinum mesh. The experiments were conducted in 1 Mole HCl solution for stainless steel sample.

3. Results and Discussion

The testing condition is the presence of 1 mole HCl solution which was prepared with distilled water. The pitting potential E_p shifts to a more negative value with increasing chloride concentration.

The plots of logarithm of $[Cl^-]$ and E_p follow a linear relationship in most of the alloy systems. The conventional austenitic steels have much higher slopes than the superstainless steels indicating a relatively small shift in pitting potential with variation in Cl^- concentration in case of high alloy stainless steels.

The potentiostatic polarization curves and table of measurement results for the test specimen recorded in 1 M HCl are presented in Figure 1 and respectively. Figure 1 shows the polarization corrosion curve of the 304 stainless steel in 1M HCl alone. The Open Corrosion Potential (OCP), E_{corr} was -0.38494 V. The specimen can be described to be protected with this potential value throughout the experimental period. This medium serves as the control for the subsequent experiment.

Results summary for the test in 1M HCl presented in Table 1 showed that the corrosion rate is 18.829 mm/yr and the corrosion polarization resistance is 24.734Ω . The corrosion current density of 0.00162 A/cm² was low and the corrosion current is 0.00162 A which was also very low. All these results data confirmed the corrosion of the test specimen 1 M HCl is under considerable.

Conc. (M)	I_{corr} (A)	I_{corr} (A/Cm ²)	b_c (V/dec)	b_a (V/dec)	R_p (Ohm)	E_{corr} Ref (V)	E_{corr} Calc (V)	E_{begin} (V)	E_{end} (V)	Corr. rate (mm/yr)
1	0.00162	0.00162	0.07586	-0.4264	24.734	-0.38383	-0.38494	-0.38742	-0.37674	18.829

Table 2: Electrochemical Parameters estimated from the polarization tests in 1 M HCl

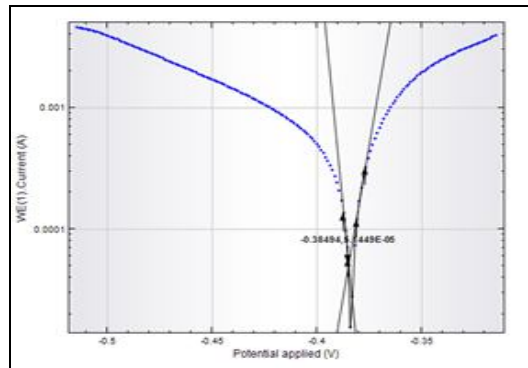


Figure 1: Showing the Potentiostatic polarization curves

The surface texture, before the action of HCl takes place on the surface of 304 grade stainless steel the picture was taken by the optical image analyser.



Figure 2: Metal Surface before action (non corroded) of 1M HCl acid

After approx. 20 min testing the sample in the 1 mole of HCl. The surface of the sample shows the severe corrosion and the image was taken under the magnification of 200X.



Figure 3: Metal surface after action (corroded surface) of 1M HCl acid

4. Conclusion

304 grade of stainless steel is more susceptible to pitting corrosion than other type of austenitic steel and its alloying elements exhibit poor corrosion resistance in 1M HCl. A good correlation seems to exist between the polarisation resistance values obtained polarisation techniques when the alloys undergo active dissolution and not when they possess passivity. Since due to the absence of Mo content the passivity of the alloy decreases in HCl, as a result there is severe corrosion of 304 in HCl solution. The anodic reactivity of stainless steels when cells were present was slightly higher. However, the cathodic reactivity was found to be drastically suppressed by the presence of cells. Despite the reduction in the general corrosion rate, cells can increase the susceptibility of local corrosion: it was speculated that this was because of the presence of occluded areas underneath the cells, which were likely to establish local chemistry that facilitates pitting corrosion.

Corrosion rates of stainless steels are the functions of Cr + Ni content, pitting resistance equivalent, PREN and induction time, time. While the presence of Cr and Ni provides a stable protective oxide film and overall strength to the alloy, PREN is the measure of resistance to pitting and corrosion rate decreases linearly with increase in PREN values. Pitting potential, E_{pit} is a logarithmic function of Cl⁻ concentration. The conventional austenitic steels show a relatively small shift in pitting potential with variation in Cl⁻ concentration. An increase in Cl⁻ concentration results in a shift to more negative (or active) E_{pit} .

5. References

1. ASM, Metals Handbook, vol. 3, Properties and Selection: Stainless Steels, Tool Materials and Special-Purpose Metals, 1980, pp. 6.
2. G. Frankel, "Pitting corrosion of metals: A review of the critical factors," 1998.
3. Electrochemistry and Corrosion: Overview and Techniques Princeton Applied Research, 801 S. Illinois Avenue, Oak Ridge, TN 37830.
4. R. P. V. Cruz, A. Nishikata, and T. Tsuru, "Pitting corrosion mechanism of stainless steels under wet-dry exposure in chloride-containing environments," Corrosion science, vol. 40, pp. 125-139, 1998.
5. T. A. Suter, "Micro electrochemical Investigations of Austenitic Stainless Steels," PhD, Materials Science and Engineering, Swiss Federal Institute of Technology Zurich, Zurich, Switzerland, 1997.
6. Y. Sun, T. Bell, Mater. Sci. Eng. A 140 (1991) 421.
7. Edwar J. Kubel Jr, Curbing Corrosion in Marine Environments, Advanced Materials and Processes, Nov. 1988.
8. Z. Szklarska-Smialowska, Pitting corrosion of metals. Houston, Tex.: National Association of Corrosion Engineers, 1986.
9. B. Leffler, "Stainless steels and their properties," AvestaPolarit AB, 1996